MULTIPHASE CATALYSTS FOR SELECTIVE REDUCTION OF NO$_x$ WITH HYDROCARBONS

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PROEFSCHRIFT

ter verkrijging van
de graad van doctor aan de Universiteit Twente,
op gezag van de rector magnificus
prof. dr. F.A. van Vught
volgens het besluit van het College voor Promoties
in het openbaar te verdedigen

door
Sergio Eduardo Maisul
egeboren op 24 September 1960
te Capital Federal (Buenos Aires), Argentini
Dit proefschrift is goedgekeurd door de promotor
Prof. dr. J.A. Lercher
en assistent-promotor
Dr. K. Seshan
Dedicated to:

my wife Agathe

(...may the sun be eternally obscured by the clouds, may the sea dry instantly, may the axis of the earth break as a fragile crystal, everything may happen, the death could cover me with its fatal crest but never will the flame of your love fade away on me). G.A. Becquer, “Rimas y Leyendas”. (free translation)

my son Benjamin and his future brothers and sisters

(...discovered with great delight that one does not love one’s children just because they are one’s children but because of the friendship formed while raising them. Gabriel García Márquez, “Love in the Time of Cholera” )
We can not predict the future, however, we can take action to give our children and their successors a more interesting, attractive and comfortable life.

Dr. Jaim Weitzmann (Scientist, founder of the Sieff institute precurso of The Weitzmann Institute of Science and 1st president of Israel), In "Jaim Weitzmann" by M. Guelehrter, Jerusalem 1967. (free translation)
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Abstract

In this chapter the problems related to the emission of NO\textsubscript{x}, the sources and the possibilities for their control are discussed. After a brief introduction, a description of the sources of NO\textsubscript{x} and the emission levels is given. The environmental and health related problems are presented. Subsequently the history, the regulations and the emission trends are summarized. Once we have described the main aspects of the NO\textsubscript{x} emission problem, the approaches for their removal are reviewed. Finally the state of the art with respect to the catalytic solutions to the problem is discussed with emphasis on the selective catalytic reduction of NO using hydrocarbons as reductant.
Chapter 1 - General Introduction

Introduction

The combustion of biomass and fossil fuels to meet the society demands for energy, release large quantities of pollutants to the environment. Among these contaminants are the nitrogen oxides (NO) which are the source of severe environmental problems. For the past thirty years great effort were made in the research directed to find solutions for the NOx problem. Nowadays two main methods for the removal of NOx from emission gases are employed. The selective catalytic reduction of NOx with NH3 (SCR), which is applied for stationary sources such as power plants and the three way catalyst (TWC), used for mobile sources such as automobiles. As will be discussed later in this chapter, in spite of the intense research, these are only partial solutions and include serious drawbacks. Alternatively selective catalytic reduction of NOx using hydrocarbons as reductant (HC-SCR) is currently attracting a great deal of interest. This manuscript is related to the worldwide effort to solve the NOx problem and presents our work in the development of a catalytic system to achieve that. The aim of this study is to gain knowledge on the selective catalytic reduction of NOx with hydrocarbons with the final goal to contribute to the development of a suitable catalysts for NOx abatement.

In this chapter the types, sources and the emission levels of nitrogen oxides, their influence on the environment and public health, their regulation, the approaches for their removal and the state of the art with respect to catalytic solutions for their removal is reviewed. Emphasis is placed on the selective catalytic reduction of NO using hydrocarbons.

1.1 The NOx pollution problem

1.1.1 Nitrogen oxides - Their origin and emission levels

Several types of nitrogen oxides with diverse physical and chemical properties exist [1](s Table1). Among these oxides the components of the polluting emission gases, formed by the combustion of biomass and fossil fuels, are mainly nitric oxide (NO) (more than 90%) and nitrogen dioxide (NO2) [2, 3]. The collective name given for the atmospheric pollutants NO and NO2 is NOx [4]. NOx is produced not only by burning of fuels and biomass, but also by lightning, oxidation of NH3 (produced by microbial decomposition of proteins in the soil) and volcanic activity. Every year more than 30 million tons of NOx are vented to the earth atmosphere [5].
Table 1 Nitrogen oxides and oxoions [1]

<table>
<thead>
<tr>
<th>Oxides of nitrogen</th>
<th>Oxidation number</th>
<th>Formula</th>
<th>Name</th>
<th>Structure (gas phase)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>+1</td>
<td>N₂O</td>
<td>Nitrous oxide</td>
<td>N₁¹⁰² O</td>
<td>Cᵥwv</td>
<td>Colorless gas, not very reactive</td>
</tr>
<tr>
<td>+2</td>
<td>NO</td>
<td>Nitric oxide</td>
<td>N₁¹⁰² O</td>
<td>Cᵥwv</td>
<td>Colorless, reactive paramagnetic gas</td>
</tr>
<tr>
<td>+3</td>
<td>N₂O₃</td>
<td>Dinitrogen trioxide</td>
<td>N=N O</td>
<td>Planar, C₃</td>
<td>Forms blue solid (m.p. −101 °C) and dissociates into NO and NO₂ in the gas phase</td>
</tr>
<tr>
<td>+4</td>
<td>NO₂</td>
<td>Nitrogen dioxide</td>
<td>¹⁴⁰ N O</td>
<td>Cᵥwv</td>
<td>Brown, reactive, paramagnetic gas</td>
</tr>
<tr>
<td>+4</td>
<td>N₂O₄</td>
<td>Dinitrogen tetroxide</td>
<td>N=N O</td>
<td>Planar, D₂h</td>
<td>Forms colorless liquid (m.p. −11 °C); in equilibrium with NO₂ in the gas phase</td>
</tr>
<tr>
<td>+5</td>
<td>N₂O₅</td>
<td>Dinitrogen pentoxide</td>
<td>N=N O</td>
<td>Planar, Cᵥwv</td>
<td>Colorless ionic solid [NO₃][NO₂] (m.p. 32 °C); unstable</td>
</tr>
</tbody>
</table>

Nitrogen oxoions

<table>
<thead>
<tr>
<th>Oxidation number</th>
<th>Formula</th>
<th>Common name</th>
<th>Structure</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>+1</td>
<td>N₂O³⁻</td>
<td>Hyponitrite</td>
<td>O¹²⁻ N=N</td>
<td>Usually acts as a reducing agent</td>
</tr>
<tr>
<td>+3</td>
<td>NO₂⁻</td>
<td>Nitrite</td>
<td>O¹²⁻ N=N</td>
<td>Weak base; acts as an oxidizing and a reducing agent</td>
</tr>
<tr>
<td>+3</td>
<td>NO⁺</td>
<td>Nitrosium (nitrosyl cation)</td>
<td>N—O⁺</td>
<td>Cᵥwv</td>
</tr>
<tr>
<td>+5</td>
<td>NO₃⁻</td>
<td>Nitrate</td>
<td>O¹²⁻ N=O</td>
<td>Very weak base; an oxidizing agent</td>
</tr>
<tr>
<td>+5</td>
<td>NO₂⁺</td>
<td>Nitronium (nitryl cation)</td>
<td>O¹¹⁰⁻ N=O⁺</td>
<td>Oxidizing agent, nitrating agent, and a Lewis acid</td>
</tr>
</tbody>
</table>
Chapter 1 - General Introduction

Table 2 shows the sources of global NO\textsubscript{x} emissions and their relative contributions. It can be seen that natural sources (such as lightning, stratosphere, soil, etc) are only a small fraction while anthropogenic activity (such as burning of fuels by power plants and vehicles) is the main source of nitrogen oxides emission. According to recent estimates [5] 21 million of NO\textsubscript{x} is emitted per year in the US alone and 95% of it is due to power sources and vehicles.

<table>
<thead>
<tr>
<th>Source</th>
<th>Contribution</th>
<th>N\textsubscript{2} [10\textsuperscript{6} Ton /yr]\textsuperscript{*}</th>
<th>[%]\textsuperscript{**}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Combustion of fossil fuels</td>
<td>10 - 22</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>Biomass burning</td>
<td>20</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>Natural sources</td>
<td>3 - 14</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>Ammonia oxidation</td>
<td>1 - 3</td>
<td>7</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{*}Reference [2], \textsuperscript{**}Reference [6].

In Table 3 an estimate of the NO\textsubscript{x} emissions due to human activity in the United States is given. It can be seen that in the USA 57% of the NO\textsubscript{x} emissions is related to stationary sources. This may vary for different countries, for example, it is estimated that in the Federal Republic of Germany 59% of the NO\textsubscript{x} is emitted by traffic [8]. According to[2] transportation is responsible in a selection of industrialized countries for 45-60% of the emissions. Globally both stationary and mobile sources contribute approximately to similar fractions of the produced emissions.

<table>
<thead>
<tr>
<th>Source</th>
<th>NO\textsubscript{x} [10\textsuperscript{6} ton/yr]</th>
<th>NO\textsubscript{x} [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transportation</td>
<td>7.3</td>
<td>43</td>
</tr>
<tr>
<td>Stationary fuel combustion</td>
<td>10.6</td>
<td>29</td>
</tr>
<tr>
<td>Industrial processes</td>
<td>0.6</td>
<td>16</td>
</tr>
<tr>
<td>Solid waste disposal</td>
<td>0.1</td>
<td>4</td>
</tr>
<tr>
<td>Miscellaneous</td>
<td>0.2</td>
<td>8</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>18.8</td>
<td>100</td>
</tr>
</tbody>
</table>
Another nitrogen oxide that is relevant due to its important role in the atmospheric pollution is N\textsubscript{2}O. It is produced mainly in the nature by microbial activity, however its level in the atmosphere continues to increase mainly due to anthropogenic activities\cite{9}. The human contribution to the release of N\textsubscript{2}O to the atmosphere is between 4.7 to 7 million ton per year (30-40% of the total emissions)\cite{10}. This includes activities such as adipic acid production for Nylon 66, nitric acid manufacture, fossil fuels and biomass combustion and the use of fertilizers \cite{9, 10}. N\textsubscript{2}O is converted into N\textsubscript{2} and NO in the stratosphere and it also contributes to the destruction of the earth’s protective ozone layer and to the green house effect.

Three types of NO\textsubscript{x} are distinguished according to the combustion process in which they were formed: (i) thermal, (ii) prompt and (iii) fuel NO\textsubscript{x}. Table 4 summarizes the combustion processes in which different types of NO\textsubscript{y} are formed. Thermal NO\textsubscript{x}, is generated by the fixation of atmospheric nitrogen and its formation is thermodynamically favored by high flame temperature and atomic oxygen concentration \cite{2, 3, 8}. Prompt NO\textsubscript{x} is produced by the formation of intermediate HCN via reaction of nitrogen radicals and hydrocarbons followed by oxidation of the HCN to NO. Prompt NO\textsubscript{x} is weakly dependent in the temperature and significant only for fuel rich flames \cite{2}. Fuel NO\textsubscript{x} is the result of the gas phase oxidation of nitrogen containing compounds in the fuel and from the heterogeneous oxidation of char nitrogen in the flame tail. However, from the point of view of NO\textsubscript{x} production, the oxidation of organic nitrogen compounds from fuel is not significant \cite{3}. Fuel NO\textsubscript{x} formation is independent of the temperature of the flame at normal combustion conditions and insensitive to the kind of organic nitrogen compound\cite{2}.

1.1.2 Environmental and health related Problems

Nitrogen oxides are a extremely deleterious to the environment and represent a serious hazard to the health \cite{2, 3, 7, 8}. The negative influence to the environment is caused by their contribution to the acid rain, smog, green house effect and to the depletion of the earth protective ozone layer. Water and soil pollution are also among the NO\textsubscript{x} detrimental effects.

Figure 1 shows the chemical transformation of NO in the atmosphere and how it affects the environment. NO is the precursor for the different nitrogen oxides. Once released into the atmosphere NO undergoes chemical transformations. It is rapidly oxidized by ozone, OH or HO\textsubscript{2} radicals to form higher oxides of nitrogen such as NO\textsubscript{2}, HNO\textsubscript{3} and HO\textsubscript{2}NO\textsubscript{2} \cite{3, 12}. Thus prevention of nitric oxide emission to the atmosphere can eliminate most of the NO\textsubscript{x} pollution problems.
Table 4 Formation of NO and NOx in combustion processes [2, references therein]

<table>
<thead>
<tr>
<th>Nitrogen Oxide</th>
<th>Area of formation</th>
<th>Mechanism/Reaction</th>
<th>Dependance</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Thermal NO</strong></td>
<td>Flame afterburner (fixation of N₂) (all fuels)</td>
<td>In excess of O₂</td>
<td>Concentration of O-atoms</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O + N₂ = NO + N</td>
<td>(dissociation of O₂),</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N + O₂ = NO + O</td>
<td>residence time, temperature</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fuel rich</td>
<td>(T &gt; 1300 ºC)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N + OH = NO + H</td>
<td></td>
</tr>
<tr>
<td><strong>Prompt NO</strong></td>
<td>Flame (all fuels) (Oxidation of intermediate HCN)</td>
<td>CN + H₂ = HCN +H</td>
<td>Concentration of O-atoms</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CN + H₂O = HCN+OH</td>
<td>(combustion of O₂),</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CN + N₂ = HCN +N</td>
<td>concentration of O₂</td>
</tr>
<tr>
<td><strong>Fuel NO</strong></td>
<td>Flame (Coal, heavy fuel- oil) (Oxidation of N containing fuels)</td>
<td>via CN-compounds</td>
<td>residence time</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(partly unknown) and via</td>
<td>concentration of O₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CN + H₂ = HCN +H</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>CN + H₂O = HCN+OH</td>
<td></td>
</tr>
<tr>
<td><strong>NO₂</strong></td>
<td>Flame Smoke ducts Chimneys</td>
<td>NO + HO₂ = NO₂ +OH</td>
<td>Quenching of combustion reactions (gas turbines)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2NO + O₂ = 2NO₂</td>
<td>O₂ and NO concentration,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>residence time, temperature</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(T &lt; 650 ºC)</td>
</tr>
<tr>
<td></td>
<td>Free atmosphere</td>
<td>NO₂ + hv = NO + O</td>
<td>O₂ concentration, light</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O + O₂ + M = O₃ + M</td>
<td>intensity,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NO + O₃ = NO₂ + O₂</td>
<td>residence time, air pollution</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M = N₂, O₂, H₂O or CO₂</td>
<td></td>
</tr>
</tbody>
</table>

The influence of nitrogen oxides to health is so adverse that exposure to concentrations of approximately 150 ppb of NO₂ is highly dangerous and could lead to permanent health damage [2]. Nitric oxide, due to its low water solubility, is able to reach all parts of the respiratory system and in this way diffuses through the alveolar cells and the capillary vessels of the lungs into the body. The health related problems are best summarized in “The Nitric Oxide Home page”, recently published on the Internet [13]. From diabetes to hypertension, cancer to drug addiction, stroke to intestinal motility, memory and learning disorders to septic shock, sunburn to anorexia, male impotence to tuberculosis, there is probably
no pathological condition where nitric oxide does not play an important role. To underline the significance that nitrogen oxides may have on the health of the citizens it is relevant to mention that recently (1998), the Nobel price in medicine was awarded for the research concerning the involvement of NO in human physiology.

**Figure 1** The cycles of NO$_x$ in the environment [11]

1.1.3 Emission regulations - History and legislation

From the historical point of view three rare meteorological events made it clear that air pollutants should be regulated [7]. The first one was in the Meuse valley in Belgium in 1930. Due to meteorological conditions a week long air stagnation caused pollutants to accumulate resulting in 60 people dead and many suffering respiratory problems. In 1948 similar conditions in Donora, Pennsylvania USA, resulted in 7000 illnesses and 20 deaths. In 1952, 4000 deaths were attributed to a four day “killer fog” in London. These cases as well as the long-term health effects of air pollution lead to governments worldwide to impose regulatory legislation on emission gases.

Further incentive to reduce the emissions is the enormous cost of the air pollution. Even though the evaluation in monetary terms is often difficult, and cases such as the global warming, plant or animal
species extinction or human mortality can not be satisfactorily evaluated in monetary terms, according to [14] estimates for the United States that take into consideration health costs, damage to materials, reduced agricultural productivity and other factors, ranged from a “conservative” $10 billion per year to $2000 billion per year. Furthermore it was calculated that benefits from implementation of air quality plan in the Los Angeles area in the USA could generate $1.5 to $7.4 billion per year billion per year. Another study, published in 1998 by the European Communities in Luxemburg [15], assessed the cost and benefits of attaining the limit values for ambient quality for various pollutants (e.g. NO$_x$ 40 μ/m$^3$ annual average of hourly values). The most important results of this study are summarized in Table 5. As can be observed the benefit of attaining a required 8% reduction in the emission of NO$_x$ is several hundreds of millions of EC larger than the cost related to the implementation of this standard.

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Required emission reduction [%]</th>
<th>Range of annual costs [millio ECU]</th>
<th>Benefit range [millio ECU]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_2$</td>
<td>10</td>
<td>4 - 48</td>
<td>(21)*</td>
</tr>
<tr>
<td>NO$_x$</td>
<td>8</td>
<td>5 - 285</td>
<td>(79)*</td>
</tr>
<tr>
<td>PM$_{10}$</td>
<td>50</td>
<td>50 - 300</td>
<td>(87 - 225)*</td>
</tr>
<tr>
<td>Lead</td>
<td>not quantified</td>
<td>12 - 40</td>
<td>3.2 - 5.8</td>
</tr>
</tbody>
</table>

*Benefits range relates to emission reduction to which the central estimate of costs refers

Another aspect of concern is the increasing numbers of emission sources such as vehicles. For example in 1988 there were about 500 million vehicles on the road worldwide, meanwhile in 1990, 50 million new vehicles were produced [8]. In Figure 2 the annual production of vehicles and a prediction of the vehicle population in the coming years is shown. The extrapolation shown in Figure 2 predicts a vehicle population of about 800 million in the near future. For all the mentioned reasons it is essential to control the presence of NO$_x$ in the environment. In 1955 an initiative to limit toxic emissions was taken in the US where clean air legislation was enacted [12]. It was followed by the Air Quality Act of 1967 and the Clean Air Amendments of 1970 and 1977. In 1990 further refinements in the pollution control were introduced. These legislation established air quality standards and provided significant reduction of emissions. Violation of these regulations carried civil and criminal penalties with larger fines or prison terms. In Table 6 an historical overview of the limits for CO, HC and NO$_x$ emissions from passenger cars in the USA is given.
Chapter 1 - General Introduction

Figure 2  Annual worldwide production of vehicles between 1950 and 1990 and trends of motor vehicle registration. [8].

Table 6  Historical overview of the limits for emissions from passenger cars in the USA [8]

<table>
<thead>
<tr>
<th>Year</th>
<th>Are</th>
<th>CO (g mil⁻¹)</th>
<th>HC (pp)</th>
<th>NOₓ (g mil⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1966 - 67</td>
<td>California</td>
<td>1.5%</td>
<td>275</td>
<td>-</td>
</tr>
<tr>
<td>1968 - 69</td>
<td>Federal &amp; California</td>
<td>1.5%</td>
<td>275</td>
<td>-</td>
</tr>
<tr>
<td>1970</td>
<td>Federal &amp; California</td>
<td>23</td>
<td>2.2</td>
<td>-</td>
</tr>
<tr>
<td>1972</td>
<td>California</td>
<td>39</td>
<td>3.2</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td>Federal</td>
<td>39</td>
<td>3.4</td>
<td>-</td>
</tr>
<tr>
<td>1975</td>
<td>California</td>
<td>9</td>
<td>0.9</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Federal</td>
<td>16</td>
<td>1.5</td>
<td>2</td>
</tr>
<tr>
<td>1980</td>
<td>California</td>
<td>8</td>
<td>0.41</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Federal</td>
<td>7</td>
<td>0.41</td>
<td>2</td>
</tr>
<tr>
<td>1981</td>
<td>Federal &amp; California</td>
<td>3.4</td>
<td>0.41</td>
<td>1</td>
</tr>
<tr>
<td>1993</td>
<td>California</td>
<td>3.4</td>
<td>0.25</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Similar to the USA, measures were taken in Japan, Australia and Switzerland. In 1985 the European community passed strict legislation for passenger cars and was followed by South Korea in 1987 and Brazil in 1988 [8]. The result of regulation efforts are reflected in Table 7, where the trends for air pollutant emissions in the United States between the years 1940 and 1995 is shown. It is seen that there was
a constant increase in the emission levels of air pollutants before 1980. Gradually after the implementation of regulations the stabilization or reduction of the emission levels took place emphasizing the benefits of emission regulation.

Table 7 Trends for Air Pollutant Emissions in the United States[16]

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon monoxide</td>
<td>93615</td>
<td>102609</td>
<td>109745</td>
<td>128079</td>
<td>115625</td>
<td>100650</td>
<td>92099</td>
</tr>
<tr>
<td>Nitrogen oxides</td>
<td>7374</td>
<td>10093</td>
<td>14140</td>
<td>20625</td>
<td>23281</td>
<td>23038</td>
<td>21779</td>
</tr>
<tr>
<td>Sulfur dioxide</td>
<td>19953</td>
<td>22358</td>
<td>22227</td>
<td>31161</td>
<td>25905</td>
<td>22433</td>
<td>18319</td>
</tr>
<tr>
<td>Lead</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>220</td>
<td>75</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>Volatile organics</td>
<td>17161</td>
<td>20936</td>
<td>24459</td>
<td>30646</td>
<td>25893</td>
<td>23599</td>
<td>22865</td>
</tr>
<tr>
<td>Particulate matter</td>
<td>15956</td>
<td>17133</td>
<td>15558</td>
<td>13044</td>
<td>7050</td>
<td>43337</td>
<td>42636</td>
</tr>
</tbody>
</table>

(Numbers in thousand short tons. N/A = not available.) Source U.S. Environmental Protection Agency, Office of Air and Radiation.

The emission legislation is a dynamic process, nowadays new steps are taken worldwide to improve the air quality. An increasing number of countries are adopting more stringent emission standards. In Table 8, the emission standards for passenger cars in the European Union in effect in 1996 are given.

Table 8 Emission standards for passenger cars in the European union (1996) [8]

<table>
<thead>
<tr>
<th>Engine type</th>
<th>Carbon Monoxide (g km(^{-1}))</th>
<th>Total hydrocarbons and nitrogen oxides (g km(^{-1}))</th>
<th>Particulate matter (g km(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline spark ignition</td>
<td>2.2</td>
<td>0.5</td>
<td>–</td>
</tr>
<tr>
<td>Direct injection diesel</td>
<td>1.1</td>
<td>0.9</td>
<td>0.1</td>
</tr>
<tr>
<td>Indirect injection diesel</td>
<td>1.1</td>
<td>0.7</td>
<td>0.08</td>
</tr>
</tbody>
</table>

As mentioned above the worldwide efforts to reduce pollutant emission result in more stringent regulations. To meet these demands technologies for emission control should constantly be improved. Figure 3 illustrates the benefits of such technological advances. In this particular case, the reduction in the black smoke (due to the switch to improved fuel sources) emphasizes the effect that these technological changes have on the environment.
1.1.4 Emission control methods

The emission control methods (deNO₃) can be divided in two main groups (i) combustion control techniques also named as clean methods and (ii) post-combustion abatement technology also called clean-up techniques or flue gas treatment [2, 12, 18].

Combustion control is a primary measure intended to minimize NOₓ formation by designing better burning devices that minimize the oxygen concentration, the flame temperature and the residence time in the combustion zone. Also the use of fuels with low levels of nitrogen content is an option. Examples of combustion control devices are the low NOₓ burners, flue gas recirculation, fuel reburning, staged combustion and water or steam injection. The combustion control technologies are the most cost-effective and energy efficient. A drawback of these techniques is sometimes the enhanced N₂O formation [19]. The main disadvantage of combustion control methods is the low NOₓ conversion (<70%) compared to some post-combustion techniques (90-99 %)[2, 20, 21].

Post-combustion techniques are secondary measures for the treatment of the flue gas already containing NOₓ. In general five methods are available for controlling gaseous emissions: absorption, adsorption, condensation, incineration and chemical reaction. Specific problems such as nitrogen oxides require often combination of methods [7]. According to the environment in which they are applied secondary methods for NOₓ control can be separated in wet and dry methods. The wet methods or chemical scrubbing are chemical oxidation/adsorption processes that are applied to small NOₓ sources and have disadvantages such as high cost and waste generation in the form of dissolved nitrates and nitrites. The dry methods include catalytic and non catalytic processes. An example of a non catalytic methods is the Selective Non-catalytic Reduction (SNCR), developed by Exxon, it is an homogeneous gas phase reduction process in which NOₓ is selectively reduced by NH₃ to N₂. This process requires low capital investment however its temperature operation window (850 °C -1050 °C) is very narrow and difficult to operate in larger facilities. In comparison to the non catalytic solutions, catalytic methods offer lower operating temperatures and are the primary method to control gas emissions [7, 19]. The possible catalytic solutions can be divided in four categories. The Selective catalytic Reduction (SCR) using ammonia as reductant, The Three Way Catalyst (TWC), the direct NO decomposition and the Selective Catalytic Reduction using hydrocarbons as reductant (HC-SCR).
Figure 3 Pittsburgh (Pennsylvania USA) before the and after the decrease in black smoke. [17]
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Among all the emission control technologies the most widely applied method is the Selective Catalytic Reduction (SCR or NH$_3$-SCR) [6, 18-21]. This method is considered the best available control technology for industrial deNOx. The technology has several variants depending on the supplier. It was first introduced in the 1970s in Japan, later in Germany and the USA. It is expected that as a result of the Clean Air Act of 1990 a wider use of SCR will be implemented.

In the SCR method the emission abatement is achieved by injecting NH$_3$ into the flue gas which with the help of a catalyst chemically reduces the NOx to N$_2$ and H$_2$O. NH$_3$ is used as a reductant because it is very selective and reacts mostly with NOx and not with O$_2$ usually present in exhausts. Although this process involves a number of reactions it can best be represented by equation (1).

\[
4\text{NO} + 4\text{NH}_3 + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \quad (1)
\]

The process operates at low temperatures 300-400°C and $\text{WO}_3/\text{TiO}_2/\text{SiO}_2$ catalyst are commonly used due to their high activity and sulfur tolerance. The major advantage of the Selective Catalytic Reduction is the high degree of NOx conversion that can be achieved (> 95% conversion) [20, 21]. This method has several known disadvantages. It is quite expensive compared to the combustion control methods. Catalyst reactor system, NH$_3$ injection unit and NH$_3$ storage is necessary. To achieve high conversions ammonia has to be injected into the flue gas before the catalyst and this requires sophisticated distribution pipes and nozzles. Anhydrous ammonia need to be transported and stored near the control unit. Furthermore oxidation of sulfur contamination in the fuel by vanadia forms SO$_2$ and SO$_3$ that subsequently form ammonium sulfate and bisulfate (by reaction of SO$_3$ with NH$_3$ and H$_2$O). These salts cause plugging and corrosion. All these problems make the operation of the utility complicated. In addition the reaction leaves 1 to 20 ppm of unreacted NH$_3$ which is a pollutant by itself.

The three way catalyst (TWC) technology is the principal method of controlling the emissions from internal combustion engines from vehicles. This catalytic treatment method has been in use since the 1979 model year [22]. The name indicates the simultaneous removal of carbon monoxide and uncombusted hydrocarbon by oxidation to CO$_2$ and H$_2$O and the reduction of nitrogen oxides to N$_2$ and O$_2$. This became possible due to the development of the O$_2$ or lambda sensor. This electronic sensor ensures that the air to fuel ratio will remain around the optimal air/fuel ratio of 14.6 wt basis. Figure 4 shows the influence of the air-fuel ratio on the operation characteristics of a three way catalyst.

If the air to fuel ratio is not in a narrow window near 14.6 the catalyst activity results in emission of larger amounts of NOx in the air rich mixture and larger emission of CO and unburned hydrocarbons in a fuel rich mixture (see Figure 4).
Figure 4 Three way catalyst simultaneous conversion of $\text{NO}_x$, CO and Hydrocarbon [23]

The three way catalysts in use nowadays are manufactured in a honeycomb monolithic form and are composed of 0.1-0.15% precious metals with a ratio of Pt to Rh of 5-1 and varying concentrations of bulk high surface area $\text{CeO}_2$ mixed with $\gamma$-$\text{Al}_2\text{O}_3$ washcoat stabilized with 1-2% of $\text{La}_2\text{O}_3$ and/or $\text{BaO}$[23]. Pt is involved in the oxidation, Rh in NO reduction while the main role of $\text{CeO}_2$ is in the storage of $\text{O}_2$ needed in the case of fuel rich conditions. The catalysts are very efficient (< 95% NOx conversion) [8, 23] provided their used under appropriate conditions. Among the problems of the TWC are their poisoning by sulfur compounds and the liberation of unburned hydrocarbons during cold start of the engine. The main problem nowadays is that the environmental regulations demand better fuel efficiency. This is achieved with engines that operate under lean burn conditions. Not only that under these conditions formation NOx is favored but in the presence of excess of $\text{O}_2$ these catalysts are not able to reduce the nitrogen oxides. The same problem exists for applications in diesel engines and power plants emissions. Toyota has pioneered a new engine - catalyst system which operates lean during cruise conditions and results in 5-6% fuel economy savings. The NOx generated is stored in an alkaline metal oxide such as BaO incorporated to the TWC. Periodically the engine goes to fuel rich conditions for a short time during which the NOx is reduced.[23]. The main problem with this method is that adsorbed sulfur oxides cause permanent deactivation of the storage function. Alternatives need to be found.

