The use of niobia in oxidation catalysis

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Abstract

This paper summarises the background to work carried out at the University of Twente on the use of niobia as a catalyst for the oxidative dehydrogenation of propane to propylene and discusses the development of promoted niobia catalysts for this reaction. Results are also presented which illustrate the use of niobia in catalysts for other reactions such as the oxidative coupling of methane, the oxidative dehydrogenation of ethane and the oxidative dehydrogenation of methanol. It appears that niobia and niobia-modified catalysts, when used in high-temperature oxidation processes, can exhibit relatively high selectivities compared with more conventional catalysts.

1. INTRODUCTION

There has of recent years been a growing interest in processes for the dehydrogenation and oxidative dehydrogenation of saturated hydrocarbons. This interest has risen from the fact that the rate of production throughout the world of liquefied petroleum gas (LPG) has increased markedly over the last ten or so years, from around 20 million metric tons per year in 1980 to around 55 million metric tons per year in 1990 [1]. LPG is made up of approximately 60% propane, 29% butane and 9% isobutane, with the balance made up predominantly of ethane and pentane. The dehydrogenation of these molecules leads directly to some of the most important building units of the petrochemicals industry, propylene, but-1-ene and isobutene, molecules normally produced as secondary products in the thermal (steam) cracking of naphthas. Although steam cracking of LPG using conventional crackers can also be carried out to bring about dehydrogenation to the corresponding olefins, the selectivities to the olefins is not great; for example, the predominant products from the steam cracking of propane are ethylene (42%) and fuel products (34%) [2].

The straightforward dehydrogenation of propane:

is endothermic with a value of ΔH° of +117 kJ mol⁻¹. In