The demand for improved fuel economy and lower emissions regulations are the driving force to develop catalytic solutions that will operate under lean conditions. As mentioned earlier the use of ammonia has several disadvantages such as ammonia slip, equipment corrosion, plugins, transport through
residential areas, etc. Thus alternatives are being investigated. One approach is the direct catalytic decomposition of NO to N\textsubscript{2} and O\textsubscript{2}. The direct decomposition of NO to N\textsubscript{2} and O\textsubscript{2} is an attractive option because it does not involve the use of reductant (see Equation (2)).

\[
\text{NO(g)} \rightarrow \frac{1}{2} \text{N}_2 + \frac{1}{2} \text{O}_2 \quad \Delta G^0 = -86 \text{kJ/mol} \quad (2)
\]

Thermodynamically the reaction is favorable up to 1000°C, however due to its high activation energy 364 kJ/mol[3] a catalyst is necessary. In their pioneering work Iwamoto et al. [24] reported in 1986 that Cu/ZSM-5 was an active catalyst for the decomposition of NO to N\textsubscript{2} at 500 °C. In a later study[25] it was shown that complete NO conversion to N\textsubscript{2} was obtained. Since then many catalysts were tested, [3], however, until now no catalyst was found to be suitable for practical application due to lack of enough activity, the inhibiting effect of oxygen and durability under reaction conditions [3, 19].

Following the research of Iwamoto et al. it was published in the patent literature that Cu-zeolites were effective catalysts for the reduction of NO\textsubscript{x} emission when applied to the exhaust of real lean burn engines, however it also was shown that the reaction taking place was not the direct decomposition of NO but the reduction of NO by hydrocarbons present in the emission gases [26]. These results are connected to the development of an alternative approach to reduce the NO\textsubscript{x} called Selective Catalytic Reduction of NO\textsubscript{x} with Hydrocarbons (HC-SCR). HC-SCR was tested already in the 1970's but was abandoned at this time due to the low selectivity to N\textsubscript{2} compared to NH\textsubscript{3}-SCR [26].

Nowadays HC-SCR is attracting a lot of interest and it is believed to be the most promising way to eliminate nitrogen oxide [3, 21, 27-29]. Low levels of unburned hydrocarbons are already present in the exhaust gases of all emitting sources and their reductive power can be utilized. In Table 9 the typical exhaust gas composition from a gasoline -powered automobile is shown. Also a second possibility for this approach could be the injection of these hydrocarbons from an external source as in the case of NH\textsubscript{3}. Since the subject of this work is essentially the HC-SCR in the following section this approach will be discussed in more detail and the state of the art with respect to the types of catalysts used in HC-SCR and mechanistic aspects will be reviewed.


Table 9 Typical exhaust gas composition from a gasoline-powered automobile [8]

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration [vol %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>71.0</td>
</tr>
<tr>
<td>CO₂</td>
<td>18.0</td>
</tr>
<tr>
<td>H₂O</td>
<td>9.3</td>
</tr>
<tr>
<td>Main Pollutants</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>0.85</td>
</tr>
<tr>
<td>NOₓ</td>
<td>0.095</td>
</tr>
<tr>
<td>HC</td>
<td>0.05</td>
</tr>
<tr>
<td>particles</td>
<td>0.005</td>
</tr>
<tr>
<td>O₂ and noble gases</td>
<td>0.7</td>
</tr>
</tbody>
</table>

1.2 Removal of NOₓ by SCR with hydrocarbons (HC-SCR) - State of the art

1.2.1 Catalyst for HC-SCR

As mentioned earlier after the initial discovery in 1986 that Cu/ZSM-5 decomposes NO, by Iwamoto et al. [24], it was independently published in 1990, by Iwamoto et al. [30] and Held et al. [31] that alkanes and alkenes are suitable for NO reduction over Cu-ZSM-5 in the presence of excess oxygen. Furthermore, in contrast to the inhibitory effect shown by oxygen in the direct decomposition of NO, in the presence of hydrocarbons a beneficial effect in the NO conversion to N₂ was found. This was the starting point of an enormous effort to develop a suitable catalyst for this process.

A large number of catalysts for HC-SCR were investigated and reported in the literature [3, 21, 27-29]. The catalysts can be divided in 5 categories: (i) oxides, (ii) zeolites, (iii) metals (mainly transition metals) supported on zeolites, (iv) supported noble metals and (v) multi-functional catalyst.

Among the oxide based catalysts that were reported to be active in the HC-SCR are: (i) simple oxides such as: Al₂O₃, SiO₂-Al₂O₃, TiO₂, ZrO₂, Fe₂O₃, CeO₂, La₂O₃ [eg. 32-35] (ii) metal oxides (eg. Cu, Co, Ni, Mn, Fe, La, Ag) [eg. 36-41] supported on silica and alumina and (iii) perovskites (eg. La₆Sr₄Al₄O₁₉) [42].

Comparing the activities of oxide based catalysts it was found that alumina is the most active (a maximum NO reduction of 32% at 300 °C was reported) while silica is not active at all [32]. There ar
several reports in the literature that the activity of the above mentioned oxides was improved by the addition of transition metals. Such is the case for Cu/Al₂O₃ [39]. Another example is Sr which was found to promote La₂O₃ [43] and Co/Al₂O₃ [36]. Oxides (bulk and supported) exhibit only moderate activity (< 400 ºC), but on the other hand there are active with a wide range of hydrocarbons [29]. Their main drawback is that they are sensitive to sulfur.

Several studies on H-zeolites such as H-Mordenite, H-ZSM-5 etc., were reported [40, 44, 46]. It is interesting to note that many had reported that protonated zeolites are not very active in the reduction of NO [40, 44, 46] while they show higher activity in the reduction of NO₂ [45, 46]. The main disadvantage zeolites have is their low activity and the negative effect of water on their performance [29].

The early findings that Cu/ZSM-5 is active in HC-SCR [30, 31] generated special interest in the transition metals supported on zeolites catalysts. Later Li et al. reported that Co/ZSM-5 was active in the HC-SCR with CH₄ [47, 48]. The high selectivity of Co supported on zeolite catalyst specially when CH₄ is the reductant resulted in a large number of publication that deal with HC-SCR over these catalysts. That is the case of Co/ZSM-5, Co/FER, Co/BEA, etc [40, 45, 47-53]. Other transition metals supported on zeolites catalysts that were reported to be active are (eg. Fe, Ga, Mn, Ce) [54-58]. In particular promising results were obtained over Fe/ZSM-5 [54, 55]. This catalyst showed high activity and durability in presence of H₂O and SO₂ which is one of the requirements for practical application due to the presence of these compounds in the emission gases. However the results of Feng et al. [54] had some problems with reproducibility, while the high activity reported by Chen et al. [55] decreased somewhat with time on stream and produced high concentrations of CO. In conclusion many transition metal-zeolite systems display good activity and selectivity to N₂. However some of these catalyst are hydrothermally unstable or show sensitivity to SO₂.

As mentioned in the previous section the role of noble metals in the reduction of NOx in the TWC is known, thus, a great deal of work was done with supported noble metals (eg. Rh/ZSM-5, Pt/ZSM-5, Pt/Al₂O₃, Pt/SiO₂, Pt/La₂O₃, Pt/ZrO₂) [59-67]. In comparison to other catalysts the main quality of the catalyst containing noble metals is their high activity at low temperatures and their high H₂O and sulfur tolerance [eg 22, 60, 64]. Regrettably these catalysts high activity is accompanied by the formation of large concentrations of N₂O, a pollutant by itself [60, 62]. Another problem with these catalyst is that in many cases their temperature activity range is very narrow.
As will be discussed in the following sections, HC-SCR consists on several reaction steps. It is difficult to find a single active phase that will catalyze several processes simultaneously and will provide satisfactory activity and durability. Multi-functional catalysts try to tackle the problem by combining active components from the categories mentioned above. In these catalysts, one function, for example catalyzes the oxidation of NO to NO$_2$ while the second function catalyzes the reaction of NO$_2$ with the hydrocarbon. This is the case of, Pd/H-ZSM-5 the physical mixture of Co/Al$_2$O$_3$ and H-ZSM-5 or Mn$_2$O$_3$ and Ce/ZSM-5 [57, 68-73].

1.2.2 Hydrocarbons as reductants in HC-SCR

As mentioned before, low levels of unburned hydrocarbons (the potential reductant of NO$_x$) are present in the emission gases and their amount and composition may vary according to the source. For example, the exhaust of a gasoline powered engine contains typically 500 to 1000 vppm of unburned hydrocarbons [7, 8]. A typical distribution of unburned hydrocarbons present in the exhaust of a gasoline engine is shown in Table 10.

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Mass [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatics</td>
<td>46.2</td>
</tr>
<tr>
<td>Olefins</td>
<td>27.5</td>
</tr>
<tr>
<td>Paraffins (C$_3$)</td>
<td>11.5</td>
</tr>
<tr>
<td>Methane</td>
<td>7.0</td>
</tr>
<tr>
<td>Paraffins (C$_2$ - C$_4$)</td>
<td>4.5</td>
</tr>
<tr>
<td>Others</td>
<td>3.3</td>
</tr>
</tbody>
</table>

A large part of the research on the use of hydrocarbons as reductants in HC-SCR was devoted to CH$_4$ [19, 21]. Not only C$_4$ is relatively safe and offers a low price and is conveniently available. Methane is 90% of the natural gas content which is widely used as fuel in many applications such as electric power generation. Lack of reactivity is one of the problems of using methane whose activation is difficult. In the past, methane was considered a non-selective reductant due to its tendency to combust with O$_2$ rather than reduce NO$_x$. However, nowadays several selective catalysts have been found and CH$_4$ is reconsidered. Alkenes and alkynes are very reactive and HC-SCR takes place in many cases already at very low temperatures (200 °C). They are a main portion of the hydrocarbons present in the emission gases (s
Table 10) and due to their reactivity they are considered as selective reductive agents. In most of the cases olefins are more effective than paraffins in NO\textsubscript{x} reduction. Further it was shown that this was independent of the carbon number [74]. The role of hydrocarbons in the HC-SCR is as important as the catalyst type. They influence the temperature at which substantial activity takes place and under special circumstances may influence the selectivity to the products. For example Burch et al.[75] reported that over Pt based catalysts the selectivity to N\textsubscript{2}O (a major drawback of these systems) was completely suppressed by the use of toluene as reductant.

1.2.3 Mechanistic aspects of the HC-SCR

Several general features are characteristic of HC-SCR catalytic activity. A common characteristic in HC-SCR is that NO\textsubscript{x} conversion reaches always a temperature of maximum activity. Further increase in temperature shows decrease in the NO\textsubscript{x} conversion. This decrease in activity is usually not related to deactivation of the catalyst but to decrease in availability of reductant due to unselective total combustion with oxygen. Another salient feature of HC-SCR is that NO\textsubscript{x} conversion is intimately related to the hydrocarbon conversion in such a way that during increasing of reaction temperature maximum NO\textsubscript{x} reduction is obtained almost simultaneously with maximum hydrocarbon conversion.

As mentioned earlier HC-SCR is complex and include several reaction steps. Even though the reaction has been subject to numerous studies the mechanism of the selective catalytic reduction with hydrocarbons is still under debate. Several types of mechanism were suggested and it may well be that more than one pathway may exist according to the reaction conditions [26,76-78]. In very rough lines three main groups of HC-SCR reaction schemes are proposed in the literature. One group is the catalytic decomposition of NO over a reduced metal site. The role of the hydrocarbon is to scavenge the adsorbed oxygen thus regenerating the active site. The second group involves the formation of partially oxidized hydrocarbon intermediates that react with NO\textsubscript{x} to yield N\textsubscript{2} while a third one emphasizes the oxidation of NO to NO\textsubscript{2} as a first essential step that it is followed by the reduction of NO\textsubscript{2} to N\textsubscript{2} by the hydrocarbon possibly via an organic-nitrogen containing intermediate. In Figure 5 the thr proposed mechanisms are summarized.
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- Catalytic decomposition of NO and subsequent regeneration of the active site by the hydrocarbon.

\[
\begin{align*}
2 \text{NO} + \text{HC} + \text{O (ads.)} & \rightarrow \text{N}_2 + 2 \text{O (ads.)} + \text{CO}_x + \text{H}_2\text{O} \\
\end{align*}
\]

- Partial oxidation of the hydrocarbon.

\[
\begin{align*}
\text{HC} + \text{O}_2 \text{ and/or NO}_x + \text{HC*} & \rightarrow \text{N}_2 + \text{CO}_x + \text{H}_2\text{O} \\
\end{align*}
\]

- Oxidation of NO to NO\(_2\) which acts as a strongly oxidizing agent.

\[
\begin{align*}
\text{NO} + \frac{1}{2} \text{O}_2 \text{ or MeO} + \text{NO}_2 + \text{HC} & \rightarrow \text{N}_2 + \text{CO}_x + \text{H}_2\text{O} \\
\end{align*}
\]

**Figure 5** Scheme of the three proposed mechanisms for HC-SCR [29]

The fact that catalysts such as Cu/ZSM-5 decomposes NO to nitrogen and oxygen in the absence of hydrocarbons provided the basis for the proposition of a decomposition mechanism [64, 79]. In contrast to the direct decomposition of NO the presence of hydrocarbon species add complexity to reaction and multiplies the possible reaction pathways. Based on transient kinetics experiments over Pt\(\gamma\)-Al\(_2\)O\(_3\) Burch *et al.* [64] proposed a NO decomposition mechanism. Decomposition of NO leaves surface bound N which may recombine with another N or NO forming N\(_2\) or N\(_2\)O, respectively. During HC-SCR experiments over Pt based catalysts with C\(_3\)H\(_6\) and C\(_3\)H\(_8\) Rottlander *et al.* [66] found higher NO conversions with propene. They argued that a decomposition mechanism should give similar NO reductions for both C\(_3\)H\(_6\) and C\(_3\)H\(_8\) because of comparable efficiency for the removal of surface oxygen. To account for discrepancies of this kind it was proposed that NO reduction occurred via carbonaceous deposits [66, 80, 81] or oxygenates [80] derived from propene. The involvement of carbonaceous deposits in the HC-SCR is supported by experiments that show sustained NO reduction activity for some time after removal of the hydrocarbon from the feed [80-84]. Pitchon *et al.* [63] argue that over Pt based catalyst no coke formation was observed.
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during SCR with propene in presence of O₂. Therefore it was proposed that partially oxidized hydrocarbons species are the intermediates in the reduction of NO to N₂ [85-87]. This view is supported by the fact that NO reduction and the oxidation of the hydrocarbon starts almost at the same temperature. However this mechanism has difficulty in explaining why propene is more effective than partially oxidized reductants such as propanol, ethanol, acetone [87].

Another approach is taken by others that claim that NO₂ derived from the oxidation of NO, is reduced by the hydrocarbon to N₂ yield [57, 68, 76, 77, 88-91]. In this mechanism reaction of NO₂ with hydrocarbon forms an organo nitrogen (-nitro,-nitroso) intermediates. Decomposition /dehydration or hydrolysis of this intermediate produce: isocyanate [33, 41, 65, 88, 92, 93], oximes [43, 76], or nitril [44, 91, 94]. Hydrolysis or reaction of these with NO, NO₂ or O₂ forms N₂. We mentioned earlier that oxygen has a positive influence on NO reduction in HC-SCR. Furthermore, NO₂ is very reactive under HC-SCR. These observations and evidence from infrared studies on the surface species present during HC-SCR support this view [33, 41-44, 65, 76, 88, 91-94].

1.2.4 HC-SCR - Future challenges

Even though that HC-SCR is a promising method and was subject to intensive research during the last years there are still many problems to overcome. As mentioned in the previous section HC-SCR is complex and involves several reaction steps. In spite of the great effort invested and that many suggestions were made the mechanism of the selective catalytic reduction with hydrocarbons remains not fully understood. Thus more relevant mechanistic studies are necessary to clarify the reaction pathways, to identify intermediates and determine the reaction active sites for the different reaction steps.

From the practical point of view catalysts that are more active than those known until today need to be found. (e.g. space velocities of 30,000 GHSV for power plants[5]). Secondly, since NOₓ emissions usually are accompanied by presence of water vapor and in many cases sulfur compounds, this catalytic activities need to be achieved in presence of water and SO₂ and should be able to be sustained for periods of months. It was already mentioned that some improvements in that respect were reported recently for Fe/ZSM-5 catalysts, however, the sensitivity towards water and sulfur compounds is still a major challenge that needs to be faced. Finally in the case of many highly active catalysts as in the case of Pt based catalysts the issue of high N₂O selectivity needs to be solved before any possible application.
1.3 Scope and structure of the thesis

The pollution of the environment by nitrogen oxides (NO\textsubscript{x}) presents a serious threat to the quality of life of the world population and in spite of the great effort made, until today only partial solutions have been found. Among the existing proposed solutions there is a promising alternative, the so-called (HC-SCR) selective catalytic reduction of NO\textsubscript{x} using hydrocarbons as reductant. To develop a catalytic solutions to the NO\textsubscript{x} first we must understand the process of HC-SCR. This knowledge will provide us with the necessary tools to achieve that. With this intentions in mind, this thesis is part of a world wide effort on the field of HC-SCR devoted to gain knowledge on the selective catalytic reduction of NO\textsubscript{x} with hydrocarbons with the final goal to contribute to the development of a suitable catalysts for the above mentioned process.

Chapter 2 describes the details of the experimental set up and of the analytical methods employed through the thesis. Among the catalyst for HC-SCR, Co based catalyst are known to be active and selective, thus as a starting point of this work, a study on the HC-SCR over a series of Co based catalysts supported on zeolites was undertaken and the results are presented in Chapter 3. Correlation between catalytic characteristics and kinetic results are employed to understand the working catalyst and this is used as basis for catalyst optimization. With the intention to prepare a multi-functional catalyst that will preserve the desired characteristics of the individual components minimizing their negative aspects catalysts based on Co-Pt supported on ZSM-5 were investigated. In Chapter 4 the results of this study are discussed. Bimetallic Co-Pt/ZSM-5 catalysts with low Pt contents (0.1 wt %) showed a synergistic effect by combining high stability and activity of Pt catalysts with the high N\textsubscript{2} selectivity of Co catalysts. Further it was found to be sulfur and water tolerant. Its positive qualities lead us to study the mechanism that takes place over this catalyst during HC-SCR. The results of an in-situ i.r mechanistic study over this catalyst is reported in Chapter 5. From the results presented in Chapter 5 a mechanism operating over the Co-Pt/ZSM-5 catalyst is proposed. The modification of Co catalyst with Pt improved the catalysts, however further improvement was found to be hindered by high selectivity to N\textsubscript{2}O. Since Rh catalyst are generally less selective to N\textsubscript{2}O, the modification of Co catalyst with Rh was studied and the results are summarized in Chapter 6. Chapter 7 presents a comparison between the Co-Pt and Co-Rh systems. Finally we evaluate the results of this study and general conclusions with suggestions for design of an optimal deNO\textsubscript{x} Catalyst.
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15. Economic evaluation of air quality targets for sulfur dioxide, nitrogen dioxide, fine and suspended particulate matter and lead, final report, XIII, 80, Office for official publications of the European Communities Luxembourg (1998).
Chapter 1 - General Introduction

CHAPTER 2

Experimental

Abstract

In this chapter the experimental techniques employed for the preparation, characterization and testing of the catalysts through this thesis are summarized and the set up for kinetic measurements is presented.
2.1 Catalysts preparation

The catalysts used in this study were based on Co, Pt and Rh supported on zeolites. The parent zeolites were ZSM-5 (Na form, Si/Al = 38.5, P.Q. Zeolites), FER (Na form, Si/Al = 30, Shell) and F (Na form, Si/Al = 10, Shell). When needed the ammonium form of the zeolites was prepared by heating first the zeolite in N₂ and subsequently in air at 500 °C for 12 hours. Then, the zeolites were ion exchanged twice with 0.1M NH₄NO₃ solution. After ion exchange the NH₄/Zeolite contained < 0.01 wt% Na as determined by atomic absorption spectroscopy.

For the preparation of catalysts three methods were employed: (i) Liquid State Ion Exchange (LSIE) (ii) Incipient Wetness (IW), and (iii) Solid State Ion Exchange (SSIE)[1]. Typical procedures for the three methods are given below.

Incorporation of Co onto the zeolites by LSIE was carried out with a Co(NO₃)₂ solution (0.01M). The NH₄+/Zeolite (5g) was suspended in the Co(NO₃)₂ solution (250ml) and stirred at 80 °C for 24 hrs. The catalyst was then filtered, washed with deionized water and dried in air at 120 °C for 8 hours. The whole procedure was repeated 3 times. For IW the NH₄⁺ exchanged form Zeolite was heated (500 °C at 2 °C/min in He and was maintained at this temperature for 12 hrs) to decompose and remove the NH₄⁺ leaving the zeolite in the acidic form. The required loading of Co(NO₃)₂·6H₂O was dissolved in the amount of water that 1g of zeolite would absorb. The metal solution was then added drop wise to the zeolite and the resultant paste was thoroughly mixed. The samples were then dried in air at 120 °C for 8 hours. SSIE was carried out by thoroughly grinding a mixture of the zeolite (eg. NH₄+/ZSM-5 (5g) with the required amounts of CoCl₂·6H₂O. The resulting mixture was heated to 500 °C at 2 °C/min in He and was maintained at this temperature for 12 hrs. During the heating cycle the samples were maintained for three hours near the melting point (80 °C) and boiling point (105°C) of Co(Cl)₂. After this procedure the catalyst was washed with de-ionized water and dried in air at 120 °C for 8 hours.

2.2 Catalyst characterization

2.2.1 Atomic absorption spectroscopy

The metal loading was determined by atomic absorption spectroscopy (AAS) with a VARIAN AAS spectrometer. The solid samples (±100 mg) were dissolved in 5 ml HF + 3 ml HCl + 1 ml HNO₃. This solution was heated on a sandbath until the sample was completely dry. Then, 3 ml HCl were added again to the sample to dissolve the remaining salts. The solution was made up to 50/100 ml in a volumetric flask and then used for the AAS measurements.
2.2.2 High resolution electron microscopy

In order to study the morphology size and distribution of metals introduced into the zeolites, high resolution electron microscopy (HREM) was employed. HREM was performed in the NCHREM Delft, The Netherlands using a Philips CM 30 T Electron Microscope with an LaB₆ filament as the source of electrons operated at 300 Kv. Samples were mounted on a microgrid carbon polymer supported on a copper grid by placing a few droplets of a suspension of ground sample in ethanol on the grid, followed by drying at ambient conditions. Elemental analysis was performed using a LINK EDX system.

2.2.3 X-ray absorption spectroscopy

In order to evaluate the oxidation state of the metal, the size and distribution of metal particles introduced into the zeolites, X-ray absorption spectra were employed (XAS). EXAFS measurements were carried out at the SRS in Daresbury on beamlines 9.2 and 8.1. The details of the cell used for EXAFS measurements can be found in ref 2. The spectra were collected in transmission mode, with a Si (220) monochromator detuned to 50% on beamline 9.2 and 70% on beamline 8.1, to remove high energy harmonics present in the beam. The analysis was carried out using standard analysis procedures [3]. Th EXAFS spectra were collected at -103 ºC in flowing He. The catalysts were activated at 500 ºC in flowing He and XANES spectra were taken during the processes. Typically the samples of the freshly prepared catalyst after activation and after reaction (i.e., exposure to 1000ppm NO, 1000ppm C₃H₆ and 5% O₂ in He between 200 ºC-500 ºC for 24 hr) were studied. For comparison the spectra of metal foil and relevant oxides (e.g., Co₃O₄, CoO PtO₂ etc) were taken as well.

2.2.4 Infrared spectroscopy

Infrared spectroscopy (IR) was employed to study the changes in the zeolite matrix after ion exchange procedures and the surface species present over the catalyst under reaction conditions. The i.r. measurements were performed in situ on a BRUKER IFS 88 FTIR spectrometer (resolution of 4 cm⁻¹) in a continuous gas flow mode using the transmission-absorption technique. The i.r. gas cell was equipped with a heatable sample holder and CaF₂ windows. For details of the setup see ref 4. Spectra were recorded in the range from 3800 cm⁻¹ to 1300 cm⁻¹ with a time resolution of 30s. The catalysts were pressed into a self supporting wafers (2 mg) and activated in flowing He at 500 ºC for one hour. Subsequently, the catalysts were heated to the required temperature and the reactant gases were brought in contact with the catalyst. Difference spectra were obtained by subtracting the spectrum of the catalyst from the spectra measured during the reaction. Both spectra were collected at the same temperature. The difference spectra
shows bands with increased intensity pointing upwards while bands with decreased intensity point downwards (negative peaks).

2.2.4 Temperature programmed desorption

Temperature-programmed desorption (TPD) of ammonia was employed to assess the zeolite acid sites. In Figure 1 a schematic drawing of the TPD apparatus is shown. Typically a 50 mg catalyst sample was evacuated in the quartz glass tube and then activated by heating to 550°C with a ramp of 10 °C/min and a dwell temperature of 30 min at a pressure of $10^{-3}$ mbar. After cooling down to room temperature ammonia was adsorbed until equilibrium was reached (equilibrium pressure ~9.5 mbar). Then the sample was evacuated for 1 hour to remove the excess and weakly adsorbed ammonia. The TPD measurement was taken from 25°C to 600°C using a heating rate of 10 °C/min. The detector was a BALZERS quadrupole mass spectrometer.

![Figure 1 Schematic drawing of the setup used for TPD experiments](image-url)
2.3 Catalyst Testing

In Figure 2 a schematic drawing of the kinetic setup is shown. The setup was composed of two gas stream lines (i) the reactants line (ii) the blank line (He). To avoid condensation all the lines were traced to a temperature of 85 °C. The gases in line (i) were mixed by means of four Brooks mass flow controllers. The He in line (ii) was used to activate the catalysts and to purge the system and was also controlled by a Brooks mass flow controller. When needed water could be added to the reactants line (i), through a septum, with the help of a syringe pump. A set of two four port valves switched the lines between the reactor and a bypass line. The reactor used was a U-shaped quartz tube with an internal diameter of 8 mm and the catalyst bed was supported by means of two plugs of quartz wool. The catalyst was pelletized, crushed and sieved to 0.3 mm-0.6 mm before use. The temperature of the catalyst bed was controlled by a Eurotherm 903P temperature controller. For catalyst testing, the catalyst was activated in situ by heating to 500 °C for 1 hr in flowing He. After activation, the flow was switched to the reactant mixture. The typical reactant gas mixture consisted of 1000 ppm NO, 1000 ppm C₃H₆, 5% O₂ balanced with He to 100%. A total gas flow of 100 ml/min was passed through the catalyst bed (0.2 g). The resulting GHSV was 15000 hr⁻¹, based on the apparent bulk density of the catalyst bed (0.5 g/cm³). Kinetic measurements were carried out at temperature intervals of 25°C between 200°C to 500°C.

The products were analyzed simultaneously by gas chromatography (Varian 3700 equipped with a TCD detector and a molecular sieve 5A column for separation of N₂, O₂ and CO and porapak Q column for N₂O, C₃H₆ and CO₂ analysis) and a chemiluminescence NO-NO₂-NOₓ analyzer (ThermoEnvironmental Instr., Model 42C, NO, NO₂ analysis) (Figure 1). To ensure sufficient sample flow for the analysis the gas stream coming out of the reactor was split and controlled with the help of two needle valves. To avoid interferences and ensure precise measurement the sample for the NOₓ analyzer was always in a constant gas matrix environment. This was achieved by diluting the stream for the NOₓ analyzer with dry air with a constant ratio (approximately 150 times volume dry air to volume of sample). The dilution was performed with an EPM 797 diluting stack gas sampler equipped with a glass critical orifice and it was maintained at a constant temperature of 60 °C to avoid condensation before dilution. The system uses an air driven aspirator which extracts the sample through a glass critical orifice then dilutes with dry air at a constant ratio determined by the size of the orifice. This ensures proper measurement conditions and reduces deposition of pollutants and condensation in the detector. The electronic components of the setup were connected to a computer that controlled the data acquisition process with the help of CSW progra (Chromatography Station for Windows, Data Apex Ltd, Czech Republic.).
Figure 2 Schematic drawing of the kinetic setup used for catalyst testing
ACKNOWLEDGMENTS

The authors thank Dr. Patricia J. Kooyman from the National Center for HREM Delft, The Netherlands, for the TEM measurements, Dr. S. Feast and I.r M. Tuchen for the assistance in the characterization and preparation of the catalysts and for making Figure 1.

REFERENCES

CHAPTER 3
On the physicochemical properties of Co/ZSM-5 prepared by ion exchange and incipient wetness impregnation

Abstract
The influence of different preparation methods (i.e. solid state or liquid phase ion exchange and impregnation) on the physicochemical properties of Co in zeolites have been studied by temperature programmed desorption (TPD), X-ray absorption spectroscopy (XAFS), Fourier Transform Infrared (FTIR) spectroscopy and by reduction of NO in presence of oxygen with propene as reductant. It was found that all the preparation routes led to Co exchanged metals ions at the bridging oxygen of Si-O-Al groups and the excess of Co was present as Co oxide clusters. The performance of the catalysts was influenced by the preparation methods and these differences are explained in terms of the oxidic Co phase.
Chapter 3 - On the physicochemical properties of Co/ZSM-5 ...

3.1 INTRODUCTION

Co/ZSM-5 is a promising catalyst for the selective reduction of NO\textsubscript{x} by hydrocarbons (HC-SCR). The first report dates back to 1992 [1] where it was shown that the material is able to selectively convert NO to N\textsubscript{2} in the presence of oxygen using, \textit{e.g.} methane as reductant. Following this report a series of other studies has been published [\textit{e.g.} 2, 3] in which the use of Co exchanged zeolites for selective NO\textsubscript{x} reduction is discussed.

Generally, it is assumed that in these catalysts Co is present either as Co\textsuperscript{2+} ions exchanged for Brønsted acid sites, or as oxidic clusters [\textit{e.g.} 4-7], however, the nature and role of Cobalt species with respect to the reduction of NO, however, is still under debate.

It has been shown [\textit{e.g.} 8-14] that the catalytic properties subtly depend upon the nature of Co involved in the catalyzed reaction, thus, several publications deal with the position and environment of Co ions in the zeolite lattice with help of computational modeling or different characterization techniques. Li \textit{et al.} [4] report that NO reduction activity is proportional to the amount of exchanged Co ions and suggest that Co\textsuperscript{2+} ions are the active site at which selective reduction takes place. Based on the difference in catalytic performance for the reduction of NO with methane over Co/ZSM5, Co/FER, Co/FAU the authors furthermore state that the position, environment and coordination of Co\textsuperscript{2+} ions, in different zeolite channel systems has a significant influence.

Over exchange of Co (i.e. exchange degrees above 100\% based on the stoichiometric ratio of Co/Al) results in the formation of oxide phases during calcination (dehydration of Co hydroxide clusters). The influence of these Co oxide clusters on the activity in the HC-SCR is still debated. Co oxide is described as inactive [1, 4-6] or detrimental for HC-SCR due to unselective hydrocarbon combustion [6, 7, 15]. Others, however, report that Co oxide forms NO\textsubscript{2} [16-19] an important intermediate in the overall reaction and thus enhances the activity of the catalyst. It is very important to note that the work described in the references above are carried out using different reductants and conditions.

Based on the above discussions it is seen that the state and distribution of Co is important in the resulting catalyst performance. Choice of different preparation methods to incorporate Co in the zeolite can be expected to determine the type of Co species in the zeolite. It is therefore the task of the present study to compare catalysts prepared by solid state or liquid phase ion exchange as well as impregnation with a salt solution.

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In order to evaluate the nature of cobalt sites resulting from the different preparation routes and on different zeolites, the catalysts have been studied by Temperature programmed desorption (TPD), X-ray absorption spectroscopy (XAFS), Fourier Transform infrared (FTIR) spectroscopy and by the activity/selectivity for the reduction of NO in presence of oxygen with propene. Correlations between structural characteristics and kinetic results are used to describe the physicochemical state of the working catalyst, which is then used as basis for further catalyst optimization.

3.2 EXPERIMENTAL

3.2.1 Catalyst preparation

The chemical composition of the catalysts investigated are compiled in Table 1. The zeolites used were ZSM-5 (Na form, Si/Al = 38.5, P.Q. Zeolites), FER and FAU (Na form, Si/Al = 10, Shell). The zeolites were heated in N$_2$ and subsequently in air at 500 ºC for 12 hours. Then, the NH$_4^+$ form of the zeolites were obtained by ion exchanged with 0.1M NH$_4$NO$_3$ solution. After ion exchange the NH$_4$/ZSM-5 contained < 0.01wt% Na as determined by atomic absorption spectroscopy.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Preparatio route</th>
<th>*Co [wt %]</th>
<th>Si/Al [mol/mol]</th>
<th>*Co/Al [mol/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co/ZSM-5 (1)</td>
<td>LSIE</td>
<td>0.7</td>
<td>38.5</td>
<td>0.3</td>
</tr>
<tr>
<td>Co/ZSM-5 (2)</td>
<td>IW</td>
<td>2.5</td>
<td>38.5</td>
<td>1.1</td>
</tr>
<tr>
<td>Co/ZSM-5 (3)</td>
<td>SSIE</td>
<td>2.8</td>
<td>38.5</td>
<td>1.2</td>
</tr>
<tr>
<td>Co/ZSM-5 (4)</td>
<td>SSIE</td>
<td>5</td>
<td>38.5</td>
<td>2.1</td>
</tr>
<tr>
<td>Co/FAU</td>
<td>SSIE</td>
<td>3.4</td>
<td>30</td>
<td>1.1</td>
</tr>
</tbody>
</table>

*Concentration of Co and Al determined by AAS.

Co was introduced by three methods, i.e., (i) liquid phase ion exchange (LSIE) (ii) incipient wetness (IW), and (iii) solid state ion exchange (SSIE)[20]. LSIE was carried out with an aqueous Co(NO$_3$)$_2$ solution (0.01M). The NH$_4^+$/zeolite (5g) was suspended in Co(NO$_3$)$_2$ solution (250ml) and stirred at 80 ºC for 24 hrs. Then it was filtered, washed with deionized water and dried in air at 120 ºC for 8 hours. Th
whole procedure was repeated 3 times. For IW preparation the NH₄⁺ exchanged form Zeolite was heated (500 °C at 2 °C/min in He and was maintained at this temperature for 12 hrs) to decompose and remove the NH₃ leaving the zeolite in the acidic form. The required amount of Co(NO₃)₂·6H₂O was dissolved in the amount of water that 1 gr of zeolite would absorb. The metal solution was then added dropwise to the zeolite and the resultant paste was thoroughly mixed. The samples were then dried in air at 120 °C for 8 hours. SSIE was carried out by thoroughly grinding a mixture of the zeolite (eg. NH₄/ZSM-5 (5g) with the required amounts of CoCl₂·6H₂O. The resulting mixture was heated to 500°C at 2 °C/min in He and was maintained at this temperature for 12 hrs. During the heating cycle the samples were maintained for three hours at 80 °C and for three hours at 105°C. After this procedure the catalyst was washed with de-ionized water and dried in air at 120 °C for 8 hours.

3.2.2 Catalyst characterization

The Co loading was determined by atomic absorption spectroscopy (AAS) with a VARIAN AAS spectrometer. The solid samples (±100 mg) were dissolved in 5 ml HF+3 ml HCl + 1 ml HNO₃. This solution was heated on a sandbath until the sample was completely dry. Then, 3 ml HCl were added again to the sample to solve the remaining salts.

The i.r. measurements were performed in situ on a BRUKER IFS 88 FTIR spectrometer (resolution of 4 c⁻¹) using the transmission-absorption technique. The i.r. cell was equipped with a heatable sample holder and CaF₂ windows [21]. The catalyst was pressed into a self-supporting wafer with approximately 1 cm diameter and activated in flowing He at 500 °C for one hour.

For temperature-programmed desorption (TPD) of ammonia a 50 mg of sample was evacuated in the quartz glass tube and then activated by heating to 550 °C with a ramp of 10 °C/min and kept at this temperature for 30 min at a pressure of 10⁻³ mbar. After cooling down to room temperature ammonia was adsorbed until reaching an equilibrium pressure of 9.5 mbar. Then the sample was evacuated for 1 hour to remove the excess and weakly adsorbed ammonia. The TPD was carried out between 25 °C to 600 °C with a heating rate of 10 °C/min using a BALZERS quadrupole mass spectrometer to detect desorbing species.

X-ray absorption spectra were measured at the SRS in Daresbury, UK, on beamline 9.2 and at Hasylab in DESY, Hamburg, Germany, on beamline ROMOII. The storage ring operated with an electron energy of 4.5 GeV and a current of 100 mA. The spectra were collected in transmission mode, with a Si (220) monochromator (SRS) and a Si (311) monochromator (DESY) which were detuned to 50% to...
remove high energy harmonics present in the beam. The weight of the sample was chosen to obtain a total absorption of 2.5. The data was collected at the Co edge (7709 eV) and analyzed with the WINXAS97 software. Data analysis was carried out using standard analysis procedures [22]. The features of the XAS spectra were compared with those of reference compounds with known oxidation state and structure.

The XAS were collected at -103°C in flowing He. The Co/ZSM-5(3) catalyst (see Table 1) was investigated under three different conditions: (i) XAS of the precursor catalyst after drying the sample in He at 100 °C, (ii) after activation in He at 500 °C and (iii) after reaction ex-situ (i.e. exposure to 1000ppm NO, 1000ppm C\textsubscript{3}H\textsubscript{6} and 5% O\textsubscript{2} in He between 200 °C-500 °C for 24 hrs).

3.2.3 Catalyst Testing

A U-shaped quartz tube with an internal diameter of 8 mm was used as reactor and the catalyst bed was supported by means of two plugs of quartz wool. The catalyst was pelletized, crushed and sieved to 0.3 mm-0.6 mm grains before use. After activation by heating to 500 °C for 1hr in flowing He, the flow was switched to a mixture of (NO/O\textsubscript{2}/C\textsubscript{3}H\textsubscript{6}/He). The typical reactant gas mixture consisted of 1000 ppm NO, 1000 to 2250 ppm C\textsubscript{3}H\textsubscript{6}, 5% O\textsubscript{2} balancing with He to 100% (one bar total pressure). A total gas flow of 100 ml/min was passed through the catalyst bed (0.2 g). The resulting GHSV was 15000 hr\textsuperscript{-1}, based on the apparent bulk density of the catalyst bed (0.5 g/cm\textsuperscript{3}). The temperature of the catalyst bed was controlled by a Eurotherm 903P temperature controller, the gas flows by four mass flow controllers (Brooks). The products were analyzed simultaneously by gas chromatography (Varian 3700 equipped with a TCD detector and a molecular sieve 5A column for separation of N\textsubscript{2}, O\textsubscript{2} and CO and porapak Q column for N\textsubscript{2}O, C\textsubscript{3}H\textsubscript{6} and CO\textsubscript{2}) and a chemiluminescence NO/NO\textsubscript{2} analyzer (Thermo Environmental Instr., Model 42C). The measurements were carried out at temperature intervals of 25 °C between 200°C to 500 °C.

3.3 RESULTS

3.3.1 Physicochemical characterization

For the catalysts prepared by LSIE (Co/ZSM-5(1)) only 0.7 wt % Co was incorporated onto the zeolite after 3 ion exchange cycles (see Table 1). Elemental analysis of the catalysts prepared by IW (Co/ZSM-5(2)) and SSIE (Co/ZSM-5(3)) showed that both preparation methods led to a higher concentration of Co (2.5 and 2.8%, respectively) in the zeolite. The i.r. spectra of the parent H/ZSM-5 zeolite and the Co/ZSM-5 catalysts prepared by the three different techniques are compared in Figure 1. All the spectra were normalized to the intensity of the lattice vibrations at 2000 cm\textsuperscript{-1} and 1880 cm\textsuperscript{-1}. On the parent H/ZSM-5 zeolite bands at 3740 cm\textsuperscript{-1} (attributed to terminal Si-OH groups), 3610 cm\textsuperscript{-1}
Chapter 3 - On the physicochemical properties of Co/ZSM-5 ...
desorption peaks (130 °C 230 °C, wide peak from 350°C to 500 °C) are observed. Co/ZSM5 (3) prepared by SSIE shows a broad peak at 180 °C and a second wide desorption from 325 °C to 500 °C, the latter could be related to two overlapping desorptions at 375 °C and 475 °C. All the Co exchanged zeolite samples show peaks that are of lower intensities than the parent H/ZSM-5. The peak at 375 °C, relating to NH₃ strongly adsorbed at the Brønsted acid sites, was used to estimate the degree of ion exchange. For Co/ZSM5 (1) LSIE sample approximately 44 % of the Brønsted acid sites were exchanged by Co²⁺ while for SSIE 53 % and 65 % for IW. The trends in the degree of ion exchange obtained by the different methods were similar to those estimated from the i.r. spectra.

**In situ** XAS were measured on Co/ZSM-5 catalyst prepared by LSIE, IW and SSIE and the spectra are shown in Figs 5-10. The EXAFS and XANES analysis of Co reference materials such as metallic foil, and oxides is shown for comparison in Figures 3 and 4 respectively.

Figure 5 shows the results of the EXAFS of the Co present in ZSM5 following the three different preparation routes. All methods lead to Co bound to Cl and/or O. After activation all the samples except that prepared by LSIE show a contribution above 2 Å that could be attributed to presence Co-O and/or Co-Co distances as in Co₃O₄ (see Figure 6).
The XANES results for the Co/ZSM-5 catalyst are shown in Figures 7 and 8. The intensity of the white line for Co on Co/ZSM-5 catalyst prepared by the different methods suggest that ionic form of Co is present (CoCl₂, CoO) (see Figs 4 and 7). After activation the XANES of Co/ZSM-5 by LSIE showed no change while that for the SSIE and IW lower intensity was observed (see Figs 4 and 8).
In order to monitor changes in the state of Co, XAS measurements were performed on the Co/ZSM-5 (3) (Table 1) precursor, after activation and after reaction \( \text{etc.} \) exposure to 1000 ppm NO, 1000 ppm \( \text{C}_3\text{H}_6 \) and 5% \( \text{O}_2 \) in He between 200 \(^\circ\text{C}\) - 500 \(^\circ\text{C}\) for 24 hr). Figs 9 and 10 show the results of this comparison. It was found that in the freshly prepared catalyst Co was present as small particles for which interatomic distances corresponding to Co-Cl (Co(Cl)\(_2\)), Co-O (CoO) were observed. After activation and reaction Co-Co and Co-O interatomic distances become dominant. Interestingly the catalyst after reaction shows very similar EXAFS spectral features to Co\(_3\)O\(_4\) reference material.

![Figure 9](image1.png)  
**Figure 9** Fourier transform of the Co edge \(k^2\) weighted EXAFS oscillation, for Co/ZSM-5 catalyst, prepared by SSIE, Comparison with Co\(_3\)O\(_4\).

![Figure 10](image2.png)  
**Figure 10** XANES of Co/ZSM5 prepared by SSIE, Comparison with Co\(_3\)O\(_4\).

### 3.3.2 Catalyst Studies

For the catalytic NO conversion with propene, under the same reaction conditions, the order of activity was Co/ZSM-5 LSIE < SSIE < IW (see Fig 11). However, there seem to be no direct correlation between the amount of Co present (Table 2) and catalyst activity in this comparison. Even though the catalyst prepared by IW was found to be the most active, converting NO already at 300 °C, this Catalyst was very unselective and produced mostly NO\(_2\), even at lower temperatures (325 °C). Under comparable conditions (e.g. 40% NO conversion, 440 °C) Co/ZSM5 catalyst prepared by SSIE showed superior selectivity to \( \text{N}_2 \) (100%) compared to IW catalyst (45%). LSIE catalyst was also very selectiv
3.3.2.1 The influence of the support

The characterization results (i.e. AAS, IR, TPD) indicated that solid state ion exchange is the most efficient method for preparing Co/ZSM-5 samples with a high degree of ion exchange. Furthermore, the kinetic data showed that by the SSIE route active and selective Co/ZSM-5 catalysts were obtained. Therefore solid state ion exchange was chosen as the preparation method to test the influence of different zeolite supports. The details of the Co containing (ZSM-5, FAU and FER) catalysts are described in Table 2.

Table 2. The NO conversions to N\textsubscript{2} as function of the temperature for a series of Co catalysts prepared by SSIE supported on different zeolites is compared in Table 2. The only nitrogen containing products observed were N\textsubscript{2} and N\textsubscript{2}O. However, at 400 °C propene conversion was complete and NO\textsubscript{2} was also observed. (see Fig12). Importantly, Co/ZSM-5 catalyst gave the maximum N\textsubscript{2} yields (see Table 2). These catalysts produced only low amounts of N\textsubscript{2}O (\textsim 2\%). Based on these, ZSM5 was chosen for further optimization of Co content.
Table 2. Comparison of NO conversion to N₂ over Co supported on zeolite catalysts

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>NO conversion to N₂ [Mol %]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>350 °C</td>
</tr>
<tr>
<td>Co/ZSM-5 (4)</td>
<td>11.9</td>
</tr>
<tr>
<td>Co/FER</td>
<td>6.9</td>
</tr>
<tr>
<td>Co/FAU</td>
<td>6.2</td>
</tr>
</tbody>
</table>

Conditions: 15000 hr⁻¹, 1000 ppm NO, 1000 ppm C₃H₆ and 5% O₂ in He.

3.3.2.2 The influence of the Co concentration

The results of NO reduction with propene over Co/ZSM-5 catalysts already reported in [24], are compiled in Table 3.

Table 3. Kinetic results for Co/ZSM-5 catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Co [wt%]</th>
<th>Co/Al [ratio]</th>
<th>Conversion¹</th>
<th>Selectivity²</th>
<th>Conversion¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>NO [mol s⁻¹ g⁻¹]</td>
<td>N₂ [mol%]</td>
<td>N₂O</td>
</tr>
<tr>
<td>H-ZSM-5</td>
<td>--</td>
<td>--</td>
<td>0.08E-07</td>
<td>100³</td>
<td>0</td>
</tr>
<tr>
<td>Co/ZSM-5 (1)</td>
<td>0.7</td>
<td>0.3</td>
<td>0.18E-07</td>
<td>96</td>
<td>4</td>
</tr>
<tr>
<td>Co/ZSM-5 (3)</td>
<td>2.8</td>
<td>1.2</td>
<td>1.28E-07</td>
<td>85</td>
<td>15</td>
</tr>
<tr>
<td>Co/ZSM-5 (4)</td>
<td>5.0</td>
<td>2.1</td>
<td>6.84E-07</td>
<td>60</td>
<td>13</td>
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</tbody>
</table>

ZSM-5 Si/Al ratio = 38.5; Conditions: At 350 °C, 1000 ppm NO, 1000 ppm C₃H₆ and 5% O₂ in He. ¹Differential Rates of conversion, ²At 30% NO conversion (by varying the contact time), ³At 2% NO conversion. (product NO₂ is observed only when C₃H₆ conversion reaches 100%).

The kinetic results showed that H/ZSM-5 had only very little activity for NO conversion. Addition of Co²⁺ ions improved the activity for NO conversion maintaining high selectivity to N₂. Increasing the Co content improved the activity of the catalysts further (higher rates of NO and C₃H₆ conversion). High Co content (5%) however, lead to lower selectivity towards N₂. Under these conditions oxidation of NO was favored as seen from the selectivity to NO₂ in Table 3. The influence of temperature on the yield and conversions for these Co/ZSM-5 catalysts was found to be similar. In agreement with the literature [e.g. 17, 18], NO conversion passed through a maximum as function of the temperature and at approximately
100% C\textsubscript{3}H\textsubscript{6} conversion, N\textsubscript{2} and N\textsubscript{2}O yields reached maximum values, NO\textsubscript{2} was observed only after 100% C\textsubscript{3}H\textsubscript{6} conversion was reached (see Fig 12). The results showed that Co/ZSM-5 (3) has a good balance between high activity and high selectivity to N\textsubscript{2}. In order to test the stability of the catalyst, temperature cycles between 200 °C to 500 °C were performed, which showed that Co/ZSM5(3) was stable. The catalyst showed an increasing activity (NO conversion) during the first cycle, however.

Figs. 13 and 14 show the variation of selectivity and yields to different products as a function of NO conversion at 350 °C over Co/ZSM-5(3). N\textsubscript{2} and N\textsubscript{2}O were the only products at low conversions. The selectivity to N\textsubscript{2} increased at the expense of N\textsubscript{2}O at higher NO conversions. This suggests that a secondary path for the formation of N\textsubscript{2} via decomposition of N\textsubscript{2}O exists. To test this, N\textsubscript{2}O was reacted over Co/ZSM5(3). The catalyst was found to be active in the reduction of N\textsubscript{2}O to N\textsubscript{2}. When C\textsubscript{3}H\textsubscript{6} conversion reached 100% (see Fig. 13 and 14 shaded area) the selectivity/yield of N\textsubscript{2} reached the maximum values. NO\textsubscript{2} was observed beyond this point. From figures 13 and 14 it is also seen that at higher NO conversions the selectivity to NO\textsubscript{2} increased rapidly at the expense of N\textsubscript{2}; the amount of N\textsubscript{2}O was almost invariant in this region.

In comparison to Co/ZSM5(3) (2.8 wt%.Co), the catalyst with lower Co concentration (Co/ZSM5(1), 0.7 wt%.Co) also showed similar trends in yields/selectivities. (see Fig. 15 and 16).
For the catalyst containing higher concentration of Co (Co/ZSM5(4), 5.0 wt%.Co) similar performance was observed at lower conversions, however, a remarkable difference was observed in the products distribution at NO conversion higher than approximately 20% (see Fig 17 and 18). At these conversions, Co/ZSM5(4) showed enhanced NO$_2$ formation. Interestingly, at even higher NO conversions
the NO₂ formation reached a maximum after which the selectivity towards N₂ improved at expense of NO₂.

3.3.2.3 Influence of water

For practical applications, good performance of the SCR catalyst is also necessary in the presence of water. The activity of Co/ZSM-5 (3) at 350 °C in the presence of 6 vol % H₂O is shown in Fig 18.

Addition of water completely suppressed NO₂ formation without affecting the NO conversion and or the stability of the catalyst (see fig 18). The selectivity to N₂ improved from 60 % N₂, 8% N₂O and 30% NO₂ without water to 96 % N₂, 4 % N₂O and 0 % NO₂ in the presence of water, at 77 % NO conversion and a space velocity of 7500 hr⁻¹. The presence of water also decreased the propen conversion from 100% to approximately 85% and caused formation of about 10 % CO. The effect of water addition was completely reversible indicating that the catalyst did not undergo any physical alterations.

3.4 DISCUSSION

The i.r. spectra of the Co/ZSM-5 catalysts show that all the preparation routes lead to Co exchanged metals ions located at the bridging oxygen of Si-O-Al groups. In the case of LSIE the catalyst contained only 0.7 wt % Co corresponding to a Co/Al mol ratio of 0.3. I.r. spectra indicate that for LSIE only about 33 % of the Brønsted acid sites were exchanged by Co³⁺. Thus, for Co/ZSM-5 prepared by LSIE, the relative small amount of Co in the catalyst is likely to be present as Co³⁺ only.

The IW and SSIE preparation methods lead to catalyst with higher Co concentrations. The i.r spectra indicate a decrease in the Brønsted acid sites corresponding to 51 % and 50 % for IW and for SSIE respectively. The molar Co/Al ratio for the catalysts prepared by these methods were near 1, which indicates that approximately 50 % of the Co is present an exchange Co³⁺. The rest of the Co found by elemental analysis should be present as Co oxide that are known to be formed over Co/ZSM-5 catalysts under oxidative conditions [5, 6, 16]. EXAFS and XANES also confirms the presence of Co oxidic phas
over Co/ZSM-5 catalyst prepared by SSIE. This is also clearly seen in the EXAFS of the catalyst equilibrated in the reaction mixture showing spectral features of Co$_3$O$_4$ (see Fig 9).

All the Co exchanged zeolite samples showed NH$_3$ TPD desorption peaks that correspond to the presence of Brønsted acid sites. These peaks are of lower intensities than the parent HZSM-5 indicating, in agreement to the i.r. measurements, that part of the Co ions were exchanged at the Brønsted acid sites. Further for the Co/ZSM5 (2) catalyst prepared by IW and Co/ZSM5 (3) prepared by SSIE the broad NH$_3$ desorption peak may be attributed to contributions from the Brønsted acid sites and Lewis centers such as Co ions (These samples contain much higher Co concentration compared to the sample prepared by LSIE and hence the contribution from Lewis acid metal ion sites can be expected to be more significant).

Thus to summarize, the difference found in the i.r., TPD and XAS results for the Co/ZSM-5 catalysts together with the Co/Al molar ratio suggest that the preparation of Co/ZSM-5 by different routes lead to catalysts with different characteristics. It seems that in the LSIE Co ions are coordinated to the Brønsted sites while for the samples IW and SSIE in addition to that, Co oxide is present.

From the catalytic measurements following observations were made: (i) addition of Co$^{2+}$ ions to HZSM-5 incorporates SCR activity, (ii) the order of increasing activity and decreasing N$_2$ selectivity was Co/ZSM-5 LSIE < Co/ZSM-5 SSIE < Co/ZSM-5 IW. (iii) increasing the Co content improved the activity of the catalysts (see Fig10 and Table 3) (iv) Higher Co content (eg, 5%), led to lower selectivity towards N$_2$. (v) an initial shift to lower temperatures on the conversions during the temperature cycling was observed and after that the catalyst activity was stable. These results indicate that in all the catalysts with Co/Al mol ratio higher than 1 there is an excess of Co present and these excess of Co should lead to Co oxide clusters formation during reaction under oxidative conditions. These oxide clusters are known to promote propene combustion [25] and NO$_2$ formation [16]. Since NO conversion follows closely the $\text{C}_3\text{H}_6$ conversion (see Fig12) and as mentioned above Co oxide clusters promote combustion, presence of Co oxide may result to increased activity of the catalyst. Also the increased NO$_2$ formation due to Co oxide clusters can increase the catalyst activity. In that respect should be noted that in experiments where NO was replaced by NO$_2$ as reactant the rates of N$_2$ formation was strongly enhanced. Thus presence of Co oxide may be beneficial for the selective catalytic reduction of NO to N$_2$. However presence in higher concentrations may result in an increased unselective combustion of propene. Under these conditions oxidation of NO to NO$_2$ is favored and the selectivity to N$_2$ strongly decreases. From the discussion above we find that the Co/ZSM-5 (3) catalyst (prepared by SSIE) shows superior performance with respect to
NO conversion and N₂ selectivity probably due to a good balance between the Co concentration and the fraction of which is exchanged or present as oxidic phase. The difference in catalytic behavior between LSIE and SSIE/IW are explained by formation of Co oxide on the latter two samples. Even though there is no clear evidence, we propose that the differences between the IW and SSIE could be related to differences in the Co oxide particle size.

Among the Co supported catalysts Co/ZSM-5 catalyst the best performance. We have seen earlier that increasing the Co content improved the activity of Co/ZSM5, however comparing different supports, the least active catalyst was Co/FAU even though it had a the higher Co content. As mentioned in the introduction, Li et al. [4, 8, 9, 26] suggested that the position, environment and coordination in different channel systems in zeolites, of Co²⁺ ions is of significance. They also reported that even though a Y zeolite had a much larger cation exchange capacity (due to low Si/al ratio) Co/Y was not active and adsorbed very little NO and they related it to the zeolite topology suggesting that over Co/Y they were Co²⁺ sites not readily accessible due to limited diffusion from the sodalite cage. Also they related to the different coordination of Co ions proposing that Co on Co/Y did not form dinitrosyls species that are necessary for NO conversion while ZSM-5 was able to position cobalt cations in its active state. Further they proposed that differences observed between Co/ZSM-5 and Co/FER for SCR (activity and selectivity for NO reduction, CH₄ combustion and SO₂ tolerance) could be related to in homogeneity of Co²⁺ sites. ZSM-5 has 2 dimensional 10 ring channel system with a ring size of 5.6x5.3Å for the straight channel and 5.1x5.5 Å for the sinusoidal channels. Ferierite has a 10 ring channel system with a ring size of 4.3x5.5Å and a 8 ring channels 3.5x4.8Å. [27]. They suggested that the sites at the entrance of the 10-member rings are less selective for NO reduction and more active in CH₄ combustion. Also Co²⁺ sites in the smaller channels of FER channels may enhance selectivity by restricting diffusion of CH₄ (kinetic diameter 3.8Å) or by suppressing O₂ adsorption, suppressing unselective combustion and thus increase NO conversion. For example in Mordenite (12 ring channel 6.5x7 Å) lower selectivity and activity were observed.

For all the catalysts it was found that the NO conversion passes a maximum as result of the decreasing availability of the reductant with increasing temperatures (it is consumed by direct oxidation) [e.g.4] or by a decreasing concentration of NO and a higher abundance of oxygen in catalyst pores [28]. NO₂ is observed only after 100% C₃H₆ conversion is reached, i.e., the reduction of NO by C₃H₆ replaced by the NO oxidation by oxygen. As mentioned before this latter reaction is catalyzed by Co oxide. It should be noted that Co/ZSM-5 catalyzes the oxidation of NO to NO₂ At a reaction temperature of 400°C, an NO
partial pressure of 1000 ppm, 50 mbar O₂ in He and a GHSV = 15000 h⁻¹. 40% NO is converted to NO₂ over Co/ZSM-5 (3)).

The selectivities/yields vs NO conversions experiments showed that at 350°C over Co/ZSM-5(3), N₂ and N₂O are primary products and that some interconversion of N₂O to N₂ occurs at higher NO conversions. Further the experiments with N₂O showed in agreement with the literature [29, 30] that Co/ZSM-5 is active in the decomposition of N₂O to N₂. We propose that also over these catalysts readsorption of N₂O occurs on Co²⁺ followed by its reduction to N₂.

The presence of 6 vol.% water had a positive influence upon the catalytic activity of Co/ZSM-5. With water in the feed the combustion of propene decreased, while the selectivity to N₂ increased and NO₂ formation was completely suppressed. It seems that water impedes propene oxidation by competing for sorption sites allowing the propene to react more selectively presumably with NO₂.

The active phases of Co/ZSM-5 catalysts appear to be cobalt oxide in the pores of the zeolite, individual ions at exchange sites. The oxide phase is involved in the oxidation of NO to N₂O and propene to COₓ as well as the formation of N₂O. The individual Co²⁺ ions at exchange sites may be involved in the adsorption of NOₓ species and their reaction with activated propene to form intermediates that decompose resulting in the formation of N₂ as well as providing a site were N₂O may decompose to N₂. The presence of water the combustion of propene assuring that propene is available for the selective reduction of NOₓ to N₂.

We have found that the Co supported on ZSM-5 prepared by SSIE with a Co/Al ratio of 1.2 showed optimal performance. In this catalyst under reaction conditions it seems that a good balance between presence of Co²⁺ and Co oxide brings about this resulting catalytic behavior.

3.5 CONCLUSIONS

The preparation method influence the state of Co in the zeolite. Even though all the preparation routes led to Co ions exchanged at the bridging oxygen of Si-O-Al groups, the excess of Co in catalysts prepared by SSIE and IW is present as Co oxide clusters.

Addition of Co²⁺ ions to H/ZSM-5 improve the activity for NO conversion, leading to high selectivity to N₂. Increasing the Co content improved further the activity of the catalysts. Excess of Co
oxide leads to lower selectivity towards N$_2$ due to unselective combustion of propene. Lack of Co oxide phase in catalysts prepared by LSIE could explain their high selectivity and their low activity.

Over Co/ZSM-5 N$_2$ and N$_2$O are primary products and that some interconversion of N$_2$O to N$_2$ occurs at higher NO conversions. Readesorption of N$_2$O occurs on Co$^{2+}$ followed by its reduction to N$_2$. The presence of 6 vol.% water retards propene oxidation allowing the propene to react more selectively presumably with NO$_2$.

The catalytically active phases of Co/ZSM-5 catalysts appear to be cobalt oxide in the pores of the zeolite, individual ions at exchange sites. The oxide phase is involved in the oxidation of NO to NO$_2$ and propene to COx as well as the formation of N$_2$O. The individual Co$^{2+}$ ions at exchange sites may be involved in the adsorption of NO$_x$ species and their reaction with activated propene to form intermediates that decompose resulting in the formation of N$_2$ as well as providing a site where N$_2$O may decompose to N$_2$. The presence of water the combustion of propene assuring that propene is available for the selective reduction of NO$_x$ to N$_2$. These aspects are discussed in detail in Chapters 4 and 5.

Finally, the Co catalyst supported on ZSM-5 and prepared by SSIE present a good compromis between high activity and selectivity to N$_2$.

ACKNOWLEDGMENTS

The authors thank Dr. S. Feast, Dr. A Jentys, Drs. L. Simon and Ir. M. Tuchen for the assistance in the characterization and preparation of the catalyst. This project was supported by the EU, in the framework of the R and D programme in the field of the environment, sub-programme: Technologies for protecting and rehabilitating the environment, Contract no. EVSV-CT-94-0535. This work was performed under the auspices of NIOK, the Netherlands Institute for Catalysis (Report number UT-98-1-02).

REFERENCES

Chapter 3 - On the physicochemical properties of Co/ZSM-5 ...

CHAPTER 4

Co-Pt/ZSM-5, a water and sulfur resistant catalyst for NO$_x$ reduction

Abstract

The selective catalytic reduction of NO by propene in the presence of excess oxygen has been studied over catalysts based on Co-Pt supported on ZSM-5. Pure Pt based catalysts are highly active, but produce large amounts of N$_2$O. Bimetallic Co-Pt/ZSM-5 catalysts with low Pt contents (0.1 wt %) show a synergistic effect by combining high stability and activity of Pt catalysts with the high N$_2$ selectivity of Co catalysts. The lower selectivity to N$_2$O is attributed to its selective conversion over Co. The catalysts also showed high water and sulfur tolerance above 350°C.
4.1 INTRODUCTION

The interest in developing new catalytic processes for the reduction of NOx under conditions of excess oxygen such as needed for stationary sources, diesel engines and lean burn Otto engines is currently very high [1,2]. Nowadays, the use of hydrocarbons as an alternative reductant is being intensively investigated [2]. While a large number of catalysts based on zeolites was proposed and tested (e.g., Cu/ZSM-5 [3,4], Co/ZSM-5 [5], Co/FER [6], Pt/ZSM-5 [7]), sensitivity towards water and sulfur compounds (or high selectivity to N₂O in the case of Pt/ZSM-5) has been found to be prohibitive to a breakthrough. Water and sulfur compounds retard reversibly and irreversibly the rate at which NOx is reduced and may under some instances completely destroy the zeolite. Impressive improvements in that respect were reported by the groups of Hall [8] and Sachtler [9] based on Fe/ZSM-5. Pt based catalyst are also very active and durable, however, during NO reduction they yield large amounts of N₂O [7,10]. Information available in the literature indicate that Co/ZSM-5 catalysts are very selective to N₂ [4,11] and also active in the reduction of N₂O to N₂ [12,13]. It was our intention to prepare a multi component catalyst that will preserve the desired characteristics of the individual components minimizing their negative aspects. In the present communication we describe a zeolite based catalyst, Co-Pt/ZSM-5 that is sulfur and water tolerant and considerably extends the limit of operation towards lower temperatures required for power plant emissions abatement. The roles of Pt and Co for the elementary steps of NOx reduction and the implications for catalyst design are discussed.

4.2 EXPERIMENTAL

The chemical composition of the catalysts investigated are compiled in Tables 1-3.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Co [wt%]</th>
<th>Pt [wt%]</th>
<th>Co/Pt [mol/mol]</th>
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</tr>
<tr>
<td>8</td>
<td>0.65</td>
<td>1.01</td>
<td>2.1</td>
</tr>
</tbody>
</table>

Concentration of Co and Pt determined by AAS.
4.2.1 Catalyst preparation

The catalysts were based on ZSM-5 and the metals were introduced via solid state ion exchange. The parent ZSM-5 (Na form, Si/Al = 38.5, P.Q. Zeolites) was heated in N₂ and subsequently in air at 500 °C for 12 hours. Then, the zeolite was ion exchanged twice with 0.1M NH₄NO₃ solution. After ion exchange the NH₄/ZSM-5 contained < 0.01wt% Na as determined by atomic absorption spectroscopy. In a typical procedure NH₄/ZSM-5 (5g) was thoroughly ground with the required amounts of CoCl₂.6H₂O and PtCl₄. The resulting mixture was heated to 500 °C at 2 °C/min in He and was maintained at this temperature for 12 hrs. During the heating cycle the samples were maintained for three hours near the melting point (80 °C) and boiling point (105°C) of Co(Cl)₂ and then near the melting point and decomposition point (370°C) of PtCl₄ for 3 hours to allow slow diffusion of the metal ions into the zeolite.

4.2.2 Catalyst characterization

High resolution electron microscopy (HREM) was performed using a Philips CM 30 T electron microscope with an LaB₆ filament as the source of electrons operated at 300 kV. Samples were mounted on a microgrid carbon polymer supported on a copper grid by placing a few droplets of a suspension of ground sample in ethanol on the grid, followed by the drying at ambient conditions. Elemental analysis was performed using a LINK EDX system.

X-ray absorption spectra were measured at the SRS in Daresbury on beamlines 9.2 and 8.1. The spectra were collected in transmission mode, with a Si(220) monochromator detuned to 50% on beamline 9.2 and 70% on beamline 8.1, to remove high energy harmonics present in the beam. The analysis was carried out using standard analysis procedures [14]. The EXAFS spectra were collected at -103 °C in flowing He. The catalysts were heated to 500 °C in flowing He or H₂ to effect activation or reduction and XANES spectra were taken during these processes.

The i.r. measurements were performed in situ on a BRUKER IFS 88 FTIR spectrometer (resolution of 4 cm⁻¹) in a continuous gas flow mode using the transmission-absorption technique. The i.r. cell was equipped with a heatable sample holder and CaF₂ windows. The catalyst (Co-Pt/ZSM-5 with 2.8 wt % Co and 0.1 wt % Pt) was pressed into a self-supporting 2 mg wafer and activated in flowing He at 500°C for one hour. Subsequently, the catalyst was brought to the required temperature and the reactant gases were flown over the catalyst.

4.2.3 Catalyst Testing

The reactor used was a U-shaped quartz tube with an internal diameter of 8 mm and the catalyst
Chapter 4 - Co-Pt/ZSM-5 a water and sulfur resistant catalyst for NOx reduction

bed was supported by means of two plugs of quartz wool. The catalyst was pelletized, crushed and sieved to 0.3 mm-0.6 mm before use. For testing, the catalyst was activated \textit{in situ} by heating to 500 °C for 1 hr in flowing He. After activation, the flow was switched to a mixture of (NO/O2/C3H6/He). The typical reactant gas mixture consisted of 1000 ppm NO, 1000 to 2250 ppm C3H6, 5% O2 balancing with He to 100%. A total gas flow of 100 ml/min was passed through the catalyst bed (0.2 g). The resulting GHS was 15000 hr⁻¹, based on the apparent bulk density of the catalyst bed (0.5 g/cm³). The temperature of the catalyst bed was controlled by a Eurotherm 903P temperature controller, the gas flow by four Brooks mass flow controllers. The products were analyzed simultaneously by gas chromatography (Varian 3700 equipped with a TCD detector and a molecular sieve 5A column for separation of N₂, O₂ and CO and porapak Q column for N₂O, C₃H₆ and CO₂ analysis) and a chemiluminescence NO-NO₂-NOₓ analyzer (Thermo Environmental Instr., Model 42C, NO, NOₓ analysis). Kinetic measurements were carried out at temperature intervals of 25°C between 200°C to 500°C. The experiments to test the influence of the addition of SO₂ were performed at the CPERI laboratories, Thessaloniki Greece.

4.3 RESULTS

4.3.1 Characterization

High resolution electron microscopy (HREM) combined with EDX analysis of the Co-Pt/ZSM-5 catalyst revealed three kind of macroscopic zones in the catalysts (see Fig 1), (a) areas with large Co particles (maximal diameter approx. 5 nm), (b) areas with highly dispersed Co and (c) areas with particles containing both Co and Pt. Differences between the catalyst before and after reaction were not observed.

Figure 1 HREM picture of Co-Pt/ZSM-5 catalyst, composition: Co 2.8 wt %, Pt 0.1 wt %
In situ EXAFS and XANES were performed on Co-Pt/ZSM-5 catalysts. Fig 2 shows the EXAFS for the Pt L_{III} edge. In the freshly prepared catalysts Pt was present as highly dispersed particles with interatomic distances corresponding to Pt-O in PtO_{2}. After activation and during reaction Pt was found to be present as small particles that resemble metallic Pt having a coordination number, N= 5 and an average Pt-Pt distance of 2.75 Å. Fig 3 shows the EXAFS for the Co edge. It was found that in the freshly prepared catalyst Co was present as small particles for which interatomic distances corresponding to Co-Cl (Co(Cl)_{2}), Co-O (CoO) were observed. During reaction Co-Co and Co-O interatomic distances become dominant. XANES of Co and Pt reference materials such as metallic foil, and oxides were taken for comparison. The intensity of the white line for Pt and Co on Co-Pt/ZSM-5 catalyst resembled Pt in a metallic state and Co in an oxidic state (see Figs 4 and 5).

**Figure 2** K^{2} weighted fourier transform EXAFS for Pt_{III} edge of Co-Pt/ZSM-5.

**Figure 3** K^{2} weighted fourier transform EXAFS for Co edge of Co-Pt/ZSM-5.

**Figure 4** XANES spectra for Pt_{III} edge of Co-Pt/ZSM-5 and reference materials Pt foil, PtO_{2}.

**Figure 5** XANES spectra for Co edg of Co-Pt/ZSM-5 and reference materials CoO, C_{3}O_{4} and Co foil.
In Fig 6 the i.r. spectra of the parent H/ZSM-5 zeolite after activation, the Co-Pt exchanged zeolite, fresh, after reduction in \( H_2 \) and after reaction are shown. The parent H/ZSM-5 zeolite has absorption bands at 3740 cm\(^{-1}\) (attributed to terminal Si-OH groups), 3610 cm\(^{-1}\) (attributed to bridging Si-OH-Al, groups), 2000 cm\(^{-1}\), 1880 cm\(^{-1}\), 1640 cm\(^{-1}\), 1480 cm\(^{-1}\) (attributed to Si-O-Si lattice overtones). The Co-Pt modified zeolite showed a large decrease of the peak at 3610 cm\(^{-1}\) and small decrease in the band at 3740 cm\(^{-1}\) indicating that the Co, Pt exchanged metals ions are located mainly on the bridging oxygen of Si-O-Al groups and to a small extent at the terminal oxygens of Si-OH groups. Normalizing the spectra for the lattice overtones at 2000 cm\(^{-1}\) and 1880 cm\(^{-1}\) allowed to estimate that approximately 50% of the protons of the Brønsted acid sites were exchanged for Co\(^{2+}\) and Pt\(^{4+}\). After reduction with \( H_2 \) at 400 °C for 1 hr, the band at 3610 cm\(^{-1}\) recovered 80% of the initial intensity indicating that approximately 20% of the exchanged metal cations were not reduced or the bridging hydroxyl groups were eliminated by dealumination. After reaction however, the band completely disappeared indicating that the Brønsted acid sites are covered by hydrocarbon species under reaction conditions.

**Figure 6** Normalized i.r. spectra of H/ZSM-5 and Co-Pt/ZSM-5 freshly prepared, after reduction and after reaction.
4.3.2 Catalytic Studies

4.3.2.1 Co/ZSM-5 catalyst

The results of NO reduction with propene over Co/ZSM-5 were presented in an earlier publication [15] and are compiled in Table 2 indicating the influence of the Co concentration on the catalytic behavior of Co/ZSM5 catalysts.

Table 2. Chemical composition and kinetic results for Co/ZSM-5 catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Co [wt%]</th>
<th>Co/Al [ratio]</th>
<th>Conversion $^1$ [mol s$^{-1}$ g$^{-1}$]</th>
<th>Selectivity$^2$ [mol%]</th>
<th>NO</th>
<th>N$_2$</th>
<th>N$_2$O</th>
<th>NO$_2$</th>
<th>C$_3$H$_6$</th>
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<td>H-ZSM-5</td>
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<td>0.08E-07</td>
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<td></td>
</tr>
<tr>
<td>Co/ZSM-5</td>
<td>5.0</td>
<td>2.1</td>
<td>6.84E-07</td>
<td>60</td>
<td>13</td>
<td>27</td>
<td>8.87E-06</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

ZSM-5 Si/Al ratio = 38.5; Conditions: At 350 °C, 1000ppm NO, 1000ppm C$_3$H$_6$ and 5% O$_2$ in He,
$^1$ Differential Rates of conversion, $^2$ At 30% NO conversion (by varying the contact time, $^3$ at 2% NO conversion. (product NO$_2$ is observed only when C$_3$H$_6$ conversion reaches 100%).

Increasing the Co content improved the activity of the catalysts (higher rates of NO and C$_3$H$_6$ conversion). High Co content (5%) however, led to lower selectivity towards N$_2$. This was the result of increased unselective combustion of propene. Under these conditions oxidation of NO to NO$_2$ was favored. EXAFS measurements suggested that the excess of Co on this catalyst (Co/Al mol ratio of 2.10) is present as Co oxide clusters. The formation of Co oxides over Co/ZSM5 is known to occur under oxidativ conditions [16-18]. These oxide clusters are known to promote propene combustion [19] and NO$_2$ formation [18].

4.3.2.2 Co-Pt/ZSM-5 catalyst

The chemical composition for Co-Pt/ZSM-5 catalysts investigated are compiled in Table 1. The influence of the addition of Pt on ZSM-5 catalysts for NO conversion is compiled in Table 3.
Co/ZSM-5 showed the lowest activity (see Table 3 differential rates for NO conversion and C\textsubscript{3}H\textsubscript{6} conversion) and the highest selectivity to N\textsubscript{2}. Pt/ZSM-5 on the contrary showed high activity, but low selectivity to N\textsubscript{2}. Addition of Pt improved the activity of Co based catalysts, resulted, however, in a small increase in selectivity to N\textsubscript{2}O. In order to optimize the performance of Pt based catalysts (NO conversion and N\textsubscript{2}O selectivity) a series of Co and Pt containing catalysts were prepared. Figures 7 and 8 show the influence of Pt content on N\textsubscript{2}O yields for a variety of bimetallic Co-Pt catalysts.

**Figure 7** Influence of temperature and Co/Pt ratio on N\textsubscript{2}O formation over Co-Pt/ZSM-5 catalysts. Conditions: GHSV=15000 hr\textsuperscript{-1}, NO = 1000 ppm, C\textsubscript{3}H\textsubscript{6} = 1000 ppm, O\textsubscript{2} = 5% in He. * Numbers in figure represent Co/Pt ratios.
Fig 7 N_2O shows yields vs temperature for all catalysts investigated. Fig 8 the N_2O yields and th temperature at which they were obtained as function of Pt content. It should be noted that Pt concentrations above 0.1 wt % increased the tendency to form N_2O. Thus, the Co-Pt/ZSM-5 material with 0.1 wt% Pt was chosen for detailed studies.

The influence of temperature on the yield and conversions for Co-Pt/ZSM-5 catalysts (0.1 wt% Pt) was found to be similar to the results found for Co/ZSM-5 [20 a, b]. NO conversion passed through a maximum as function of the temperature, at approximately 100% C_3H_6 conversion, N_2 and N_2O yields reached maximum values and NO_2 was observed only after 100% C_3H_6 conversion is reached.

In order to test the stability of Co-Pt/ZSM-5 cycles of increasing and decreasing temperature between 200 ºC to 500 ºC were explored. In the first cycle a 25 ºC shift to lower temperatures on the conversions curves was observed, however, after this first cycle the catalyst was very stable. Fig 9. shows the time on stream performance of this catalyst at 300ºC underlining good stability, high activity and high selectivity to N_2 (87 % N_2 selectivity at 67 % NO conversion).

In contrast to the results obtained using propene as reactant, CH_4 was less efficient for the selective reduction of NO to N_2 over Co-Pt/ZSM-5. When CH_4 was used, the main product was NO_2 , even when the hydrocarbon was not fully converted. Note that with C_3H_6 NO_2 was observed only after all the propen was converted.

4.3.2.2.1 Detailed kinetic study and reaction pathway analysis

![Figure 8](image1.png)

**Figure 8** Time on stream behavior of Co-Pt/ZSM-5 Conditions: 300 ºC, GHSV=5250 hr^-1, NO = 1000 ppm, C_3H_6 = 2250 ppm, O_2 = 5% in He. At ~ 100 % C_3H_6 conversion,

![Figure 9](image2.png)

**Figure 9** Influence of the Pt content on N_2O yields for Co-Pt/ZSM-5 catalysts. Conditions: GHSV = 15000 hr^-1, 1000 ppm NO, 1000 ppm C_3H_6, 5% O_2, in He. *numbers in figure indicate the temperatures at which maximum N_2O yields were obtained for each catalyst.
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Fig. 10 and 11 show the variation of selectivity and yields to different product as a function of NO conversion at 350 °C over Co-Pt/ZSM-5. At low conversions only N₂ and N₂O were formed, but not NO₂ (note that propene conversion was below 100 %). The selectivity to N₂ increased at expense of N₂O at higher NO conversions. When C₃H₆ conversion reached 100% the selectivity/yield of N₂ reached the maximum values. NO₂ was observed beyond this point. Under typical reaction conditions, at NO conversions higher than 60%, the selectivity to NO₂ increased rapidly at the expenses of N₂.

The increased N₂ selectivity at expenses of N₂O selectivity at higher NO conversions suggests that a secondary path for the formation of N₂ via decomposition of N₂O, exists. To test this, N₂O was reacted over Co-Pt/ZSM-5. While the catalyst was active in the reduction of N₂O to N₂, the rates were an order of magnitude lower than for NO conversions.

In order to clarify the role of the different reactants in the formation of N₂, experiments varying the feed composition were performed. At 350°C passing NO alone over Co-Pt/ZSM-5, N₂ or N₂O were not detected in the gas phase. An NO/O₂ mixture produced exclusively NO₂. When NO and C₃H₆ were co-fed small amounts of N₂ and N₂O were observed as products. The same products were also observed when NO was passed over the catalyst previously exposed for few hours to 2000 ppm propene in He. When NO, C₃H₆ and O₂ were passed simultaneously significant selective reduction of NO to N₂ took place. When C₃H₆ alone was passed over the catalyst a C₃H₆ conversion of approximately 15% was obtained, however, gas phase products were not observed. Under these conditions passing oxygen resulted in CO₂ formation.
An *in situ* infrared spectroscopic study performed on Co-Pt/ZSM-5 [21], revealed that Co-(NO$_2$), Co-(NO$_3$) are present under reaction conditions. These species are related to NO$_2$ and indicated that NO$_2$ could be an intermediate in the formation of N$_2$. To investigate this possibility experiments comparing the reactivity of NO and NO$_2$ were performed. It was found that the rates of N$_2$ formation were twice with NO$_2$ as reactant. The parent H/ZSM-5 zeolite also produced considerable amounts of N$_2$ from NO$_2$. This contrasts with its inactivity for the conversion of NO. Note that H/ZSM-5 with higher concentration of acids sites (Si/Al = 10) was more active than the standard sample used.

4.3.2.2 Influence of water and SO$_2$

At 350 °C the presence of water (up to 6%) did not influence the NO conversion and the stability of the catalyst. Additionally, water improved the selectivity to N$_2$ at the expense of NO$_2$ (from 48 % N$_2$, 9 % N$_2$O and 43% NO$_2$ without water to 71 % N$_2$, 8 % N$_2$O and 21 % NO$_2$ in the presence of water), at 82% NO conversion. At a higher space velocity (19500 h$^{-1}$) addition of water completely suppressed NO$_2$ formation without affecting the NO conversion (from 68 % N$_2$, 14 % N$_2$O and 18% NO$_2$ to 90 % N$_2$, 9 % N$_2$O and 0 % NO$_2$, at 62% NO conversion). The presence of water also decreased the propene conversion from 100% to approx. 85%. The effect of water addition was completely reversible indicating that the catalyst did not undergo alterations at 350°C. Similarly 200 ppm SO$_2$ also did not affect the stability, but slightly decreased the activity.

4.4 DISCUSSION

4.4.1 Characterization

*In situ* EXAFS and XANES showed that in the freshly prepared Co-Pt/ZSM-5 catalysts Pt is present as highly dispersed Pt oxide particles, while Co is present as small particles with Co-Cl, Co-O indicating that these particles are oxidized (containing some chloride). After activation and during reaction Pt is reduced while Co stays in an oxidic state. I.r. spectroscopy showed that on Co-Pt/ZSM-5 approximately 50% of the protons of the strong acid sites were exchanged for Co$^{2+}$ and Pt$^{4+}$. Recovery of 80% of the Brønsted acid sites after reduction suggest their liberation as metal particles are formed. The HREM and EDX analysis indicate that the materials are heterogeneous on microscopic scale. Two types of regions appear to exist: (1) Large Co and Co/Pt particles are found to be scattered over the sample and are probably Co oxidic clusters. (2) Cobalt highly dispersed and most likely still attached to the bridging oxygen of an ion exchange site.
4.4.2 Catalytic Studies

In agreement with the literature, see ref [20a] the kinetic results show that the parent H/ZSM-5 has very little activity for NO conversion. Addition of Co$^{2+}$ ions to H/ZSM-5 improve the activity for NO conversion, leading to high selectivity to N$_2$. The addition of Pt further enhanced the activity. The rates of NO conversion doubled in the presence of small amount (0.1 wt %) of Pt corresponding to a Co/Pt molar ratio of 70. However, the improvement of activity by the addition of Pt resulted in higher selectivity to N$_2$O. It should be emphasized that the catalytic properties observed are not a linear combination of the activity of the two metals, but indicate a more complex behavior. In comparison to only Co based catalyst, Pt improves the activity at lower temperatures, while the presence of Co improves the selectivity to N$_2$ (See Table 3). The roles of the different components are discussed below.

4.4.3 Mechanistic aspects

Under oxidizing conditions NO$_2$ is formed from the reaction of NO with O$_2$ over the ZSM-5 based catalysts. When NO, C$_3$H$_6$ and O$_2$ were passed simultaneously, a significant selective reduction of NO to N$_2$ took place. Further, the experiments presented for NO alone did not show any evidence for the formation of N$_2$ or N$_2$O via decomposition of NO. In order to obtain N$_2$ and N$_2$O it is, therefore, necessary for a reductant such as propene to participate in the reaction. Correspondingly, when NO was passed over the catalyst previously exposed to propene or when NO and C$_3$H$_6$ were co-fed low NO conversions (<10%) to N$_2$ and N$_2$O were observed. However, only when O$_2$ was present significant conversion of NO to N and N$_2$O occurred and thus oxygen is associated, directly or indirectly, with the activation of NO. The role of O$_2$ is tentatively associated by many authors with the formation of NO$_2$ which is reduced by hydrocarbon to N$_2$ [22 a-h]

As regards the role of propene, exposing the catalyst to propene resulted in the deposition of carbon containing species (evidenced by combustion with oxygen pulses). In situ i.r. spectroscopy[21] indicated that at low temperatures propene was deposited on the acid sites as coke or oligomers. With increasing temperature these oligomers are combusted (i) to CO$_2$ and water by O$_2$ and (ii) to CO$_2$, water and N$_2$ by NO. The former is the unselective combustion and the latter results in selective reduction of NO. A subtle balance between these two pathways exist and as the temperature rises unselective combustion is favored. Correspondingly, we also observed an optimum in the selective formation of N$_2$ as a function of temperature.

Additional evidence for the involvement of carbonaceous species in the reduction of NOx comes from the experiments using methane. At lower temperatures in the presence of methane NO was converted
exclusively to NO$_2$. In contrast to propene, methane is not expected to decompose and deposit oligomers or coke at these temperatures [23] and is combusted by oxygen.

From the temperature vs yields curves it is seen that NO conversion follows propene conversion closely. Since platinum is very active for hydrocarbon oxidation it is logical to find enhanced activity by the addition of platinum. The positive effects of Pt addition found when using propene as reductant are not beneficial in the case of methane. Pt catalyzes very efficiently not only hydrocarbon combustion, but also the oxidation of NO to NO$_2$. Since methane is neither reactive enough at low temperatures nor blocks the sites for NO oxidation the overall result is the observed formation of NO$_2$ at low temperatures and the unselective combustion of methane at high temperatures.

During the catalytic experiments the N containing products observed are NO$_2$, N$_2$O, and N$_2$. In the following section selectivity to these components are discussed with a view to understand the reaction sequence in the reduction of NO to N$_2$.

The Pt based catalysts give high N$_2$O selectivity (Table 3). The increased yield to N$_2$O was pronounced at lower temperatures (see Fig 7). Burch et al. [20b] proposed that over Pt, NO decomposition takes place. In this mechanism NO decomposition leads to adsorbed N and O atoms on the Pt surface. N atoms may recombine or react with an undissociated adsorbed NO molecule resulting in the formation of N$_2$ and N$_2$O respectively. They suggested that lower temperatures favor N$_2$O formation, because at these temperatures NO adsorbs not dissociatively. The observation that Pt catalysts are active at low temperatures could explain their high selectivity to N$_2$O. However, even at 350°C Pt/ZSM-5 displayed a much higher selectivity to N$_2$O than the other catalysts (see Table 3). As showed above, NO decomposition is not significant over Co-Pt/ZSM-5.

Alternatively, the possibility that during the reduction of NO with hydrocarbons, an intermediate N containing organic compound (2-nitrosopropane or its isomer (CH$_3$)$_2$C=NOH) is formed [22 f, 24, 25] and that it react further to yield N$_2$O [22 f,25] is discussed in literature. Sachtler et al. [22f] proposed that the reaction of acetone oxime with (NO)$^+$ is a step in which N$_2$O is formed over Cu/ZSM-5. They further show that there is an additional route in which N$_2$O can be reduced to N$_2$. Our yield conversion plots show a secondary conversion (decomposition) of N$_2$O to N$_2$ [Fig 9, 10] in agreement with this suggestion. Since Pt is a poor N$_2$O decomposition catalyst [26] we observe higher N$_2$O selectivities in our experiments with Pt-ZSM5.

For Co, Pt and Co-Pt/ZSM-5 catalysts, the NO conversion passes a maximum, which has been ascribed previously to result from the decreasing availability of the reductant with increasing temperatures (it is consumed by direct oxidation)[20a] or by a decreasing concentration of NO and a higher abundance of oxygen in catalyst pores [20b]. NO$_2$ is observed only after 100% C$_3$H$_6$ conversion is reached, i.e. the
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reduction of NO by C₃H₆ replaced by the NO oxidation by oxygen. This latter reaction is catalyzed both by Co and Pt as deduced from separate experiments. In that context it should be noted that Pt containing catalysts are well suited for oxidation of NO to NO₂ [27]. Indeed, it is observed that Co-Pt/ZSM-5 catalyzes the oxidation of NO to NO₂ readily in the absence of propene. (At a reaction temperature of 350°C, an NO partial pressure of 1000ppm, 50 mbar O₂ in He and a GHSV= 15000 hr⁻¹ 64% NO is converted to NO₂). The initial shift to lower temperatures on the conversions during the temperature cycles was the result of a transformation on the catalyst. This is attributed to the formation of Co oxide clusters (see Fig. 5) which promote combustion [19] and NO₂ formation [18, 28] leading to increased activity of the catalyst.

At this point it is relevant to discuss the role of the Co oxidic phase present on the catalyst. There is controversy in the literature with respect to the effect of Co oxide on the selective catalytic reduction of NO to N₂. Some groups describe Co oxide as not active [5, 17], as detrimental for the reaction due to unselective hydrocarbon combustion[17, 29, 30], while others report Co oxide is active and beneficial due to the enhanced formation of NO₂ [18, 28, 31, 32]. It is very important to notice that the work described in the references above are using different reductants and conditions. The impact that these oxidic clusters may have on the SCR activity is strongly dependent on factors such as the reactivity of the specific hydrocarbon or in the temperature at which the SCR takes place. It is proposed that for hydrocarbons which are reactive at lower temperatures such as propene (as opposed to methane or propane) there is a beneficial effect in the presence of oxidic phase. The beneficial role of Co oxide as mentioned earlier via enhanced formation of NO₂ is discussed in the following section. At high temperatures the beneficial effects are lost due to unselective combustion that becomes the dominant reaction pathway.

4.4.4 Reaction path analysis

From the variation of selectivities with the conversion for Co-Pt/ZSM-5 at 350 °C it can be recalled that N₂ and N₂O are primary products and that some interconversion of NO to N₂ occurs at higher NO conversions. Since the experiments with N₂O showed that Co-Pt/ZSM-5 and Co/ZSM-5 are both active in the decomposition of N₂O to N₂ and combined with the fact that Pt catalyzes N₂O formation, we propose that readsoption of N₂O occurs on Co⁷⁺ followed by its reduction to N₂. Note that Co/ZSM-5 has been reported to reduce N₂O efficiently to N₂ [10, 12]. Therefore, the difference in N₂O selectivities among catalysts that contain only Pt and the ones with Co and small amounts of Pt can be due to the interconversion of N₂O to N₂.

While the parallel formation of N₂ and N₂O and its secondary conversion into N₂ has been well established by the variations in the conversion, the role of NO₂ is more difficult to assess. NO₂ is only
observed once all propene has been consumed. However, it has been found that the rate of NO$_2$ reduction by propene is about twice as fast as the reduction of NO. Thus, it is possible that in the presence of propene any NO$_2$ formed is immediately converted either to NO or N$_2$. It should be emphasized that the conversion of NO$_2$ should proceed via surface bound nitrate species, because the reaction of NO$_2$ with adsorbed propene will result in the reduction of NO$_2$ to NO [33]. In the presence of oxygen these species will form nitroso groups generated from the adsorption of NO on the Co-Pt/ZSM-5 samples. Conceptually, the appearance of NO$_2$ in the products will then also depend upon the temperature at which the reaction is performed, as the thermal stability and the reducibility of the nitrates are the key parameters, which determine its concentration.

The Brønsted acid sites are completely covered with propene oligomers under the reaction conditions used (see Fig. 6). While the discussion in the literature on the role of these deposits is controversial [34 a-g], the i.r. spectra presented suggest the presence of propene oligomers (sorbed as alkoxy groups) than partially oxidized surface species. These oligomers may interact with NO and become (partially) oxidized, but NO$_2$ in such a reaction is only converted to NO and not to N$_2$ [33]. It is speculated that hydrocarbons that are transformed into such an oligomer will only participate in NO reduction, if cracked as an olefinic fragment. Thus, it is concluded that the Brønsted acid sites do not directly participate in the reduction of NO, but provide a site for storage of hydrocarbons. If one accepts that the reaction proceeds via nitrites as intermediate the reaction on HZSM5 has to be related to the presence of extra lattice alumina, which is able to form aluminum nitrate.

The presence of 6 vol.% water exerted a moderate and positive influence upon the catalytic properties of Co-Pt/ZSM-5. With water in the feed the combustion of propene decreased, while the selectivity to N$_2$ increased with less NO$_2$ being formed. It is unclear at present whether water impedes propene oxidation or whether it reduces its sorption and oligomerization providing more olefins to react with the chemisorbed nitrate species.

Also the presence of 200 ppm SO$_2$ did only slightly decrease the activity for NOx reduction. Similar to what was observed with water the lower activity was compensated by a higher selectivity to N$_2$. This was mainly achieved via reducing the combustion of propene. As SO$_2$ is chemisorbed by forming sulfite (or in the presence of oxygen surface sulfate) with a Lewis acid base pair, it is concluded that the cobalt oxide or extra lattice alumina are the sites poisoned by water and SO$_2$.

4.4.5 The role of the various catalyst components

The active phases of Pt modified Co/ZSM-5 catalysts appear to be cobalt oxide in the pores of the zeolite, individual ions at exchange sites and metallic Pt particles. The role of the different phases
seem to be a complex series of simultaneous reactions. The oxide phase and the Pt particles are involved in the oxidation of NO to NO$_2$ and propene to COx as well as the formation of N$_2$O. The individual Co$^{2+}$ ions at exchange sites may be involved in the adsorption of NOx species and their reaction with activated propene to form intermediates that decompose resulting in the formation of N$_2$ as well as providing a site were N$_2$O may decompose to N$_2$. With respect to the reactants, the role of propene is mainly to react with NOx species and secondarily to facilitate the removal of oxygen and to keep Pt in a reduced state. Oxygen seems essential for the formation of NO$_2$ and to help avoiding the formation of substantial coke deposits. The presence of water and to a lesser extent SO$_2$ seems to retard the combustion of propene assuring that propene is available for the selective reduction of NOx to N$_2$.

4.5 CONCLUSIONS

Electron microscopy and XAS analysis of the samples indicate that three catalytically active phases are formed with the present catalyst. Over this catalyst NO is reduced by propene to N$_2$ and N$_2$O. The latter product can be also converted to N$_2$ over the present catalyst in a secondary reaction. At least a part of NO is oxidized to NO$_2$ (presumably adsorbed on Lewis acid base sites of the catalyst surface in the form of nitrates) and reacts with propene. The Lewis acid sites are partly blocked in the presence of water and SO$_2$. The blockage by water or SO$_2$, however, is compensated by the reduced combustion of propene leading so to higher N$_2$ yields. Evidence for a specific role of the Bønsted acid sites was not noted in the present study.

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CHAPTER 5

Reaction path analysis and *in situ* i.r. spectroscopic study of the surface species during the selective catalytic reduction of NO over Co-Pt/ZSM-5

Abstract

*In situ* i.r. spectroscopy was employed to study the adsorbed species present under SCR reaction conditions over Co-Pt/ZSM-5 catalyst. Formation of carbonaceous deposits, partially oxidized species, organo-nitro/nitro/nitrite/nitrate species and nitrile was observed. The correlation between changes observed in the absorption band related to nitrile species and the catalytic activity of Co-Pt/ZSM-5 suggest that nitrile species are involved in the formation of N₂. A mechanism in which adsorbed hydrocarbons react with NOx compounds to form organo-nitro intermediate is proposed. The nitrile originated from the organo-nitro intermediate in an acid catalyzed hydrolysis form NH₄⁺ ions. These NH₄⁺ ions then reduce NOₓ to N₂.
5.1 INTRODUCTION

Substantial interest in the selective catalytic reduction (SCR) of nitrogen oxides in the presence of excess oxygen exists in order to reduce emissions from stationary and mobile sources [1,2]. In particular the use of hydrocarbons as reductant is promising [2]. Group VIII metals supported on carriers such as oxides, zeolites have been reported as catalysts [1-13]. Previously [3a-b] we have shown that a bimetallic Co-Pt/ZSM-5 catalyst is very efficient in the selective reduction of NO with propene. The catalyst shows a synergistic effect by combining high activity of Pt catalysts with the high N₂ selectivity shown by Co catalysts. Furthermore, the catalyst also shows water and SO₂ tolerance which is an essential requirement for practical applications.

In spite of the intense research, the mechanism of the selective catalytic reduction with hydrocarbons is still under debate. Over some catalysts, e.g. Cu/ZSM-5, NO decomposes to nitrogen and oxygen in the absence of hydrocarbons, and hence a decomposition mechanism was proposed [4 a-b]. The mechanism of reduction of NO in the presence of hydrocarbons, however, is more complex. Based on transient kinetics experiments over Pt/γ-Al₂O₃, Burc et al. [4a] suggested that the role of hydrocarbon was to scavenge oxygen and keep the Pt surface reduced to allow decomposition of NO. The decomposition of NO leads to surface bound N and O. Recombination of N with another N or NO leads to N-N pairing and to the formation of N₂ or N₂O, respectively. Rottlander et al. [5] argued that C₃H₆ and C₃H₈ would remove oxygen from the surface with comparable efficiency and thus should give similar NO reductions. However, higher NO conversions were observed with propene. To account for this, alternate suggestions were made, that NO reduction occurred via carbonaceous deposits [5-7] or oxygenates [6] derived from propene. Evidence for the NO reduction by carbonaceous deposits is supported by the fact that catalytic activity was retained for some time after the alkene was removed from the feed [6,7,8 a-c]. However, Pitchon et al. [9] claim that over Pt based catalyst, during SCR with propene in presence of O₂, no hydrocarbon deposition took place. In accordance to that partially oxidized hydrocarbons are claimed to be the reducing agents [10 a-c]. This is inferred from the fact that the reduction of NO starts almost at the same temperature where the oxidation of the hydrocarbon occurs. Although compounds such as propanol, ethanol, acetone showed SCR activity, propene was more effective [10c].

Many authors claim yet another route, involving NO₂, formed from the reaction of NO and O₂, which preferentially react with the hydrocarbon to yield N₂ [11 a-h]. The sequence consists of the formation of organo nitrogen (-nitro, -nitroso) intermediates by reaction of NO₂ with hydrocarbon. These species produce by decomposition/dehydration or hydrolysis: isocyanate [11c, 12-14], oximes [11f, 15a], or nitril [11g, 15a-b]. Subsequent hydrolysis or reaction of these with NO, NO₂ or O₂ forms N₂.

Catalysts reported for the reaction are based on acidic supports, however, the role of the acid sites
is also a subject of controversy. For Cu/ZSM-5, Hayes et al. [11g] and Kharas et al. [16] suggested that acid sites are not involved in the reaction. They based this on their kinetic results which indicate that NO reduction takes place exclusively on Cu ions and do not depend on the acid site concentration. On the other hand the beneficial effect of acid sites in SCR was reported on several publications [15a, 11b, 17a-e]. Some proposed that the role of the acid sites was to oxidize NO to NO₂ [e.g. 11b]. Others proposed that over the acid sites NO and NO₂ react to form NO⁺, which reacts further with hydrocarbons to form organic intermediates [15a]. Further, the acid sites also catalyze the hydrolysis of these intermediates and lead to the formation of N₂. Suggestion was also made that protonation of adsorbed hydrocarbon takes place over the acid sites generating carbocations, that react with NO₂ from the gas phase to form N₂ [17e].

This discussion summarized how difficult and complex to understand the reactions of NOx with hydrocarbons are. The complexity also suggests that more than one pathway may exist under typical operating conditions. [11f, 11h, 18a-b]. The purpose of this study is to clarify the role of the different reactants (propene, O₂, NO) and of the different catalyst functions (Co, Pt, acid sites) on the SCR of NO over Co-Pt/ZSM-5. In situ i.r. spectroscopy is employed in this work to identify the reacting species, their origin and which of these are involved in the formation of N₂.

5.2 EXPERIMENTAL

A Co-Pt/ZSM-5 catalyst with 2.8 wt % Co, 0.1 wt % Pt and a ZSM-5 zeolite with Si/Al ratio 38.5 was used in this study. Please insert here nevertheless the preparation study. The details of the catalyst are given elsewhere [3b].

5.2.1 I.r. Spectroscopy

The spectra were recorded in situ on a BRUKER IFS 88 FTIR spectrometer (resolution 4 c⁻¹) in a continuous gas flow mode using the transmission-absorption technique. The i.r. gas cell was equipped with a heatable sample holder and CaF₂ windows. All i.r. spectra were recorded in the range from 3800 cm⁻¹ to 1300 cm⁻¹ with a time resolution of 30 s. The catalyst was pressed into a self supporting wafer (2 mg) and activated in flowing He at 500 °C for one hour. Difference spectra were obtained by subtracting the spectrum of the catalyst from the spectra measured during the reaction. Both spectra were collected at the same temperature. The difference spectra shows bands with increased intensity pointing upwards while bands with decreased intensity point downwards (negative peaks). After activation, the following series of experiments were performed:

(i) Reaction of propene at 350 °C : Co-Pt/ZSM-5 was heated to 350 °C and a mixture of 2000 ppm C₃H₆
in He was passed over the catalyst at rate of 10 ml/min. Spectra were collected every minute for 30 minutes and then at 1 hour intervals. After 19 hours the catalyst was purged with pure He and finally brought in contact with a mixture of 5% O₂ in He for 10 min.

(ii) Reaction of NO between 40 °C - 500 °C: Co-Pt/ZSM-5 was heated to 40 °C and 1000 ppm NO in H was passed over the catalyst (10 ml/min.). Spectra were recorded every 30 seconds for 10 minutes and then at 10 minute intervals for one hour. The catalyst was heated to 200 °C in He. The flow was switched to NO/He and the temperature was increased with 10 °C/min from 200-500 °C. During the temperature increase i.r. spectra were recorded at temperature intervals of 25 °C.

(iii) Reaction of NO and O₂ between 40 °C - 500 °C: The procedure was identical to that described under (ii), but in this case the mixture was contained 1000 ppm NO and 5% O₂ in He.

(iv) Reaction of NO, C₃H₆ and O₂ between 200 - 500 °C: The catalyst was heated to 200 °C in He. Then, a mixture of 1000 ppm NO, 2000 ppm C₃H₆ and 5% of O₂ in He was passed over the catalyst. Spectra were recorded every 30 seconds for 10 minutes and then at intervals of 0.5 hours. Subsequently, the temperature was increased linearly from 200-500 °C and the i.r. spectra were measured (see section ii).

(v) The influence of water addition at 350 °C: The catalyst was brought to 350 °C in He. Then, a mixture of 1000 ppm NO, 2000 ppm C₃H₆ and 5% of O₂ in He was passed over the catalyst. After one hour at this temperature, 5% water vapor was added to the reactant gas mixture by means of a syringe pump. After 90 minutes the water addition was stopped. Finally the catalyst was purged with flowing He for 48 hours. Spectra were recorded during the experiment and after the purging period.

5.3 RESULTS

Figs. 1-6 show the results of the IR measurements. Tables 1-3 summarize the wavenumbers observe and their assignment (see Appendix).

5.3.1 Activation of the catalyst

In Fig. 1 the FTIR spectra of the parent H/ZSM-5 and of the Co-Pt/ZSM-5 after activation in H at 500 °C are shown. H/ZSM-5 displays absorption bands at 3740 cm⁻¹ (terminal Si-OH groups), 3610 cm⁻¹ (bridging Si-OH-Al, groups), 2000 cm⁻¹, 1880 cm⁻¹, 1640 cm⁻¹, 1480 cm⁻¹ (Si-O-Si lattice overtones) [19]. Co-Pt/ZSM-5 shows a reduced intensity of the peak at 3610 cm⁻¹ and small decrease in the band at
3740 cm\(^{-1}\). This indicates that the exchanged metals ions, Co\(^{2+}\) and Pt\(^{4+}\), are located mainly on the bridging oxygen of Si-O-Al groups and to a small extent at the terminal oxygens of Si-OH groups.

5.3.2 Reaction of propene

Fig. 2 shows the i.r. spectra for Co-Pt/ZSM-5 after exposure to 2000 ppm C\(_3\)H\(_6\) in He at 350 °C as a function of time. Table 1 summarizes the observed bands and their assignments (see Appendix ).

At the first minute of reaction, the two peaks corresponding to OH bands (3740 cm\(^{-1}\) and 3610 cm\(^{-1}\)), decreased with the exposure. This is deduced from the appearance of two negative bands at these wavenumbers. The changes for the band at 3610 cm\(^{-1}\) were more intense than those of the band at 3740 cm\(^{-1}\).

In the C-H stretching region (3200-2800 cm\(^{-1}\)) bands appeared at 3100 cm\(^{-1}\) (=CH\(_2\)), 3070 (=CH), 2956 (=CH\(_3\)) and 2917 (=CH\(_2\)). These bands grew slowly and after 5 minutes they merge into two broad bands with peaks at 3120, and 2970 cm\(^{-1}\).
Bands appeared also at 1670 cm\(^{-1}\) (C=O), 1625 cm\(^{-1}\) (C=C), during the first minute. After 2 minutes of reaction new bands appeared at 1580 and 1540 cm\(^{-1}\). After 30 minutes the peak at 1670 cm\(^{-1}\) remained as a shoulder while the peaks at 1580 cm\(^{-1}\) and 1540 cm\(^{-1}\) became dominant. Finally after 19 hours only the peak at 1580 cm\(^{-1}\) (sh 1540 cm\(^{-1}\)) was observed (See Table 1 for assignment).

Additionally, bands were observed at 1439 and 1380 cm\(^{-1}\). These bands grew steadily with time, however, after 19 hours only the band at 1439 cm\(^{-1}\) (sh 1380 cm\(^{-1}\)) was found (see Table 1 for assignments). After 19 hours the propene stream was stopped and the catalyst was purged with He for 10 minutes at 350 °C. The spectra did not indicate changes during that period. When a mixture of 5% O\(_2\) in He was passed over the catalyst at 350°C these bands decreased only marginally and were visible even after 4 hours.

### 5.3.3 Reaction of NO

Fig. 3 shows the i.r. spectra for Co-Pt/ZSM-5 after exposure to 1000 ppm of NO in He at 40 °C as a function of time. Table 2 summarizes the observed bands and their assignments (see Appendix).

At the first moments of NO adsorption negative peaks appeared at 3744 cm\(^{-1}\) and 3610 cm\(^{-1}\) indicating absorption on silanol and Brønsted acid sites. In parallel a positive broad band grew slowly at 3500 cm\(^{-1}\) indicating interactions between NO and the Brønsted acid sites [20]. Initially, bands were also observed at 2131, 1910 (broad band with shoulder at 1935 cm\(^{-1}\) and 1896 cm\(^{-1}\)), 1813, 1633, 1601 and 1580 cm\(^{-1}\) (shoulder at 1540 cm\(^{-1}\)). Based on previous reports the band at 2131 cm\(^{-1}\) is...
attributed to weakly adsorbed NO$_2$+ or NO$^+$ [15a-b, 20 - 23, 24a], that at 1935 cm$^{-1}$ to Co(NO), those at 1896 and 1813 cm$^{-1}$ to Co(NO)$_2$, while the bands between 1633-1540 cm$^{-1}$ appear to be related to Co-NO$_2$. Co-ONO and/or Co-ONO$_2$ species [11d, 11g, 15b, 21, 24a-27]. Relevant examples are included in Table 2. With time the broad band at 1910 cm$^{-1}$ transormed into two well separated peaks at 1935 cm$^{-1}$ and 1896 cm$^{-1}$. The assignment of these bands is discussed below. After one hour on stream the main spectral features were intense bands bands between 1633-1540 cm$^{-1}$ and small ones at 2130, 1935, 1890 and 1813 cm$^{-1}$.

Fig 4. shows the change in the adsorbing species as function of the temperature. At 200 ºC the negative band at 3740 cm$^{-1}$ disappeared, while at 375 ºC also that at 3610 cm$^{-1}$ disappeared. Above 425ºC all sorbed species had been desorbed.

**5.3.4 Reaction of NO and O$_2$**

The results of the exposure of Co-Pt/ZSM-5 to a mixture of 1000 ppm of NO and 5 % O$_2$ in He were similar to those obtained when only NO was adsorbed over the catalyst. However, in the presence of oxygen the bands between 1700-1400 cm$^{-1}$ were slightly more intense, the peaks between 2130 - 1813 cm$^{-1}$ were smaller than in the absence of oxygen. Above 450 ºC adsorbed species were also not detected in this case.

**5.3.5 Reaction of NO, C$_3$H$_6$ and O$_2$**

Fig. 5 shows the i.r. spectra for Co-Pt/ZSM-5 after exposure to 1000 ppm of NO, 2000 ppm C$_3$H$_6$ and 5% of O$_2$ in He at 200 ºC as a function of time. Table 1-3 summarizes the observed bands and their assignments (see Appendix ).

Immediately after exposure to the gas mixture a negative peak was observed at 3610 cm$^{-1}$, while only after 0.5 hours a very small negative peak appeared at 3744 cm$^{-1}$. A broad band between 3500-3200 cm$^{-1}$ developed even more slowly. With time on stream bands around 3200-3100 cm$^{-1}$ (aromatic =C-H and
Chapter 5 - Reaction path analysis and *in situ* i.r. spectroscopic study ...

Figure 5 I.r. spectra of the surface species formed by the reaction of NO, O₂ and C₃H₆ over Co-Pt/ZSM-5, Conditions: 200° C, NO 1000 ppm, O₂ 5% and C₃H₆ 2000 ppm in He.

Figure 6 I.r. spectra of the surface species present under reaction conditions over Co-Pt/ZSM-5, Conditions: 350° C, NO 1000 ppm, O₂ 5% and C₃H₆ 2000 ppm in He.

...=CH₃), 3000- 2800 cm⁻¹ (-CH, -CH₂, -CH₃), 2260 cm⁻¹, 2160 cm⁻¹ related to isocyanate (-NCO) groups and/or nitrile groups (-NC) [11g,12, 13, 15b, 28, 29] increased continuously in intensity. Bands due to Co(NO)₂ at 1896 cm⁻¹ and 1813 cm⁻¹ initially appeared, however, they disappeared with time. From the beginning of the exposure a multiply structured group of bands was observed between 1750 and 1300 cm⁻¹. For the sake of clarity these bands are divided into three regions, i.e., between 1750-1635 cm⁻¹, 1635-1500 cm⁻¹ and 1500-1300 cm⁻¹. The bands at 1750-1630 cm⁻¹ are attributed to C=C and C=O stretching vibrations, 1635-1500 cm⁻¹ to surface NOx species (Table 2), oxygenates (carboxylate, carbonate, formate) or coke and 1500-1300 cm⁻¹ to allylic, formate, and/or carbonate type species (Table 1).

Fig. 6 shows the change in the spectra upon heating from 200 to 500 °C. All the bands in the region 3800-2800 and 1500-1300 cm⁻¹ decreased. In contrast, the bands at 2260 cm⁻¹ (sh 2230, 2160 cm⁻¹) and at 1750-1500 cm⁻¹ increased continuously with temperature reaching a maximum at 300 °C. All the bands, except those between 1600-1300, disappear completely at 500 °C. This is in contrast to the experiments were propene was absent and adsorbed species were not observed beyond 450 °C. Thus,
the bands are obviously related to propene and the possible surface chemistry under these reaction conditions will be discussed below (See Fig. 2 and Table 1-3).

5.3.6 The influence of water

Addition of 5% water vapor to the reactant gas mixture at 350°C did not induce significant changes in the infrared spectra. However, a temporary decrease in the intensity of bands at 2250 cm⁻¹, 1800-1750 cm⁻¹ was observed, which was reverted after a short while. Bands at 3200-3100, 1585 and 1850-1700 cm⁻¹ continued varied similarly as in the absence of water. Water and reaction gases were then switched off, and the catalyst was left in flowing He for 48 hours. Significant changes in the spectra were not observed during that period.

5.4 DISCUSSION

Weak (silanol groups) and strong (bridging hydroxyl groups) acid sites of Co-Pt/ZSM-5 are covered under typical reaction conditions. The process occurs faster on the bridging hydroxyl groups and slower on the SiOH groups. This is attributed to the formation of propene oligomers at the acid sites existing typically as alkoxy groups. This is in line with the knowledge that Brønsted acid sites have strong tendency to adsorb and oligomerize olefines. This is for example shown elegantly by Eisenbach et al. [30] during sorption of 1-hexene over Pt/Y at 350 °C. Note that characteristic bands of C-H bonds in aromatic molecules and of C=O and C=C groups (at 1670 cm⁻¹ and 1625 cm⁻¹ respectively) indicate a quite complex surface chemistry beyond oligomerization. While the presence of these bands is reproducibly observed, the attribution of these bands based on group frequencies is still speculative. Hayes et al. [11g] showed that passing propene alone at 300 °C over Cu/ZSM-5 caused the appearance of a band at 1670 cm⁻¹ and they assigned it to the C=O stretching of propen-2-al (acrolein). The oxygen necessary to form acrolein was proposed to originate from the oxo bridges between Cu²⁺ ions or hydroxyl species. Finocchio et al. showed [31] that Co₃O₄+x caused propene oxidation to acrylate species already at RT indicating the consumption of lattice O²⁻ anions. Mo-Ga oxide catalysts also form acrolein at 200 °C in absence of oxygen [32]. The results mentioned above supports the presence of partially oxidized species such as acrolein over the catalysts formed by reduction of the metal-oxygen bonds.

It has been reported in a previous paper that a Co oxide phase exists in the catalyst [3a]. Conceptually, that phase could be the source of oxygen needed for the propene species seen in Fig.2. Furthermore, in the presence of oxygen both Pt and CoOx catalyze this reaction. However, also the presence of bidentate carbonate O=CO₂ (C=O vibration 1530-1620 cm⁻¹, 1620-1670 cm⁻¹) [32] cannot
be ruled out. Hayes et al. [11g] found over Cu/ZSM-5 a band at 1590 cm\(^{-1}\) and they assigned it to asymmetric C-O stretching vibration of a surface carboxylate. Such reactions are well known for adsorption of ketones and aldehydes on oxide surfaces.

The results discussed above show that partially oxidized species are formed over the catalyst, but show also the difficulty to describe unequivocally the nature of the sorbed species. The role of these intermediates is unclear at present. Controversially, the oxidized molecules (such as aldehydes, alcohols, ketones etc) were proposed to be intermediates in the SCR of NO to N\(_2\) [10 a-c] or only in the unselective combustion of propene [11g]. For the present case the surface species were very stable and resisted purging with He at 350 ºC and even the presence of 5% O\(_2\) in the feed stream.

It is known from the literature that oxidation of C\(_3\)H\(_6\) proceeds via \(\pi\)-allyl complexes [33]. The \(\pi\)-allyl complexes may undergo selective oxidation of the methyl C-H allylic bond by nucleophilic oxygen to produce acrolein. We observed at reaction temperatures bands that could be assigned to allyl species (1435 cm\(^{-1}\), sh 1380 cm\(^{-1}\)) and acrolein (1620 cm\(^{-1}\), 1670 cm\(^{-1}\)). However, under the reaction conditions the chances are that acrolein, once formed, is an intermediate in the combustion of propene. The coke that is formed can also be combusted unselectively, but most of it stays as spectator species over the acid sites during reaction (Fig.6). Before discussing the role of intermediates derived from propene in SCR, it is the surface chemistry of NO will be addressed.

Experiments with NO alone (Fig. 3, 4) indicate interactions between the Brönsted acid sites as well as with Co and NO even at reaction temperatures (350 ºC). As was mentioned above, we assigned the band at 1935 cm\(^{-1}\) (sh) to Co(NO) and 1896 cm\(^{-1}\) (sh) together with 1813 cm\(^{-1}\) to Co(NO)\(_2\). The peak at 1910 cm\(^{-1}\), which was not assigned earlier, may originate from distorted Co(NO)\(_2\) [11d]. Ailor et al. [15b] proposed that the presence of Co\(^{2+}\) ions at different locations on ZSM-5 could lead to the appearance of more than one type of nitrosyls. The band at 1910 cm\(^{-1}\) has also been attributed to adsorbed N\(_2\)O\(_3\) [25], however N\(_2\)O\(_3\) is thermally unstable and since the band is present only temporarily at 40 ºC we rule out any significance of this under the reaction conditions. Further the i.r. spectra of the adsorption of NO at 40 ºC indicate presence of Co-NO\(_2\), Co-ONO and/or Co-ONO\(_2\) species (Fig.3 Table 2). This is in accordance with NO adsorption studies over transition metal (oxides) supported on zeolites eg. (Cu/ZSM-5 [24a], Co/ZSM-5 [15b], CaY [25], etc). The formation of this species can be explained as follows by the reaction of NO with surface oxygen to form NO\(_2\) (Co-Pt/ZSM-5 is active in the oxidation of NO to NO\(_2\) [3b]). NO\(_2\) reacts further over Co to form Co-NO\(_2\), Co-ONO and/or Co-ONO\(_2\) species. The oxygen for the nitrate formation will be provided from the cobalt oxide clusters or the zeolite lattice or the hydroxyl group at the Co\(^{2+}\) sites [24 a-b]. NO disproportionation at low temperatures has also been suggested as reaction pathway for NO\(_2\) formation [21, 25, 34a-b]. In general, the adsorption of NO in the presence or in th
absence of O$_2$ over Co-Pt/ZSM-5 led to similar results. The slightly more intense bands between 1700 and 1400 cm$^{-1}$ indicate that formation of Co-NO$_2$, Co-ONO and/or Co-ONO$_2$ compounds was slightly enhanced by the presence of oxygen. Note that formation of NO$_2$ from NO in the absence of O$_2$ is also indicative of the Co oxide phase.

Under simulated reaction conditions, i.e. in the presence of NO, C$_3$H$_6$ and O$_2$ (Fig. 6), peaks at 2260 cm$^{-1}$ and at 2160 cm$^{-1}$ were assigned to isocyanate (-NCO) or nitriles (-CN) species [35]. Bands in this region were reported in various spectroscopic studies for the selective catalytic reduction of NO [11-13, 15b, 28, 29]. For example, on CuZSM-5 [11g] the band at 2260 cm$^{-1}$ was assigned to nitriles, rather than to isocyanates based on water instability of the latter. Similarly in [36] over γ-Al$_2$O$_3$ a band at 2228 cm$^{-1}$ was assigned to isocyanate rather than nitrite on the basis of the instability of the former in the presence of water. Over Co/ZSM-5 [15b] based on isotopic substitutions, the bands at 2270 and 2173 cm$^{-1}$ were attributed to -NCO species adsorbed on Al$^{3+}$ and -CN species on Co$^{2+}$ respectively. Over CoOx/ZSM-5 a band at 2220 cm$^{-1}$ was attributed to -NCO adsorbed on Co$_3$O$_4$[28]. Over Pt/Al$_2$O$_3$, bands at 2140 cm$^{-1}$ and 2232, 2254 cm$^{-1}$ were assigned to CN species and NCO respectively [12]. Over Pt/SiO$_2$ -NCO [13] was reported at 2174 cm$^{-1}$ and was proposed as intermediates in the formation N$_2$.

During our experiments over over Co-Pt/ZSM-5 at 350 ºC addition of water to the feed did not have influence the i.r spectra. Under these conditions isocyanates are expected to readily hydrolyze. Thus, based on water sensitivity we conclude that nitriles (-CN) species rather than isocyanate (-NCO) species are present during reaction conditions.

Having established the presence of nitrile type species on the surface of the catalyst, we will now try to trace its origin and its possible involvement in the formation of nitrogen. To start with we have shown earlier that absorptions at 1439 cm$^{-1}$, 1380 cm$^{-1}$, when propene was passed over the catalyst at 350 ºC, indicated presence of allylic species derived from propene. Further, during the NO adsorption experiments species formed that were assigned to Co-NO$_2$, Co-ONO and/or Co-ONO$_2$ species. These NOx compounds can react with carbonaceous deposits or allylic species to form organo-nitro intermediates [11f-g]. In the presence of propene and NO organo-nitroy/-nitroso species have been proposed [11g, 11f, 15a,etc]. This nitro (R-CH$_2$-NO$_2$) or nitroso (RCH$_2$-NO) fragments may isomerize to an oxime (R-CH=NOH) [11f-g, 15a]. Dehydration of this oxime forms the nitrile, R-CHCN. During our experiments, the peaks assigned to nitriles (-CN) species grew as function of the temperature until 300ºC. Above that temperature they started to react or decompose. Note that this coincides with the temperatures at which high SCR activity was observed [3a-b]. More work, however, is needed to unequivocally demonstrate the participation of the nitriles in the NOx reduction.

At this point, we would like to speculate on the role of Brönsted acid sites for the SCR reaction.
We have reported earlier that [3b], for H-ZSM5 catalytic activity did depend on acid site concentration, \textit{i.e.}, decreasing Si/Al ratio [thus higher Brønsted acid concentration] increased the NO$_2$ conversion to nitrogen. We speculate that these acid sites catalyze the hydrolysis of the organo nitrile species, generating, \textit{in situ}, sorbed ammonium ions (again on the Brønsted acid sites), which then reduce the NO to N$_2$. In this context it is interesting to note that the acid catalyzed hydrolysis of nitriles leads to amides (R-C=ONH$_2$) which react further to yield carboxylic acids (RC=OOH) and ammonium ions [15a, 29]. Bands related to carboxylates were indeed found in our studies. (see Figure 6). Note also that bands for ammonium ions (3300-3100 cm$^{-1}$) [35] were also found under the reaction conditions in this study (see Fig 6). The conversion NO over NH$_4^+$ containing zeolites in excess of oxygen was reported recently [36].

To summarize, the i.r. spectra presented are compatible with the following sequence of the SCR of NO$_x$ over Co-Pt/ZSM-5. Propene is activated over the catalyst via \textit{π}-allyl species on the metal sites. Propene is also deposited over the acid sites as coke. The \textit{π}-allyl complexes undergo selective oxidation to form partially oxidized compounds for e.g. acrolein. These are combusted to CO$_2$, CO and H$_2$O. NO is oxidized over CoOx and Pt to NO$_2$. Nitrite/nitrate type compounds are directly formed from NO$_2$ by interaction with Co or CoOx or from the reaction Co$^{2+}$(NO), Co$^{4+}$(NO)$_2$ with oxygen or NO. These NO$\_x$ compounds react with allylic species to form organo-nitro (R-CH$_2$-NO$_2$) or nitroso (RCH$_2$-NO) intermediates. These isomerize (the organo nitro group first is reduced to a nitroso group) to yield an oxime (R-CH=NOH). Dehydration of this oxime forms the nitrile R-CHCN. This nitrile is decomposed by acid catalyzed hydrolysis to NH$_4^+$ ions. In the last step, the NH$_4^+$ ions reduce NO$\_x$ to N$_2$.

**5.5 CONCLUSIONS**

Using \textit{in situ} i.r. spectroscopy it has been shown that over Co-Pt/ZSM-5 propene is oligomerized under reaction conditions to coke over the acid sites and/or undergoes allylic oxidation to acrolein. Coke and acrolein over metal(oxide) sites result in direct combustion to COx and H$_2$O. Pt (and to lesser extent CoOx) catalyze this. In parallel organo-(-nitro/-nitroso), nitrite/nitrate and nitrile species are formed. We propose that over Co-Pt/ZSM-5, NO$\_x$ compounds react with allylic species to form organo-nitro intermediates (nitro (R-CH$_2$-NO$_2$) or nitroso (RCH$_2$-NO)). The intermediates are transformed to an oxime (R-CH=NOH) that dehydrates to form a nitrile (R-CHCN). Correlation between changes observed in the absorption band related to nitrile species and the catalytic activity of Co-Pt/ZSM-5 led us to speculate that nitrile species are involved in the formation of N$_2$. Acid catalyzed hydrolysis of the nitril results in the formation of NH$_4^+$ ions on Brønsted acid sites. Finally, the NH$_4^+$ ions reduce NO$\_x$ to N$_2$. 


ACKNOWLEDGMENTS

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REFERENCES


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APPENDIX - Infrared absorption bands assignmen

**Table 1.** The assignments of the infrared bands - sorption of propene.

<table>
<thead>
<tr>
<th>I.r. absorption (cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3740</td>
<td>-OH stretching (terminal Si-OH weak acid sites) [19]</td>
</tr>
<tr>
<td>3610</td>
<td>-OH stretching (bridging Si-OH-Al strong acid sites) [19]</td>
</tr>
<tr>
<td>2000, 1880 1640, 1480</td>
<td>lattice overtones Si-O-Si [19]</td>
</tr>
<tr>
<td>3120</td>
<td>=C-H stretching (aromatic, ethylenic) [35]</td>
</tr>
<tr>
<td>1670</td>
<td>C=O stretching [35] (adsorbed acrolein.) [11g, 32]</td>
</tr>
<tr>
<td>1625</td>
<td>C=C stretching [35] (adsorbed acrolein) [11g, 32]</td>
</tr>
<tr>
<td>1580</td>
<td>C=C stretching (aromatic coke)[30, 37], C=O vibration (adsorbed carbonate)[12, 31, 32], O-C-O sym. stretch,(formate,carboxylate) [31, 32]</td>
</tr>
<tr>
<td>1540</td>
<td>C=O vibration adsorbed carbonate, formates [12, 35]</td>
</tr>
<tr>
<td>1439</td>
<td>allylic species [11g, 33], carbonates, formates [12, 31, 32].</td>
</tr>
</tbody>
</table>
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1380 allylic species[33]O-C-O stretching asym.vibrations formate ions [12,31,32]

**Table 2.** The assignments of the infrared bands. -Sorption of NO

<table>
<thead>
<tr>
<th>I.r. absorption (cm(^{-1}))</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3744, 3610</td>
<td>O-H stretching, acid sites [see propene], negative bands due to interaction with NO</td>
</tr>
<tr>
<td>2131</td>
<td>weak adsorbed NO(_2) [11d], NO(_2^+) adsorbed on acid sites [15b, 22, 23], reversible adsorbed NO(_2^+) [21] NO(_2) species [38], NO reacting with ELO [24a], NO(^+[15a])</td>
</tr>
<tr>
<td>1910</td>
<td>Co-NO secondary species mononitrosyl [11d, 15b], N(_2)O(_3) [25]</td>
</tr>
<tr>
<td>1896, 1813</td>
<td>1890, 1810 Co(NO)(_2) [11d] dinitrosyl , 1894 1815 [15b, 21]</td>
</tr>
<tr>
<td>1633</td>
<td>Nitro species 1627 Co-NO(_2) [11d], 1628 Cu-NO(_2) [26], nitrito NO(_3) , nitrate NO(_3); [15b]</td>
</tr>
<tr>
<td>1601</td>
<td>Cu NO(_3^-) monodentate nitrate ions 1594 [26], Cu covalent nitrat nitrito1605 [26] Cu(NO(_3))(_2) Co bidentate nitrito 1595 [11d], Co-O(_2)N=O bidentate nitrate 1599 [15b]</td>
</tr>
<tr>
<td>1580</td>
<td>CuNO(_3^-) bidentate nitrate 1572 [26], Co-O(_2)N=O bidentate nitrate 1599 [15b, 25], bidentate, monodentate nitrate 1575 [27], organo nitro 1570 [11g]</td>
</tr>
<tr>
<td>1540</td>
<td>Co NO(_3^-)1540 nitrato compound [11d], MO(_2)N=O bidentate nitrate [23], 1545 cm(^{-1}) bidentate nitrat nitrato PtO(_2)N=O [24a]</td>
</tr>
<tr>
<td>1527</td>
<td>CoONO nitrito 1526 [26],1528 [15b], 1530 [28]</td>
</tr>
</tbody>
</table>

**Table 3.** The assignments of the infrared bands. - Observed under reaction conditions

<table>
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<tr>
<th>I.r. absorption (cm(^{-1}))</th>
<th>Assignment</th>
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<tbody>
<tr>
<td>3500-3200 (br)</td>
<td>NH(_4^+) , NH(_3) species [35]</td>
</tr>
<tr>
<td>2260 2160</td>
<td>isocyanate (-NCO)nitriles (-CN) species [35], CuZSM-5 nitriles 2260 [11g], CoZSM-5 NCO species adsorbed on Al(^{3+}) 2270 -CN species on Co(^{3+}) 2173 [15b]-NCO adsorbed on Co(_2)O(_2) 2220 c (^{-1}) [28], Pt/Al(_2)O(_3) on-CN species at 2140 -NCO at 2232, 2254,[12], PtSiO(_2) -NCO at 2174 [13], -NCO γ-Al(_2)O(_3) 2228 [36]</td>
</tr>
<tr>
<td>1585</td>
<td>organo nitro 1570 [11g]</td>
</tr>
</tbody>
</table>
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CHAPTER 6
Selective catalytic reduction of NO to $N_2$
over Co-Rh/ZSM-5 catalysts

Abstract

The selective catalytic reduction of NO by propene in the presence of excess oxygen has been studied over catalysts based on Co-Rh supported on ZSM-5. Compared to Co exchanged ZSM-5 catalysts, bimetallic Co-Rh/ZSM-5 shows improved activity, while maintaining high $N_2$ selectivity. In situ i.r. spectroscopy was employed to study the adsorbed species present during selective catalytic reaction of NO with propene. Based on these results, a mechanism in which adsorbed hydrocarbons react with NO to form organo-nitro intermediates are proposed and the route to the formation of $N_2$ from these compounds is discussed.
Chapter 6 Selective catalytic reduction of NO to N₂ over Co-Rh/ZSM-5 catalysts

6.1 INTRODUCTION

Selective Catalytic Reduction (SCR) of NOx to N₂ in presence of oxygen is an essential step in the clean up of power plant emissions. Group VIII metals supported on carriers such as oxides and zeolites have been reported to be potential catalysts [1-2]. Previously, we have reported that Co-Pt/ZSM-5 catalysts are active, stable and selective for the reduction of NO [3]. We found, however, that the most active catalysts with a relatively high Pt loading showed enhanced selectivity towards N₂O. While Co-Pt/ZSM-5 catalysts are a stable, active and reasonably tolerant towards water and SO₂ during the reduction of NO with propene in presence of oxygen, N₂O formation needs to be minimized.

Rh, may be a useful alternative to Pt in bimetallic catalysts, as it is a key component of the three-way catalyst which is efficient in the catalytic reduction of NOx to N₂ from the gasoline engine exhausts [4,5]. Additionally, in comparison to Pt/γ-Al₂O₃, Rh/γ-Al₂O₃ yields lower amounts of N₂O during reduction of NOX [5]. Thus, a series of Rh containing catalysts for the reduction of NO with propene has been studied. In order to better understand the catalytic chemistry, kinetic and in situ i.r spectroscopic experiments have been carried out. The role of Rh, in the bimetallic catalysts is discussed.

6.2 EXPERIMENTAL

6.2.1 Catalyst preparation

The catalysts were prepared via solid state ion exchange. The parent ZSM-5 (Na form, Si/Al = 38.5, P.Q. Zeolites) was first heated in N₂ and subsequently in air at 500°C for 12 hours. Then, the zeolite was ion exchanged twice with 0.1M NH₄NO₃ solution. For the preparation of the catalysts, the NH₄ form of ZSM-5 (5g) was thoroughly ground with the required amounts of CoCl₂·6H₂O and RhCl₃·3H₂O (Aldrich Chemicals). The resulting mixture was heated to 500 °C at 2 °C/min in He and was maintained at this temperature for 12 hrs. During the heating cycle the samples were maintained for three hours near the melting point (80 °C) and boiling point (105°C) of Co(Cl)₂, and RhCl₃·3H₂O (100 °C). The catalysts were pelletized, crushed and sieved to 0.3-0.6 mm fractions. The chemical composition of the catalysts investigated are compiled in Table1.

6.2.2 Kinetic measurements

An u-shaped quartz tube with an internal diameter of 8 mm was used as reactor and the catalyst bed was supported by means of two plugs of quartz wool. Catalysts were activated in situ by heating to 500°C for 1hr in flowing He. After this, the flow was switched to reactant mixture. Typically, it consisted of 1000 ppm NO, 1000 to 2250 ppm C₃H₆ and 5% O₂ balanced with He to 100%. A total gas flow of 100
ml/min was passed through the catalyst bed (0.2 g). The resulting GHSV was 15000 hr⁻¹, based on the apparent bulk density of the catalyst bed (0.5 g/cm³). The temperature of the catalyst bed was controlled by a Eurotherm 903P temperature controller, the gas flows by four mass flow controllers (Brooks). Kinetic measurements were carried out between 200ºC and 500ºC. The products were analyzed simultaneously by gas chromatography (Varian 3700 equipped with a TCD detector, a molecular sieve 5A column for separation of N₂, O₂ and CO and porapak Q column for N₂O, C₃H₆ and CO₂ analysis) and a chemiluminescence NO-NO₂ analyzer (Thermo Environmental Instr., Model 42C, NO, NO₂ analysis).

Table 1. Characteristics of the catalysts studied

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Si/Al [mol/mol]</th>
<th>Co [wt%]</th>
<th>Rh [wt%]</th>
<th>Co/Rh [mol/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-ZSM5</td>
<td>38.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Co/ZSM5</td>
<td>38.5</td>
<td>2.8</td>
<td>0.0</td>
<td>∞</td>
</tr>
<tr>
<td>Co-Rh/ZSM5 (1)</td>
<td>38.5</td>
<td>2.8</td>
<td>0.1</td>
<td>49</td>
</tr>
<tr>
<td>Co-Rh/ZSM5 (2)</td>
<td>38.5</td>
<td>2.8</td>
<td>0.5</td>
<td>10</td>
</tr>
<tr>
<td>Co-Rh/ZSM5 (3)</td>
<td>38.5</td>
<td>2.8</td>
<td>1.0</td>
<td>5</td>
</tr>
<tr>
<td>Rh/ZSM5</td>
<td>38.5</td>
<td>0</td>
<td>0.1</td>
<td>0</td>
</tr>
</tbody>
</table>

6.2.3 Catalyst characterization

High resolution electron microscopy (HREM) was performed using a Philips CM 30T electron microscope with an LaB₆ filament operated at 300 kV. Samples were mounted on a microgrid carbon polymer (supported on a copper grid) by placing a few droplets of a suspension of ground sample in ethanol on the grid, followed by the drying at ambient conditions. Elemental analysis was performed using a LINK EDX system.

I.r. measurements were performed *in situ* on a BRUKER IFS 88 FTIR spectrometer (resolution of 4 cm⁻¹) in a continuous gas flow in the transmission-absorption mode. The i.r. cell was equipped with a heatable sample holder and CaF₂ windows. The catalyst was pressed into a self-supporting wafer and activated in flowing He at 500ºC for one hour. Subsequently, the catalyst was brought to the required temperature and the reactant gases were introduced over the catalyst. Reactant mixtures with different compositions were used, details are given at appropriate sections. Spectra were recorded in the range from 3800 cm⁻¹ to 1300 cm⁻¹ with a time resolution of 30 s. Difference spectra were obtained by subtracting the spectrum of the activated catalyst from the spectra measured during the reaction. Co-Rh/ZSM-5 with 2.8
wt % Co, 0.1 wt % Rh was used.

6.3 RESULTS

6.3.1 Kinetic measurements

Table 2 summarizes the kinetic results obtained over the catalysts studied. As reported earlier, H-ZSM5 shows very little activity for SCR of NO (see Table 1). Introduction of Co leads to high SCR activity giving also high yields of N₂. Addition of Rh improved the activity of Co/ZSM5 while maintaining high selectivity to N₂ (see Table 2).

Table 2. Kinetic results for the ZSM-5 based catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion¹</th>
<th>Selectivity²</th>
<th>Conversion¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NO [mol.s⁻¹.g⁻¹]</td>
<td>N₂ [mol%]</td>
<td>N₂O [mol%]</td>
</tr>
<tr>
<td>H-ZSM-5</td>
<td>0.08E-07</td>
<td>100³</td>
<td>0</td>
</tr>
<tr>
<td>Co/ZSM-5</td>
<td>1.28E-07</td>
<td>85</td>
<td>15</td>
</tr>
<tr>
<td>Rh/ZSM-5</td>
<td>0.82E-07</td>
<td>66</td>
<td>34</td>
</tr>
<tr>
<td>Co-Rh/ZSM-5 (1)</td>
<td>1.61E-07</td>
<td>86</td>
<td>14</td>
</tr>
</tbody>
</table>

ZSM-5 Si/Al ratio = 38.5; Conditions: At 350 °C, 1000ppm NO, 1000ppm C₃H₆, 5% O₂, in He, ¹Differential Rates of conversion, ²At 30% NO conversion (by varying the contact time, ³at 2% NO conversion. (product NO₂ is observed only when C₃H₆ conversion reaches 100%).

Figure 1 shows conversion and yields as a function of temperature for the Co-Rh/ZSM-5(1) catalyst. As for Co/ZSM-5 [3, 6], the NO conversion passed through a maximum as function of temperature. The maximum of activity (N₂ and N₂O yields) was found at the temperature at which the C₃H₆ conversion reached 100%. NO₂ was observed only after all C₃H₆ was converted. The yield of N₂ was, however, constant between 400
In order to explore the role of the Rh content, a series of catalysts were prepared (Table 1). NO conversions for these catalysts are shown in Fig 2. It can be seen that increasing Rh content did not lead to improved activity. Furthermore, the higher Rh content did not lead to improved N₂ selectivity (See Fig 3). Thus, further experiments were carried out with the catalyst containing the lowest Rh content.

Figure 3 shows the selectivities to different products as a function of NO conversion at 350 °C. N₂ and N₂O were the only products at low conversions. Selectivity to N₂ increased at the expense of N₂O with increasing NO conversions suggesting that a secondary path for the formation of N₂ from N₂O is likely.

In order to probe the secondary formation of N₂ from N₂O, N₂O was reacted over Co-Rh/ZSM-5. The catalyst was found to be active in the reduction of N₂O (10.8 % conversion at 350 °C and a GHSV of 15000 hr⁻¹) to N₂ (100 % selectivity) and the rates were comparable to those of a catalyst containing no Rh, i.e. Co/ZSM-5. The shaded area in Figure 4 represents conditions of 100 % C₃H₆ and 500 °C (see Fig 1).
conversion. When the C₃H₆ conversion reached 100 %, the selectivity to N₂ also reached its maximum value. NO₂ was observed beyond this point. Further increase in NO conversion caused NO₂ to increase rapidly at the expense of N₂.

6.3.2 Influence of water and SO₂

Figure 5 shows the influence of the presence of 5% water vapor in the feed on the catalytic activity of CoRh/ZSM-5-1. At 350 ºC the presence of water decreased the NO conversion somewhat, but improved the N₂ selectivity. This effect was reversible. Fig. 6 shows that as in the case of water, also the addition of 200 ppm SO₂ decreased the activity and improved the N₂ selectivity. However, the catalyst was irreversibly poisoned by SO₂. After the removal of SO₂ from the feed the catalyst did not recover its initial activity.

Figure 4 Influence of conversion on selectivity over Co-Rh/ZSM-5. Conditions: 350 ºC, 1000 ppm NO, 2200 ppm C₃H₆, 5% O₂ in He.

Figure 5 Influence of water. Conditions: GHSV= 7500 hr⁻¹ Co-Rh/ZSM-5 (1) Co 2.8 wt %, Rh 0.1 wt %, 350 ºC, 1000 ppm NO, 2000 ppm C₃H₆, 5% O₂, in He, 5.4% H₂O.

Figure 6 Influence of SO₂ Conditions: GHSV= 7500 hr⁻¹ Co-Rh/ZSM-5 (1) Co 2.8 wt %, Rh 0.1 wt %, 350 ºC, 1000 ppm NO, 2000 ppm C₃H₆, 5% O₂, in He, 200ppm SO₂.
6.3.3 Catalysts characterization

Figure 7 shows the high resolution electron microscopy (HREM) picture of a Co-Rh/ZSM-5 catalyst before and after use. For the fresh catalyst HREM combined with EDX analysis revealed that Rh and Co were distributed in an inhomogeneous pattern. Individual Co and Rh particles between 1-3 nm were observed, while indications of combined particles were not detected. Differences between the size of Rh particles of fresh and used catalysts were not found, while the Co containing particles grew considerably after use.

Figure. 7 High resolution electron microscopy pictures of Co-Rh/ZSM-5 (1) Co 2.8 wt %, Rh 0.1 wt % (a) fresh, (b) after exposure to water and SO$_2$ under reaction conditions.

In Fig. 8, the i.r. spectra of the activated parent H-ZSM-5 and Co-Rh/ZSM5 are shown. H/ZSM-5 has absorption bands at 3740 cm$^{-1}$ (attributed to terminal Si-OH groups), 3610 cm$^{-1}$ (attributed to bridging Si-OH-Al, groups), 2000 cm$^{-1}$, 1880 cm$^{-1}$, 1640 cm$^{-1}$, 1480 cm$^{-1}$ (attributed to Si-O-Si lattice vibration overtones). A large decrease of the peak at 3610 cm$^{-1}$ in the latter sample indicates that the Co and Rh metals cations are located on the bridging oxygen of Si-O-Al groups. A small peak at 3673 cm$^{-1}$ is assigned to extra-framework Al-OH groups caused by dealumination during ion exchange [7]. Normalizing the spectra by the intensity of the lattice vibration overtones at 2000 cm$^{-1}$ and 1880 cm$^{-1}$ allowed to estimate that approximately 50 % of the protons of the Brønsted acid sites were exchanged for Co$^{2+}$ and Rh$^{3+}$.
Chapter 6 Selective catalytic reduction of NO to \( \text{N}_2 \) over Co-Rh/ZSM-5 catalysts

6.3.4 *In situ* i.r. mechanistic studies

In Figs. 9 - 11 the *in situ* i.r. spectra in the presence of various feed compositions are shown. Tables 3-5 summarize the observed bands and their assignments. Fig.9 shows the i.r. spectra of Co-Rh/ZSM-5 after exposure to 2000 ppm \( \text{C}_3 \text{H}_6 \) in He at 350 °C (reaction temperature) as a function of time. After the catalyst was contacted with propene two peaks corresponding to OH bands (3740 cm\(^{-1}\) and 3610 cm\(^{-1}\)) appeared as two negative bands. In the C-H stretching region (3200- 2800 cm\(^{-1}\)) two broad bands appeared with peaks centered at 3100 (aromatic =CH), and 2970 cm\(^{-1}\) \((-\text{CH}_3\)). Bands appeared also at 1666 cm\(^{-1}\) (C=O, aldehyde), 1620 cm\(^{-1}\) (C=C, alkene), 1570 cm\(^{-1}\) (C=O of carbonate, C=C of aromatic coke or O-C-O of carboxylate). See Table 3 for details of band assignments. After 30 minutes on stream the band at 1666 cm\(^{-1}\) was seen only as a shoulder, while that at 1570 cm\(^{-1}\) became dominant. In the low frequency region bands were observed at 1452 and 1380 cm\(^{-1}\) growing steadily with time.
Figure 10 shows the adsorbed species over Co-Rh/ZSM-5 after exposure to 1000 ppm of NO in He at different temperatures after equilibration. Table 4 summarizes the observed bands and their assignments. Negative peaks appeared at 3744 cm\(^{-1}\) and 3610 cm\(^{-1}\) indicating absorption on silanol and Brønsted acid sites. The broad band at 3500 cm\(^{-1}\) indicates hydrogen bonding between the NO species and the acid sites [8]. In addition, a broad band at 1894 cm\(^{-1}\) and sharp peaks at 1814 cm\(^{-1}\), 1633 cm\(^{-1}\), 1601 cm\(^{-1}\) and 1579 cm\(^{-1}\) were observed. Based on previous reports the band 1894 and 1814 cm\(^{-1}\) are attributed to Co(NO)_2, the bands between 1633-1579 cm\(^{-1}\) to Co-NO_2, Co-ONO and/or Co-ONO_2 species [9]. With increasing temperature all the bands decreased in intensity and at 475 °C no significant absorptions were observed in the i.r. spectra.

The results of the exposure of Co-Rh/ZSM-5 to a mixture of 1000 ppm of NO and 5 % O_2 in He were similar to those obtained when only NO was adsorbed over the catalyst. However, the bands observed by adsorbing NO alone were slightly more intense in the 1894 - 1813 cm\(^{-1}\) region. At 500°C in the presence of oxygen no more adsorbed species were found.

Figure 11 shows the i.r. spectra over Co-Rh/ZSM-5 after exposure to 1000 ppm of NO, 2000
Chapter 6 Selective catalytic reduction of NO to N\textsubscript{2} over Co-Rh/ZSM-5 catalysts

ppm C\textsubscript{3}H\textsubscript{6} and 5% of O\textsubscript{2} in He as function of the temperature. Table 5 summarizes the observed bands and their assignments. Negative peaks developed at 3610 c\textsuperscript{-1} and 3744 c\textsuperscript{-1} and a broad band between 3500-3200 cm\textsuperscript{-1} appeared. Bands were also observed at 3200-3100 cm\textsuperscript{-1} (CH stretching vibrations of unsaturated hydrocarbons), 3000-2800 c\textsuperscript{-1} (stretching vibrations of saturated -CH\textsubscript{2}, -CH\textsubscript{3} groups) and at 2246 c\textsuperscript{-1} and 2160 c\textsuperscript{-1} (isocyanate -NCO and/or nitrile -NC [9(b), 10] groups.

A complex group of bands band appeared between 1750 and 1300 cm\textsuperscript{-1}. For the sake of clarity we divide the bands into three groups, i.e., between 1750-1635 cm\textsuperscript{-1}, 1635-1500 cm\textsuperscript{-1} and 1500-1300 cm\textsuperscript{-1}. The bands at 1750-1630 cm\textsuperscript{-1} correspond to C=C and C=O stretching vibrations, 1635-1500 cm\textsuperscript{-1} to surface NOx species (Table 4), oxygenates (carboxylate, carbonate, formate) or coke (Table 3), and those 1500-1300 cm\textsuperscript{-1} to allylic, formate, and /or carbonate type species (Table 3).

With increasing temperature all bands in the region 3800-2800 and 1500-1300 cm\textsuperscript{-1} decreased in intensity. In contrast the bands at 2246 c\textsuperscript{-1} (sh 2160 cm\textsuperscript{-1}) and between 1750-1500 cm\textsuperscript{-1} grew continuously reaching a maximum at 325 °C. The bands at 3000-2800 c\textsuperscript{-1} (-CH\textsubscript{1}, -CH\textsubscript{2}, -CH\textsubscript{3}) region disappeared at 475°C, while the rest of the bands were still present at 500°C. Note that this is in contrast to the experiments in the absence of propene when bands were not observed at temperatures higher than 475 °C.

6.4 DISCUSSION

H/ZSM-5 has very little activity for NO conversion. Addition of Co\textsuperscript{2+} ions improved the activity with high selectivity to N\textsubscript{2}. The addition of small amounts of Rh (0.1 wt%) enhanced the activity further. Simultaneously with the improvement of the activity the high selectivity to N\textsubscript{2} was maintained. Note in this context that the addition of Pt also enhanced the activity for NO conversion, however presence of Pt enhanced the selectivity to N\textsubscript{2}O [3]. However, unlike Pt, Rh caused only limited improvement in NO conversion with respect to the pure Co containing catalysts.

The NO conversion follows the hydrocarbon oxidation closely. Maximum NO conversion is always observed, when the propene conversion approaches completion. Note that with respect to propene combustion Pt (TOF = 2.10\textsuperscript{4}.s\textsuperscript{-1}, [3]) has a lower propene combustion activity than Rh (TOF = 1.10\textsuperscript{4}.s\textsuperscript{-1}, Table 2). We speculate that this is the reason for the comparatively moderate improvement in activity upon addition of Rh to Co-ZSM-5 compared to the addition of Pt. The fact that increasing Rh contents did not improve activity might be related to poor dispersion of Rh. The HREM measurements (see Fig 7) indicat this already for the lowest Rh containing sample. Also, the similar catalytic activities for propene conversion over all Rh containing samples point to a similar concentration of exposed Rh in all samples studied.

Yield conversion curves indicate that N\textsubscript{2} and N\textsubscript{2}O are primary products and that some
interconversion of N₂O to N₂ occurs at higher NO conversions. Separate experiments show that Co-Rh/ZSM-5 is active in the reduction of N₂O to N₂ and that the rate is similar to that over Co/ZSM-5. This indicates, that readsorption and decomposition of N₂O is related solely to the presence of Co²⁺.

Let us now discuss the surface species observed over the bimetallic catalyst. In the presence of propene, at reaction temperatures, the weak (silanol groups) and strong (bridging hydroxyl groups) acid sites of ZSM5 are covered. Additionally characteristic bands aromatic C-H vibrations are detected. These are attributed to strong adsorption of olefines, oligomerization and aromatization on the Brønsted acid sites which ultimately leads to coke[11]. The i.r. spectra also could indicate the presence of C=O, C≡C groups (bands at 1665 cm⁻¹ and 1620 cm⁻¹, respectively) related to aldehydes or ketones [10 (d)] in agreement with literature [9 (b), 12]. Such partially oxidized species are formed by the reduction of metal-oxygen entities (Co-oxid clusters). The presence of bands due to allyl species (1435 cm⁻¹, shoulder 1380 cm⁻¹) and acrolein (1620 cm⁻¹, 1670 cm⁻¹) suggests that the oxidation of C₃H₆ proceeds via α-allyl species. Under the reaction conditions acrolein is a likely intermediate in the combustion of propene [3, 9 (b)]

In the presence of NO the i.r. spectra show evidence for chemisorbed NO such as Co(NO)₂, Co-NO₂, Co-ONO and/or Co-ONO₂ (Fig.10 Table 4). These spectra are rather similar to the spectra observed earlier with NO adsorbed on Co-ZSM-5 [9 (a)-(c)]. It is speculated that the NO₂ derived adsorbed species result from the incorporation of lattice oxygens and/or from NO disproportionation (3NO → NO₂ + N₂O) [9 (d), 9(f), 14]. It is important to note that over Co-Rh/ZSM-5, the presence Q did not enhance formation of the NO₂ derived species indicating that the participation of the lattice oxygen and the disproportionation are more important than the direct oxidation by adsorbed oxygen. We would like to mention in this context that Rh is known to decompose NO and promote N-pairing of adsorbed NO molecules [4, 15].

The bands related sorbed species were found up to relatively high temperatures. For example the C-H stretching bands disappeared only at 475°C, while other bands were even present at 500°C. This indicates that over Co-Rh/ZSM-5 combustion is not very fast allowing the presence of hydrocarbon species over the catalyst surface even at high temperatures. The presence of nitrogen containing species at high temperatures could be related with the fact that NO dissociates easily on Rh and even at high temperatures is able to compete with O₂ to react over Rh surfaces [4]. We speculate that this specific property allows the constant conversion of NO to N₂ as the temperature increases in contrast to Pt containing catalysts [3] for which the yield to N₂ drastically decreased above 350 °C.

Under the reaction conditions, presence of isocyanate (-NCO)/nitriles (-CN) species and the changes in their intensities at temperatures where SCR activity increases strongly suggest their involvement in the reaction. Since isocyanate is not stable in presence of water [3] (and water is generated in the oxidation of propene) we attribute the bands to nitrile rather than isocyanate species. Combined with the high
concentration of NO\textsubscript{2} derived species we suggest that the nitriles are formed from these surface compounds.

Overall, the following reaction scheme is proposed. Propene is activated over the catalyst via a π-allyl species on the metal sites. NO\textsubscript{x} reacts with allylic species to form organo-nitro (R-CH\textsubscript{2}-NO\textsubscript{2}) or nitroso (RCH\textsubscript{2}-NO) intermediate. These isomerize (the organo-nitro species losing oxygen to the catalyst) to form an oxime (R-CH=NOH). Dehydration of this oxime forms the nitrile R-CH\textsubscript{2}CN. The nitrile, once formed is hydrolysed and oxidized over Lewis acid/base pairs (extra lattice alumia, Co-oxide clusters) to NH\textsubscript{3}, CO\textsubscript{2} and water. Finally NH\textsubscript{3} or the NH\textsubscript{4}\textsuperscript{+} ions for Brönsted acid sites reduce NO\textsubscript{x} to N\textsubscript{2}. In parallel, propene forms oligomers and coke on Brönsted which combusts unspecifically. In agreement with previous results [3] the presence of water and SO\textsubscript{2} seems to retard the (oligomerisation and) combustion of propene making propene available for the selective route of reduction of NO\textsubscript{x} to N\textsubscript{2}.

6.5 CONCLUSIONS

A Co-RhZSM-5 catalyst with 0.1 wt% Rh content is shown to be active, selective and stable under reaction conditions for the reduction of NO with propene in the presence and absence of water. The addition of small amounts (0.1 wt%) of Rh enhanced the activity of Co/ZSM-5 while maintaining high selectivity to N\textsubscript{2}.

The active phases of Rh modified Co/ZSM-5 catalysts appear to be Co-oxide in the pores of the zeolite, Rh metal particles, and Lewis acid/base pairs of the zeolite. It is suggested that the reaction sequence involves the formation of organo-nitro species that ultimately decompose to ammonia, CO\textsubscript{2} and water. Ammonia is speculated to be the actual transient reducting agent. The specific role of Rh lies on the one hand in the more efficient activation of the hydrocarbon and on the other hand in providing a route to activate nitrogen even at high temperatures. The latter property allows the stable conversion of NO to N\textsubscript{2} at higher temperatures, even under conditions of 100\% hydrocarbon conversion. In a side reaction, Brönsted acid sites lead to oligomerization of propene and unspecific combustion. The presence of water and SO\textsubscript{2} retard the combustion of propene assuring that propene is available for the selective reduction of NO\textsubscript{x} to N\textsubscript{2}.

ACKNOWLEDGMENTS

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Netherlands, for the HREM measurements. This work was performed under the auspices of NIOK, the Netherlands Institute for Catalysis. (Report number UT-98-1-02).

REFERENCES

   (b) S. E. Maisuls, K. Seshan, S. Feast and J. A Lercher, Selective catalytic reduction of NOₓ to nitrogen over bimetallic catalysts, part A, Characterization and kinetic studies, submitted to Appl.Catal., B Environmental.

**APPENDIX - Infrared absorption bands assignment**

**Table 3. The assignments of the infrared bands - sorption of propene.**

<table>
<thead>
<tr>
<th>I.r. absorption (cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3740</td>
<td>-OH stretching (terminal Si-OH weak acid sites) [7]</td>
</tr>
<tr>
<td>3610</td>
<td>-OH stretching (bridging Si-OH-Al strong acid sites) [7]</td>
</tr>
<tr>
<td>2000, 1880, 1640, 1480</td>
<td>lattice overtones Si-O-Si [7]</td>
</tr>
<tr>
<td>3120</td>
<td>=C-H stretching (aromatic, ethylenic) [10(d)]</td>
</tr>
<tr>
<td>2970</td>
<td>-CH₃ [10(d)]</td>
</tr>
<tr>
<td>1666</td>
<td>C=O stretching [10(d)] (adsorbed acrolein.) [9(b), 12]</td>
</tr>
<tr>
<td>1620</td>
<td>C=C stretching [10(d)] (adsorbed acrolein) [9(b), 12]</td>
</tr>
<tr>
<td>1570</td>
<td>C=C stretching (aromatic coke) [11, 16] C=O vibration (adsorbed carbonate) [10(a), 12, 17] O-C-O sym.stretching (formate, carboxylate) [12, 17]</td>
</tr>
<tr>
<td>1439</td>
<td>allylic species [9(b), 18], carbonates, formates [10(a), 12, 17].</td>
</tr>
<tr>
<td>1380</td>
<td>allylic species [18] OCO stretching asym.vibrations formate ions [10(a), 12, 17]</td>
</tr>
</tbody>
</table>

**Table 4. The assignments of the infrared bands - Sorption of NO**

<table>
<thead>
<tr>
<th>I.r. absorption (cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3744, 3610</td>
<td>O-H stretching, acid sites [see propene], negative bands due to interaction with NO</td>
</tr>
<tr>
<td>1896, 1813</td>
<td>1890, 1810 Co(NO)₂ [9(a)] dinitrosyl, 1894 1815 [9(c, d)]</td>
</tr>
<tr>
<td>1633</td>
<td>Nitro species 1627 Co-NO₂ [9(a)], 1628 Cu-NO₂ [9(g)], nitrito NO₂, nitrate NO₃ [9(c)]</td>
</tr>
<tr>
<td>1601</td>
<td>Cu NO₃ monodentate nitrate ions 1594 [9(g)], Cu covalent nitrat nitrito1605 [9(g)] Cu(NO₃)₂ Co bidentate nitrito 1595 [9(a)], Co-O₂N=O bidentate nitrate 1599 [9(c)]</td>
</tr>
<tr>
<td>1580</td>
<td>CuNO₃ bidentate nitrate 1572 [9(g)], Co-O₂N=O bidentate nitrate 1599 [9(c, f), bidentate, monodentate nitrate 1575 [9(h)] organo nitro 1570 [9(b)]</td>
</tr>
</tbody>
</table>
Table 5. The assignments of the infrared bands.- Observed under reaction conditions

<table>
<thead>
<tr>
<th>I.r. absorption (cm$^{-1}$)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3500-3200 (br)</td>
<td>NH$_4^+$, NH$_3$ species [10(d)]</td>
</tr>
<tr>
<td>2246 2160</td>
<td>isocyanate (-NCO) nitriles (-CN) species [10(d)], CuZSM-5 [9(b)] nitriles 2260, CoZSM-5 NCO species adsorbed on Al$^{3+}$ 2270, -CN species on Co$^{3+}$ 2173, [9(c)], 2220 cm$^{-1}$ -NCO adsorbed on Co$_3$O$_4$ [10(c)], Pt/Al$_2$O$_3$ [10(a)] on-CN species at 2140, -NCO at 2232, 2254, PtSiO$_2$[10b] -NCO at 2174, -NCO γ-Al$_2$O$_3$ 2228 [10(e)]</td>
</tr>
<tr>
<td>1575</td>
<td>organo nitro 1570 [9(b)]</td>
</tr>
</tbody>
</table>
CHAPTER 7

Comparison of Co-Pt/ZSM-5 and Co-Rh/ZSM-5 Catalysts for Selective Catalytic Reduction of NO to N₂

Abstract

The selective catalytic reduction of NO by propene in the presence of excess oxygen over bimetallic catalysts based on Co-Pt and Co-Rh supported on ZSM-5 is compared. Co-Pt/ZSM-5 and Co-Rh/ZSM-5 catalyst are active and selective under reaction conditions. At lower temperatures Pt modified Co/ZSM-5 catalysts are more active in the SCR of NO probably due to the high activity of Pt on the activation of propene. Further, the interconversion of \( \text{NO} \) to \( \text{N₂} \) activity is proposed as the cause of higher \( \text{N₂} \) selectivity of Co-Rh/ZSM-5 catalysts. It was found that the SCR activity of these catalysts correlates to the levels of sorbed species found by IR spectroscopy under reaction conditions. The mechanism operating for SCR of NO to \( \text{N₂} \) over both catalyst is similar.
Chapter 7 - Comparison of Co-Pt/ZSM-5 and Co-Rh/ZSM-5 catalysts ...

7.1 INTRODUCTION

There is a great deal of interest in developing new catalytic processes for the selective catalytic reduction (SCR) of NOx in the presence of excess oxygen [1,2]. Several catalysts based on zeolites were found active for this reaction using hydrocarbons as reductants [e.g. 3-7]. However due to the lack of sufficient activity, selectivity and or stability, a suitable catalytic system has not yet been developed this process.

We have reported earlier, in agreement with the literature that zeolite (for e.g. HZSM-5) by itself is not active and that introduction of Co incorporates the SCR activity giving high N₂ selectivity [8-11]. For stationary sources, such as power plants, it is desirable to achieve high SCR activity at lower temperatures. Co-ZSM-5 based catalysts (e.g. Co/ZSM-5) are active at relatively higher temperatures and hence for cleaning up power plant emission further modification of Co based catalysts is required. A typical characteristic of SCR activity is that NO conversion follows hydrocarbon conversion closely [2, 10]. Thus it seems logical that enhanced catalytic activity can be achieved by the incorporation to the catalytic system of a second component, such as Pt, which is active in the oxidation of hydrocarbons. Alternatively addition of Rh, which is known to decompose NO and promote N-pairing of adsorbed NO molecules [12], could improve the catalytic performance of the Co based catalyst.

In previous studies we found that addition of small concentrations of Pt, Rh indeed, improved the activity of Co/ZSM5 while maintaining high selectivity to N₂ [8,9,13]. However, catalysts based on Pt or Rh show differences in their catalytic behavior. Detailed studies to compare the two catalysts are undertaken in order to understand the reasons therefore and help in the design of an optimal catalyst.

7.2 EXPERIMENTAL

7.2.1 Catalyst preparation

The catalysts were prepared via solid state ion exchange. The parent ZSM-5 (Na form, Si/Al = 38.5, P.Q. Zeolites) was first heated in N₂ and subsequently in air at 500°C for 12 hours. Then, the zeolite was ion exchanged twice with 0.1M NH₄NO₃ solution. For the preparation of the catalysts, the NH₄ form of ZSM-5 (5g) was thoroughly ground with the required amounts of CoCl₂.6H₂O and PtCl₄. Or RhCl₃.3H₂O. The resulting mixture was heated to 500 °C at 2 °C/min in He and was maintained at this temperature for 12 hrs. During the heating cycle the samples were maintained for three hours near the melting point (80 °C) and boiling point (105°C) of Co(Cl)₂, and RhCl₃.3H₂O (100 °C). The catalysts were pelletized, crushed and sieved to 0.3-0.6 mm fractions. The chemical composition of the catalysts investigated are compiled in Table1.
Table 1. Characteristics of the catalysts studied

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Si/Al [mol/ mol]</th>
<th>*Co [wt%]</th>
<th>Pt or Rh [wt%]</th>
<th>Co/M (M = Pt, Rh) [mol/ mol]</th>
<th>Pt or Rh **Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-ZSM-5</td>
<td>38.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Co/ZSM-5</td>
<td>38.5</td>
<td>2.84</td>
<td>0.00</td>
<td>∞</td>
<td>-</td>
</tr>
<tr>
<td>Co-</td>
<td>38.5</td>
<td>2.80</td>
<td>0.10</td>
<td>49</td>
<td>1 - 3</td>
</tr>
<tr>
<td>Co-Pt/ZSM-</td>
<td>38.5</td>
<td>2.74</td>
<td>0.13</td>
<td>70</td>
<td>&lt; 0.8</td>
</tr>
</tbody>
</table>

*In all catalyst Co is present as Co $^{2+}$ and as Co oxide clusters [9,13], ** by HREM

7.2.2 Kinetic measurements

The reactor used was a U-shaped quartz tube with an internal diameter of 8 mm and the catalyst bed was supported by means of two plugs of quartz wool. Catalysts were activated in situ by heating to 500 °C for 1 hr in flowing He. After this, the flow was switched to reactant mixture. The typical reactant gas mixture consisted of 1000 ppm NO, 1000 to 2250 ppm C$_3$H$_6$, 5% O$_2$ balancing with He to one bar. A total gas flow of 100 ml/min was passed through the catalyst bed (0.2 g). The resulting GHSV was 15000 hr$^{-1}$, based on the apparent bulk density of the catalyst bed (0.5 g/cm$^3$). The temperature of the catalyst bed was controlled by a Eurotherm 903P temperature controller, the gas flows by four mass flow controllers (Brooks). Kinetic measurements were carried out at temperature intervals of 25°C between 200°C to 500°C. The products were analyzed simultaneously by (i) gas chromatography (Varian 3700 equipped with a TCD detector, a molecular sieve 5A column for separation of N$_2$, O$_2$ and CO and porapak Q column for N$_2$O, C$_3$H$_6$ and CO$_2$ analysis) and (ii) a chemiluminescence NO-NO$_2$-NO$_x$ analyzer (Thermo Environmental Instr., Model 42C, NO, NO$_2$ analysis).

7.2.3 Catalyst characterization

High resolution electron microscopy (HREM) was performed using a Philips CM 30 T machine with an LaB$_6$ filament operated at 300 kV. Samples were mounted on a microgrid carbon polymer (supported on a copper grid) by placing a few droplets of a suspension of ground sample in ethanol on the grid, followed by the drying at ambient conditions. Elemental analysis was performed using a LINK EDX system.
I.r. measurements were performed in situ on a BRUKER IFS 88 FTIR spectrometer (resolution of 4 cm⁻¹) in a continuous gas flow in the transmission-absorption mode. The i.r. cell was equipped with a heatable sample holder and CaF₂ windows. The catalyst was pressed into a self supporting 2 mg wafer and activated in flowing He at 500°C for one hour. Subsequently, the catalyst was brought to the required temperature and the reactant gases were introduced over the catalyst. Reactant mixtures with different compositions were used, details are given at appropriate sections. Spectra were recorded in the range from 3800 cm⁻¹ to 1300 cm⁻¹ with a time resolution of 30s. Difference spectra were obtained by subtracting the spectrum of the catalyst from the spectra measured during the reaction.

7.3 RESULTS

7.3.1 Kinetic measurements

Table 2 summarizes the kinetic results obtained over the catalysts studied. From the Table it can be seen that compared to Co/ZSM-5, incorporation of small amount of Pt (0.1 wt %) almost doubles the activity for NO conversion, while the effect of Rh is less significant. The Rh modified catalyst, however, shows (at the same NO conversion) improved selectivity to N₂. Figure 1 shows the N₂ yields as a function of temperature for Co-Pt/ZSM-5 and Co-Rh/ZSM-5 catalysts. Co-Pt/ZSM-5 shows higher N₂ formation at lower temperatures (275°C - 350°C) while at higher temperatures (375 °C - 500°C) Co-Rh/ZSM-5 is able to produce higher levels of N₂ than Pt.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>*NO Conversion [mol. s⁻¹·g⁻¹]</th>
<th>**Selectivity [mol%]</th>
<th>*C₃H₆ Conversion [mol. s⁻¹·g⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>N₂</td>
<td>N₂O</td>
</tr>
<tr>
<td>Co/ZSM-5</td>
<td>1.28E-07</td>
<td>85</td>
<td>15</td>
</tr>
<tr>
<td>Co-Rh/ZSM-5</td>
<td>1.61E-07</td>
<td>86</td>
<td>14</td>
</tr>
<tr>
<td>Co-Pt/ZSM-5</td>
<td>2.36E-07</td>
<td>80</td>
<td>20</td>
</tr>
</tbody>
</table>

ZSM-5 Si/Al ratio = 38.5; Conditions: At 350 °C, 1000ppm NO, 1000ppm C₃H₆ and 5% O₂ in He, *Differential Rates of conversion, **At 30% NO conversion (by varying the contact time. (product NO₂ is observed only when C₃H₆ conversion reaches 100%).

As in the case of Co/ZSM-5 [8, 9, 13], for both Co-Pt/ZSM-5 and Co-Rh/ZSM-5 catalysts NO conversion passes through a maximum as function of temperature, the maximum being at the temperature where C₃H₆ conversion reaches 100% (see Fig.2). N₂ and N₂O yields also reach maximum values at this temperature. However for Co-Rh/ZSM-5 (as in the case of Co/ZSM-5) the N₂ yields remain constant at
higher temperatures. For Co-Pt at higher temperatures (\( > 350 \, ^\circ C \)) the yields of \( N_2 \) drop. This is one significant difference between the catalysts while considering applications in different temperature regions. In both catalysts \( NO_2 \) is observed only after 100% \( C_3H_6 \) conversion is reached [8, 9, 13].

To study the sequence of product formation, yield vs conversion studies were performed at 350°C for both catalysts. In these catalysts \( N_2 \) and \( N_2O \) were the only products at low conversions. Selectivity to \( N_2 \) increased at the expense of \( N_2O \) with increasing NO conversions suggesting that a secondary path for the formation of \( N_2 \) from \( N_2O \) is likely in both catalysts. To probe this the activity of all the catalysts for the decomposition of \( N_2O \) to \( N_2 \) is compared in Table. 3. Co/ZSM-5 showed the highest activity for \( N_2O \) decomposition. However the rates \( N_2O \) decomposition were only marginally lower for the Co-Rh catalyst. Co-Pt/ZSM-5 was less effective than Co/ZSM-5 or the Rh modified catalyst. The support H-ZSM-5 was significantly less active than the rest of the catalysts.
Table 3. Rates of decomposition of N₂O to N₂ over the studied catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>* N₂O Conversion [mol. s⁻¹.g⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H/ZSM-5</td>
<td>0.71E-08</td>
</tr>
<tr>
<td>Co/ZSM-5</td>
<td>4.50E-08</td>
</tr>
<tr>
<td>Co-Rh/ZSM-5</td>
<td>4.02E-08</td>
</tr>
<tr>
<td>Co-Pt/ZSM-5</td>
<td>1.90E-08</td>
</tr>
</tbody>
</table>

Conditions: At 350 °C, 1000 ppm NO, 2000 ppm C₃H₆ and 5% O₂ in He, *Differential Rates of conversion.*

Further kinetic measurements showed that the rates of N₂ formation when NO₂ was the reactant instead of NO were almost doubled. At 350 °C presence of 6% vol water had only a moderate influence on NO conversion but improved the N₂ selectivity in both catalysts. The effect of water was reversible. In presence of 200 ppm SO₂ Co-Pt/ZSM-5 was only slightly affected while Co-Rh/ZSM-5 was deactivated and after removal of SO₂ from the fed the initial catalyst activity did not recover [9, 13].

7.3.2 Catalyst characterization

The i.r. spectra of the Co-Pt and Co-Rh catalysts, compared to the parent H-ZSM-5, showed a large decrease of bands at 3610 cm⁻¹ and small decrease in the band at 3740 cm⁻¹ indicating that the Co, Pt and or Rh ions are located mainly on the bridging oxygen of Si-O-Al groups and to a small extent at the terminal oxygens of Si-OH groups [9, 13]. Normalizing the spectra for the lattice overtones at 2000 cm⁻¹ and 1880 cm⁻¹ allowed to estimate that approximately 50% of the Brønsted acid sites were exchanged for Co²⁺ and Pt⁴⁺ or Rh³⁺. Over Co-Rh/ZSM-5 an additional small peak was present at 3673 cm⁻¹ assigned to extra framework Al-OH groups (dealumination during ion exchange procedure). On exposure to the reactant mixture the acid bands completely disappeared for both catalysts indicating that the acid sites were covered by reacting species under reaction conditions.

HREM combined with EDX analysis revealed that both catalysts are microscopically inhomogeneous. In the case of Co-Pt/ZSM-5, Pt particles size were below the detection limit (< 0.8 nm) while in the case of the Rh catalyst particles of approximately 1-3 nm were observed [8,9, 13].
7.3.3 In situ i.r. mechanistic studies

Figs. 3- 5 show the results of the I.r. measurements with various feed compositions. The assignments of the observed i.r. band frequencies are summarized in Chapters 5 and 6.

Fig. 3 shows a comparison of the i.r. spectra for Co-Pt/ZSM-5 and Co-Rh/ZSM-5 after exposure to 2000 ppm C₃H₆ in He at 350 ºC (reaction temperature) as a function of time. For both catalysts the peaks at 3740 cm⁻¹ (terminal Si-OH groups), 3610 cm⁻¹ (bridging Si-OH-Al, groups) decreased with the exposure. This is deduced from the appearance of two negative bands at these wave numbers. In the C-H stretch region (3200-2800 cm⁻¹) two broad bands with peaks centered at 3100 (aromatic =CH and =CH₂), and 2970 cm⁻¹ (-CH₃) are observed. Also bands at 1670 cm⁻¹ (C=O, aldehyde), 1620 cm⁻¹ (C=C, alkene), 1570 cm⁻¹ (C=O of carbonate, C=C of aromatic coke or O-C-O of carboxylate) were observed [14].

In the first moments of the reaction Co-Pt/ZSM-5 showed stronger intensity at the 1670 cm⁻¹ band, however after 10 minutes all the absorption peaks over Co-Rh/ZSM-5 started to become more

Figure 3 Comparison of the i.r spectra for the reaction of propene as function of time over Co-Pt/ZSM-5 and Co-Rh/ZSM-5. Spectra measured at identical conditions: 2 mg catalyst, 2000 ppm C₃H₆ in He.
intense and this difference remained as a function of time.

Figure 4 shows the adsorbed species over the catalyst after exposure to 1000 ppm of NO in He at different temperatures after equilibration. For both catalysts negative peaks appeared at 3744 cm\(^{-1}\) and 3610 cm\(^{-1}\) indicating absorption on silanol and Brønsted acid sites. In parallel a positive broad band at 3500 cm\(^{-1}\) indicated interaction between the NO species and the acid sites [15]. Further, a broad band at 1894 cm\(^{-1}\) and sharp peaks at 1814 cm\(^{-1}\), 1633 cm\(^{-1}\), 1601 cm\(^{-1}\) and 1579 cm\(^{-1}\) were observed. Based on previous reports the band at 1894 and 1814 cm\(^{-1}\) are attributed to Co(NO\(_2\))\(_2\), while the bands between 1633-1579 cm\(^{-1}\) to Co-NO\(_2\), Co-ONO and/or Co-ONO\(_2\) species [14]. With increasing temperature all the absorptions decreased and finally at 450 °C no significant absorptions were observed in the i.r. spectra of Co-Pt/ZSM-5 while over Co-Rh/ZSM-5 all absorptions were still present. Over Co-Rh/ZSM-5 the results in the presence of 1000 ppm of NO and 5 % O\(_2\) in He were similar to those obtained when only NO was adsorbed. In contrast over Co-Pt/ZSM-5 presence of O\(_2\) caused a slight enhancement in the absorption bands related to Co(-NO\(_x\)) sorbed species mentioned earlier. In general the intensity of the i.r. bands over Co-Rh were more intense than over Co-Pt at all conditions.

Fig. 5 shows i.r. spectra after exposure to 1000 ppm of NO, 2000 ppm C\(_3\)H\(_6\) and 5% of O\(_2\) in He at different temperatures. Negative peaks at 3610 cm\(^{-1}\) and 3744 cm\(^{-1}\), and a broad band between 3500-3200 cm\(^{-1}\) appeared. Bands were observed in the regions 3200-3100 cm\(^{-1}\) (CH stretch, aromatic/ethylenic), 3000-2800 cm\(^{-1}\) (-CH, -CH\(_2\), -CH\(_3\)), 2246 cm\(^{-1}\), 2160 cm\(^{-1}\) related to (isocyanate -NCO and/or nitrile -NC for both catalysts. A complex band appeared in the region 1750-1300 cm\(^{-1}\). For the sake of clarity we divide the band in three regions, i.e., between 1750-1635 cm\(^{-1}\), 1635-1500 cm\(^{-1}\) and 1500-1300 cm\(^{-1}\). The bands in the region 1750-1630 cm\(^{-1}\) correspond to C=C and C=O stretching, 1635-1500 cm\(^{-1}\) to surface NO\(_x\) species, oxygenates (carboxylate, carbonate, formate) or coke, and 1500-1300 cm\(^{-1}\) to allylic, formate, and/or carbonate type species. As seen in fig 5 Co-Rh/ZSM-5 displays stronger absorptions (indicating presence of larger concentrations of sorbed species) on the regions related to sorbed hydrocarbons/coke, surface NO\(_x\) species and partially oxidized propene. Interestingly the band related to isocyanate -NCO and/or nitrile -NC is more intense for Co-Pt at 350 °C, at higher temperatures the intensity seems similar.
Figure 4 Comparison of the IR spectra for the reaction of NO as function of temperature over Co-Pt/ZSM-5 and Co-Rh/ZSM-5. Spectra measured at identical condition: 2 mg catalyst, 1000 ppm NO in He.
Figure 5 Comparison of the ir spectra under reaction conditions over Co-Pt/ZSM-5 and Co-Rh/ZSM-5 as function of temperature. Spectra measured at identical condition: 2 mg catalyst., 1000 ppm NO., 2000 ppm C₃H₆ ans 5% O₂ in He.

7.4 DISCUSSION

We found in our experiments that Co catalyst modified with Pt (even in small amounts (0.1 wt %) shows enhanced SCR activity(see rates NO and propene conversion). Unlike Pt, Rh caused only limited improvement in NO conversion [8, 9, 13]. We have previously found that the Rh catalysts were less active in the combustion of propene ( Pt (TOF = 2.10^-4 .s⁻¹, ) , Rh (TOF = 1.10^-4 .s⁻¹, ) [9,13] Table2). The differences in the hydrocarbon combustion activity may explain why Co-Pt/ZSM-5 shows higher activity for NO reduction. Comparison of N₂ yields (Fig. 1) indicates maxima at 325°C for Co-Pt , however, for Co-Rh at higher temperatures the N₂ yields remain constant. To recall i.r. experiments over Co-Rh the bands related to NOₓ species and (−CH, −CH₂, −CH₃) disappeared only at 475°C and 500°C respectively while the rest of the bands were still present at500°C. Over Co-Pt the bands related to NOₓ species and (−CH, −CH₂, −CH₃) disappeared at lower temperatures (ie. 425 °C). Thus we see a direct correlation between N₂ yields and the surface species mentioned above.
This results indicate that over Co-Rh/ZSM-5 combustion is limited allowing presence of hydrocarbon species over the catalyst surface even at high temperatures. With increasing temperature these oligomers are either combusted unselectively, from the SCR point of view, to CO$_2$ and water by O$_2$ or selectively to N$_2$, CO$_2$ and water by NO. As the temperature rises unselective combustion is favored thus an optimum in the selective formation of N$_2$ as a function of temperature is found. For Pt modified catalysts this optimum is reached at slightly lower temperatures due to its higher activity for hydrocarbon conversion. Also enhanced formation of NO$_x$ surface species at higher temperatures takes place over Co-Rh/ZSM-5. The presence of N'-containing compounds at high temperatures could be related with the fact that NO dissociates easily on Rh and even at high temperatures is able to compete with O$_2$ to react over Rh surfaces [12, 16]. Results are similar in the presence of NO, NO and O$_2$ or with the complete reactant mixture. This indicates that the correlation made with the individual reactants is relevant for reaction conditions.

Yields vs conversion plots indicated for both catalysts that N$_2$ and N$_2$O are primary products and interconversion of N$_2$O to N$_2$ at higher NO conversions [8, 9, 13]. Both catalysts Co-Pt/ZSM-5 and Co-Rh/ZSM-5 are active, the latter more active, in the decomposition of N$_2$O to N$_2$ (see Table 3). In previous studies decomposition of N$_2$O to N$_2$ was attributed mainly to the presence of Co$^{2+}$ ions [8, 9, 13]. Rh catalysts are also known to be active in this secondary route for the formation of N$_2$ [17]. These observations show why Rh modified catalysts are more selective to N$_2$ than Pt catalysts.

To summarize, the results presented are compatible with the following sequence of the SCR of NO$_x$ over the catalysts [13,14]. Propene is activated over the catalyst via π - allyl species on the metal sites. Propene is also deposited over the acid sites as coke. The allyl complexes undergo selective oxidation to form partially oxidized compounds for eg. acrolein. These are combusted to CO$_2$, CO and H$_2$O. NO is oxidized over CoOx and Pt/Rh to NO$_2$. Nitrite/nitrate type compounds are directly formed from NO$_2$ by interaction with Co or CoOx or from the reaction Co$_{y}$(NO), Co$_{y}$(NO)$_2$ with oxygen or NO. These NOx compounds react with allylic species to form organo-nitro (R-CH$_2$-NO$_2$) or nitroso (RCH$_2$-NO) intermediates. These isomerize (the organo nitro group first is reduced to a nitroso group) to yield an oxime (R-CH=NOH). Dehydration of this oxime forms the nitril R-CHCN. This nitrile is decomposed by acid catalyzed hydrolysis to NH$_4^+$ ions. In the last step, the NH$_4^+$ ions reduce NOx to N$_2$.

The mechanistic sequence seems to be similar. Presence of Rh in comparison to Pt enhanced interconversion of N$_2$O to N$_2$ thus showing better nitrogen selectivity. Rh catalysts by virtue of being able to stabilize intermediated at high temperatures provides for optimal activity at high temperatures.
Further, both catalysts show tolerance to water. The Pt catalyst is also tolerant to SO₂ but the Rh catalyst is deactivated more easily. In conclusion, considering these facts and the cost of Rh, Co-Pt/ZSM-5 catalyst is the optimal choice.

### 7.5 CONCLUSIONS

Co-Pt/ZSM-5 and Co-RhZSM-5 catalyst with low noble metal content (0.1 wt%) are active and selective for the SCR of NO to N₂. At lower temperatures Pt modified Co/ZSM-5 catalysts are more active in the SCR of NO than the Rh modified Co/ZSM-5 probably due to the high activity of Pt on the activation of propene.

A correlation was found between the SCR activity of the catalysts and the amount of sorbed species found under reaction conditions by IR spectroscopy. In that respect, presence of larger concentration of surface sorbed species found under reaction conditions over Co-Rh/ZSM-5, specially at higher temperature, correlates with the constant yields obtained at higher temperatures.

Selectivity vs conversion plots indicate that over both catalysts N₂ and N₂O are primary products and interconversion of N₂O to N₂ takes place at higher NO conversions. Since in relation to Pt, Co and Rh catalysts are efficient in the decomposition to N₂O to N₂, this activity explains the higher N₂ selectivity of Co-RhZSM-5 catalysts. From the others points of view the mechanism operating for SCR of NO to N₂ over both catalyst is similar.

### ACKNOWLEDGMENTS

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REFERENCES

CHAPTER 8

Summary / Samenvatting
8.1 SUMMARY

The combustion of fuels, to meet the society demands for energy, result in the emission of large quantities of nitrogen oxides (NO\textsubscript{x}) to the environment. These pollutants cause severe environmental problems and present a serious hazard to the health. Nowadays, two methods for the control of NO\textsubscript{x} emissions are employed. The selective catalytic reduction of NO\textsubscript{x} with NH\textsubscript{3} (SCR), (for stationary sources such as power plants) and the three way catalyst (TWC), (for mobile sources such as automobiles). These are only partial solutions and include serious drawbacks. An alternative approach to the control of NO\textsubscript{x} emissions that is currently investigated worldwide is the Selective Catalytic Reduction of NO\textsubscript{x} using hydrocarbons as reductant (HC-SCR). Almost every exhaust gases of emitting sources contain low levels of unburned hydrocarbons, thus these hydrocarbons can be utilized to reduce NO\textsubscript{x} to N\textsubscript{2}. For the reasons mentioned above the development of a catalyst for this process is highly desirable.

Among the catalysts proposed for HC-SCR are Co based catalysts which are known to be active and selective in this process. However these catalysts need still to be improved for practical applications. In Chapter 3, as starting point of this work, a series of studies on Co based catalysts supported on zeolites are reported. Correlation between catalytic characteristics and kinetic results are employed to understand the working catalyst and this is used as basis for catalyst optimization. The influence of different preparation methods on the state of the Co ions in the zeolite have been studied by Temperature programmed desorption (TPD), X-ray absorption spectroscopy (XAFS) and Fourier Transform Infra Red (FTIR) spectroscopy. The reduction of NO in presence of oxygen with propene was also used to characterize the catalysts. It was found that the preparation method influenced the state of Co in the zeolite and that the excess of Co is present as Co oxide clusters. Increasing the Co content improved the activity of the catalysts, however excess of Co oxide led to lower selectivity towards N\textsubscript{2} due to unselective combustion of propene. Over Co/ZSM-5, N\textsubscript{2} and N\textsubscript{2}O were found to be primary products and at higher NO conversions, some interconversion of NO to N\textsubscript{2} takes place probably through readsoption of N\textsubscript{2}O on Co\textsuperscript{2+} followed by its reduction to N\textsubscript{2}. From the results obtained it was proposed that cobalt oxide in the pores of the zeolite and the individual ions at exchange sites are the active phases of Co/ZSM-5 catalysts. The oxide phase seems to be involved in the oxidation of NO to NO\textsubscript{2} and propene to CO\textsubscript{x} while the individual Co\textsuperscript{2+} ions at exchange sites, in the adsorption of NO\textsubscript{x} species and their reaction with activated propene to form intermediates that decompose resulting in the formation of N\textsubscript{2} as well as providing a site where N\textsubscript{2}O might decompose to N\textsubscript{2}. The presence of water retards the combustion of propene assuring that propene is available for the selective reduction of NO\textsubscript{x} to N\textsubscript{2}. Finally it was concluded that Co catalyst supported
on ZSM-5 and prepared by SSIE presented a good compromise between high activity and selectivity to N₂.

Since HC-SCR consists of several reaction steps, it is difficult to find a single active phase that will catalyze all the processes simultaneously. Multi-functional catalyst try to tackle the problem by combining several active catalytic phases. In Chapter 4, this approach is exemplified with the Co-Pt/ZSM-5 catalysts. Pt based catalyst are known to be very active and durable in HC-SCR, however, on drawback of these catalysts is their high selectivity to N₂O. As mentioned before Co/ZSM-5 catalysts are very selective to N₂ and also active in the reduction of N₂O to N₂ thus, Co-Pt/ZSM-5 catalysts were prepared to preserve the desired characteristics of the individual components minimizing their negative aspects. The characterization of these catalysts showed that over freshly prepared Co-Pt/ZSM-5 catalysts Pt is present as highly dispersed as Pt oxide particles, while Co is present as small oxidized particles containing some chloride. During reaction Pt is reduced while Co stays in an oxidic state. The materials are heterogeneous on microscopic scale. Two types of regions appear to exist: (1) Large Co and Co/Pt particles are found to be scattered over the sample and are probably Co oxidic clusters. (2) Cobalt highly dispersed and most likely still attached to the bridging oxygen of an ion exchange site. It was found that addition of Pt enhanced the activity of Co catalysts, however, the improvement of activity by the addition of Pt resulted in higher selectivity to N₂O. Co-Pt/ZSM-5 catalysts with low Pt contents (0.1 wt %) showed a synergistic effect by combining high stability and activity of Pt catalysts with the high N₂ selectivity of Co catalysts. Further it was found to be sulfur and water tolerant.

In Chapter 5 an in-situ i.r mechanistic study over Co-Pt/ZSM-5 catalysts is described. Formation of carbonaceous deposits, partially oxidized species, organo-nitro/ nitro/ nitrite/ nitrate species and nitril was observed. It has been shown that over Co-Pt/ZSM-5 propene is oligomerized under reaction conditions to coke over the acid sites and/or undergoes allylic oxidation to acrolein. Coke and acrolein over metal(oxide) sites result in direct combustion to CO₂ and H₂O. From the results described it is seen that over Co-Pt/ZSM-5, NOx compounds react with allylic species to form organo-nitro intermediates (nitro (R-CH₂-NO₂) or nitroso (R-CH₂-NO)). The intermediates are transformed to an oxime (R-CH=N=NOH) that dehydrates to form a nitrile (R-CHCN). Correlation between changes observed in the absorption band related to nitrile species and the catalytic activity led us to speculate that nitrile species are involved in the formation of N₂. Acid catalyzed hydrolysis of the nitrile results in the formation of NH₄⁺ ions on Brønsted acid sites. Finally, the NH₄⁺ ions reduce NOₓ to N₂.
In Chapter 4 the most active catalysts, having higher Pt loadings showed enhanced selectivity towards N₂O. Another noble metal that is used for catalytic control of NOx (major component of the TWC) is Rh. Since Rh catalyst are less selective to N₂O, the modification of Co catalyst with Rh presented an interesting alternative, thus, a series of Rh containing catalysts have been studied. The results are discussed in Chapter 6. A Co-RhZSM-5 catalyst with 0.1 wt% Rh content was shown to be active, selective and stable under reaction conditions. The addition of Rh even in small amounts (0.1 wt%) enhanced the activity of Co/ZSM-5 while maintaining high selectivity to N₂. A mechanism similar to the one proposed for Co-Pt/ZSM-5 catalyst seems to be operating also over Rh modified Co catalysts. Finally it was observed that in the presence of SO₂ caused an irreversibly deactivation of the catalysts.

Summarizing the main findings of the multi phase catalysts prepared in this work, Chapter 7 presents a comparison between the Co-Pt and Co-Rh systems. Both catalyst showed to be active and selective under reaction conditions. At lower temperatures Pt modified Co/ZSM-5 catalysts were more active in the SCR of NO probably due to the high activity of Pt on the activation of propene. Further, the interconversion of N₂O to N₂ activity was proposed as the cause of higher N₂ selectivity of Co-Rh/ZSM-5 catalysts. The presence of larger concentration of surface sorbed species found under reaction conditions over Co-Rh/ZSM-5, specially at higher temperature, correlated with the constant yields obtained at higher temperatures.

Selectivity vs conversion plots indicated that over both catalysts N₂ and N₂O are primary products and interconversion of N₂O to N₂ takes place at higher NO conversions. The mechanism operating for SCR of NO to N₂ over both catalyst is similar. Both catalysts show tolerance to water, however, Rh catalyst is deactivated by SO₂. It was concluded, considering these facts and the cost of Rh that Co-Pt/ZSM-5 catalyst is the optimal choice.
8.1 SAMENVATTING

Het verbranden van fossiele brandstoffen, om aan de vraag naar energie te voldoen, resulteert in de emissie van grote hoeveelheden stikstof oxiden (NO$_x$) in het milieu. Deze luchtverontreinigers veroorzaken ernstige milieu problemen en zijn een serieuze bedreiging voor de gezondheid. De huidig methoden die worden ingezet voor de vermindering van de NO$_x$ uitstoot, zijn als volgt. De selectieve katalytische reduktie van NO$_x$ met NH$_3$ (SCR), (voor stationaire bronnen, zoals elektrische centrales) en de drie-weg-katalysator (TWC), (voor mobiele bronnen, zoals auto’s). Dit zijn echter alleen maar gedeeltelijk oplossingen, die serieuze tekortkomingen met zich mee brengen. Een alternatieve benadering voor de controle van NO$_x$ uitstoot, die wereldwijd op dit moment wordt onderzocht is de selectieve katalytische reduktie van NO$_x$, waarbij koolwaterstoffen worden gebruikt als reducerend agens. Bijna alle uitlaatgassen bevatten kleine hoeveelheden onverbrande koolwaterstoffen (benzine), en dus kunnen deze gebruikt worden voor de reduktie van NO$_x$ naar N$_2$. Voor de redenen hierboven genoemd is de ontwikkeling van een katalysator voor dit proces van groot belang.

Tussen de katalysatoren di genoemd worden als mogelijke materialen voor dit proces, bevinden zich cobalt (Co) bevattende katalysatoren, waarvan bekend is dat ze aktief en selectief zijn voor dit proces. Echter, deze katalysatoren moeten nog steeds worden verbeterd voordat ze praktisch toepasbaar zijn. In Hoofdstuk 3 wordt, om te beginnen, een serie van experimenten van op Co gebaseerde katalysatoren gedragen door zeolieten, getoond. Korrelatie tussen katalytische eigenschappen en kinetische resultaten worden gebruikt om de werkende katalysator te kunnen begrijpen en dit wordt gebruikt als basis voor een verdere optimalisatie van de katalysator. De invloed van verschillende preparatie methoden op de toestand van de Co ionen in de zeoliet, werden bestudeerd door Temperature programmed desorption (TPD), X-ray absorption spectroscopy (XAFS) and Fourier Transform Infra Red (FTIR) spectroscopy. De reduktie van NO in de aanwezigheid van zuurstof met propeen werd ook gebruikt voor de karakterisatie van d katalysatoren. Met behulp van deze methoden werd geconcludeerd dat de preparatie methode invloed had op de toestand van de Co ionen in de zeoliet en dat de overmaat aan Co aanwezig is als Co oxide clusters. Toename van de Co concentratie verbeterde de activiteit van de katalysatoren, echter een overmaat aan Co leidde tot een lagere selectiviteit naar N$_2$, vanwege de onselectieve verbranding van propeen. Over Co/ZSM-5 werd voornamelijk N$_2$ en N$_2$O gevonden, en bij hogere NO omzettingen werd zelfs de interconversie van N$_2$O naar N$_2$ gevonden, waarschijnlijk veroorzaakt door een readsorptie van N$_2$O op de Co$^{2+}$ ionen gevolgd door reduktie tot N$_2$. Uit de verkregen resultaten werd voorgesteld dat Co oxide in de poriën van de zeoliet en de individuele ionen op de uitgewisselde plaatsen de aktieve fasen van de Co/ZSM5 katalysatoren
vormen. De oxide fase lijkt deel te nemen in de oxidatie van NO tot NO₂ en propeen naar COₓ, terwijl de individuele Co²⁺ ionen op de uitgewisselde plaatsen helpen in de adsorptie van NOₓ deeltjes en hun reactie met geactiveerd propeen om intermediaten te vormen die uit een vallen in N₂ alsmede het aanbieden van een lokatie voor de mogelijke omzetting van N₂O tot N₂. De aanwezigheid van water remt de verbranding van propeen, er van uitgaande dat propeen aanwezig is voor de selectieve omzetting van NOₓ naar N₂. Het resultaat van deze studie was dat Co katalysatoren, gedragen op ZSM-5 en bereid met de vaste stof ion uitwisseling (SSIE) een goed compromis bezaten tussen hoge activiteit en selectiviteit naar N₂.

Omdat HC-SCR uit verschillende reaktie stappen bestaat is het erg moeilijk om een enkele actieve fase te vinden die alle processen simultaan katalyseert. Multi-functionele katalysatoren proberen het probleem op te lossen door meerdere actieve katalytische fasen te combineren. Een voorbeeld van zo’n aanpak wordt beschreven in Hoofdstuk 4 met de Co-Pt/ZSM-5 katalysatoren. Op Pt gebaseerd katalysatoren zijn bekend om hun grote activiteit en duurzaamheid in HC-SCR, echter, een minpunt is hun grote selectiviteit voor de vorming van N₂O. Zoals al eerder gezegd zijn Co/ZSM-5 katalysatoren erg selectief voor de vorming van N₂ en ook aktief in de reduktie van N₂O naar N₂ en dus werden Co-Pt/ZSM-5 bereid, die de gewenste eigenschappen van de afzonderlijke componenten behouden en de negatieve aspecten onderdrukken. Karakterisatie van deze katalysatoren hebben aangetoond dat in ongebruikt Co-Pt/ZSM-5 de Pt aanwezig is als fijn verdeeld Pt oxide deeltjes, terwijl Co aanwezig is als klein geoxideerde deeltjes waarin zich ook nog wat chloride bevindt. Tijdens de reaktie wordt Pt gereduceerd, terwijl Co in zijn geoxideerder toestand verblijft. De materialen zijn heterogeen op microscopische schaal. Twee gebieden schijnen te bestaan: (1) grote Co and Co/Pt deeltjes verspreid over het monster en waarschijnlijk zijn dit Co oxide clusters. (2) Cobalt in grote mate verspreid en waarschijnlijk nog steeds verbonden met het gebrugde zuurstof van een uitgewisselde site. Verder werd gevonden dat de toevoeging van Pt verhoogde de aktiviteit van de Co katalysatoren, maar de verbetering in aktiviteit door de toevoeging van Pt resulteerde in een hogere selectiviteit voor N₂O. Co-Pt/ZSM5 katalysatoren met een lage Pt belading (0.1 wt %) vertoonden een synergetisch effect door het samenvoegen van de hoge stabiliteit en activiteit van de Pt katalysatoren met de hoge N₂ selectiviteit van de Co katalysatoren. Ook werd gevonden dat de katalysatoren zwavel en water tolereren.

In Hoofdstuk 5 wordt een in situ i.r. mechanistische studie over Co-Pt/ZSM-5 katalysatoren beschreven. De vorming van koolstofhoudende afzettingen, gedeeltelijk geoxideerde deeltjes, organo-nitro /nitro/ nitriet/ nitraat deeltjes en nitril werden waargenomen. Ook wordt getoond dat over Co-Pt/ZSM-5, propeen wordt geoligomeriseerd onder reaktie condities tot coke over de zure plaatsen en/of allylisch oxidatie tot acroleine. Coke en acroleine over metaal (oxide) plaatsen resulteerde in de direkte verbranding
tot CO en H2O. De beschreven resultaten laten zien dat over Co-Pt/ZSM-5, NOx verbindingen reageren met allylische deeltjes tot organo-nitro intermediëren (nitro (R-CH2-NO2) of nitroso (R-CH2-NO)). De intermediëren worden omgezet in een oxide (R-CH=NOH), dat dehydrateerd tot een nitril (R-CHCN).

Korrelatie tussen waargenomen veranderingen in de i.r. absorptie band en de katalytische activiteit van leid ons ertoe te speculeren dat nitril deeltjes deelnemen in de vorming van N2. Zuur gekatalyseerde hydrolys van nitril resulteert in de vorming van NH4+ ionen op Bronsted zure plaatsen. En uiteindelijk worden de NH4+ ionen gereduceerd tot N2.

In Hoofdstuk 4, de meest aktieve katalysatoren met de hogere Pt ladingen vertoonden toenomen selectiviteit tot N2O. Een ander edel metaal dat wordt gebruikt voor de katalytische beheersing van NOx (een belangrijke component van de TWC) is Rh. Omdat Rh katalysatoren minder selectief zijn in N2O, gaf de modificatie van Co katalysatoren met Rh een interessant alternatief; dus een serie van Rh bevattend katalysatoren werd bestudeerd. De resultaten staan beschreven in Hoofdstuk 6. Een Co-Rh/ZSM-5 katalysator met 0.1 wt % Rh belading bleek erg aktief, selectief en stabiel onder reactie omstandigheden. De toevoeging van Rh, zelfs in kleine hoeveelheden (0.1 wt %), verhoogde de activiteit van Co/ZSM-5, terwijl een hoge selectiviteit in N2 gehandhaafd bleef. Een vergelijkbaar mechanisme als voor de Co-Pt/ZSM-5 lijkt ook voor de Rh gemodificeerde Co katalysatoren te gelden. Ook werd waargenomen dat de aanwezigheid van SO2 een irreversibele deactivering van de katalysatoren teweeg bracht.

De belangrijkste resultaten van de multi fase katalysatoren bereid in dit werk samenvattend presenteert Hoofdstuk 7 een vergelijking tussen de Co-Pt en Co-Rh systemen. Beide katalysatoren tonen aktief en selectief te zijn onder reactie omstandigheden. Bij lage temperaturen blijken Pt gemodificeerd Co/ZSM-5 katalysatoren aktiever te zijn in de SCR of NOx, waarschijnlijk vanwege de hogere activiteit van Pt in de aktivering van propeen. Verder, de interconversie van N2O naar N2 activiteit werd gezien als de oorzaak voor de hogere N2 selectiviteit van Co-Rh/ZSM-5 katalysatoren. De aanwezigheid van grote hoeveelheden oppervlakte geadsorbeerde deeltjes, onder reactie omstandigheden over Co-Rh/ZSM-5 katalysatoren, voornamelijk bij hogere temperaturen, kwam overeen met de constante opbrengsten, zoals verkregen bij hogere temperaturen.

Grafieken van selectiviteit uitgezet tegen conversie laten zien dat over beide katalysatoren N2 en N2O primaire produkten zijn en interconversie van N2O in N2 vindt plaats bij hogere NO conversies. Het mechanisme voor de SCR van NO naar N2 over beide katalysatoren is vergelijkbaar. Beide katalysatoren
vertonen tolerantie voor water, echter, de Rh katalysator wordt gedeactiveerd door SO₂. Geconcludeerd werd, deze resultaten en de kostprijs van Rh in beschouwing nemend, dat Co-Pt/ZSM-5 katalysatoren de optimale keuze is.
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At the last stages of this thesis I was contemplating what the future was about to bring, and among other things I remember words about the promotion date and “the light at the end of the tunnel”. I also remember how these words were not encouraging enough due to the possibility that this light was related to an incoming train. However time has proven me wrong and in this happy occasion I want to thank all of you. Since for a strange and mysterious reason technology allowed the human kind to put a man in the moon but not to choose an arbitrary number of pages on a thesis (only packages “quantum” of 16 pages at one time), there will be a lot of free pages until the 144 magic number of pages will be fulfilled. I would like to thank so many and for so many different reasons that is particularly nice to have sufficient free space. So let’s go...

First of all I wish to thank the Dutch people for their hospitality. In the last years The Netherlands has become the place where my home is and also, as a country, it became a second home. Not only because of the traditional good relations with my home country and several historical reasons but after the experience of visiting and living in several countries, I feel it is fair to say, that The Netherlands is one of the countries where being a foreigner can be a pleasant experience and the chances are that it will be. I excuse myself for generalizing, however I think that this is mainly due to a high respect for personal freedom, lack of extreme chauvinism and a great deal of tolerance, qualities that are rare to find in many other countries. A word of advice, even though it all sound very nice, it can also have serious consequences for example, as result of the qualities described above, the Dutch, without hesitation will speak other foreign language, this may cause a severe delay in the development of your own personal Dutch language skills. On the other hand it also will provide you with an invaluable excuse for not speaking yet Dutch. You may live several years in the country before noticing that there is another language, at least until a baby at home begins to pronounce strange words that seem to have sense to any one else but you.

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and specially for accepting together with Marco to be paranymphs. I am sure that at the defense you two will be able to support me and help me to write all the answers in the blackboard, and further that the song that you will write for the party will be very kind and without any sarcasm, like I expect. Talking of Laszlo reminds me of thanking also Fiona for interesting conversations. To Marco I thank not only for translating the summary to Dutch and being my paranymph, but for his social personality, his readiness to help at any time anyone even at cost of losing his own limited time. For his unlimited curiosity for others, (just remember curiosity kills the cat). It was nice to share the office with you even if later I gave up because of the irresistible and intoxicating attraction of a private docent room equipped with lots of MHz and Gigabytes. To Laszlo L, thanks for sharing common interest in music and interesting discussions. To Ibolya and Boriska for their hospitality. Martyn for a few breaks with mr. Marlborough and small talks during coffee time. To Olivier, it was nice to exchange words in Spanish with you, some jokes and wish you success in your studies. To Isaac it was very nice to work with you in DeNO, and I wish you that you will find many more good catalyst as the case of your Ni catalyst. I believe that this catalyst is so good only because you prepared completely from the beginning including the zeolite itself, bravo! Another “DeNOxing” colleague, Takeshi, it was very nice to work with you, your serious approach to work, your efficiency and tendency to solve problems independently make it easy for me to pass to you my beloved set up in which I spend the longest days of my life.

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Sergio E. Maisuls

Enschede February 14th 2000
Curriculum Vitae

Sergio Eduardo Maisuls, son of Luis Benjamin Maisuls and Dora Jinich, was born on the 24th of September 1960 in Capital Federal (Buenos Aires), Argentina. From 1973 to 1977 he attended the National High School Reconquista in Capital Federal. After completing his studies he moved to Israel. In 1978 he began to study Hebrew while working in agriculture and the manufacture of irrigation devices at the agricultural center (“kibbutz”) Hatzor at Ashdod. During 1979 he studied at the Preparatory Program in Science at the Hebrew University of Jerusalem. Between the years 1980 to 1984 he studied at the Ben-Gurion University of the Negev Beer-Sheva where he obtained his B. Sc. degree in chemistry. In September 1984 he started his studies of master in chemistry at the Feinberg Graduate School of the Weizmann Institute of Science at Rehovot and his research project was performed under the supervision of Dr. Iren Debra Feinstein-Jaffe and Prof. Joost Manassen at the Materials research department. The project involved the preparation of novel organometallic polymers of chromium, molybdenum and tungsten with bifunctional aryldiisocyanides ligands, their characterization and the investigation of their electronic properties. In March 1987 he obtained his M.Sc. degree in (Organometallic-Inorganic) Chemistry.

After graduation he was invited to work as a Research scientist at the Department of Inorganic Chemistry of the University of Bayreuth in Germany under the supervision of Dr. Karin Weiss. The research was related with the preparation characterization and investigation of the catalytic properties of heterogeneous bimetallic methathesis catalysts. Due to his military service duties, he postponed his Ph.D. studies, and in January 1988 he was recruited by the IDF (Israel Defense Forces). In 1989 he graduated from the IDF Military Officers School and continued the rest of his service as scientist. In January 1993 he ended his duties with the rank of captain. During 1993 and 1994 he worked as Plant Analytical Chemist at the Central Laboratories of “Carmel Olefins”, the Petrochemical Industries in Haifa, under the supervision of the chief chemist and head of the laboratories, Dr. Raanan Aloni. The work dealt with different aspects on the production of Polypropylene, Polystyrene, Polyethylene and Ethylene, as well as with the research, development and implementation of new analytical techniques. From July 1995 he worked as a Ph.D. student at the Catalytic Processes and Materials Department at the Faculty of Chemical Technology from the University of Twente in The Netherlands under the supervision of Prof. Dr. J.A. Lercher on the Selective Catalytic Reduction of NOx with Hydrocarbons in presence of excess oxygen. The results of his research work are described in this thesis.
**List of publications**

1. Organometallic Coordination Polymers of the Group VI Transition Metals with Aryldiisocyanides S. E. Maisuls
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2. Chromium, Molybdenum and Tungsten Organometallic Polymeric Networks with Aryldiisocyanides Ligands.
   I. Feinstein-Jaffe and Sergio E. Maisuls,

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4. Heterogeneous Bimetallic Methathesis Catalyst by Reaction of Fisher-type Carbene Complexes with Reduced Phyllips Catalyst.
   K. Weiss, W. Guthman and S.E. Maisuls,

5. Syntheses of heterogeneous, bimetallic methathesis catalysts by reactions of Fischer type carbene and carbyne complexes with reduced Phyllips catalyst,
   K. Weiss, W. Guthman, M. Denzner and S.E. Maisuls

6. Water and sulfur resistant pt-based zeolite catalysts for NOx reduction
   S. E. Maisuls, S. Feast, K. Seshan, J.G. van Ommen and J.A Lercher,

7. Selective catalytic reduction of NOₓ to nitrogen over bimetallic catalysts, part A, Characterization and kinetic studies,
   S. E. Maisuls, K. Seshan , S. Feast and J. A Lercher,

8. Selective catalytic reduction of NOₓ to nitrogen over bimetallic catalysts,. Part B *In situ* i.r. spectroscopic study of the surface species during reaction
   S. E. Maisuls, K. Seshan and J. A Lercher

9. Selective catalytic reduction of NOₓ to nitrogen over Co-Rh/ZSM-5 catalysts,
   S. E. Maisuls, K. Seshan and J. A Lercher

10. On the physicochemical properties of Co/ZSM-5 prepared by ion exchange and incipient wetness impregnation,

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*Publications 1 to 5 not included in this thesis*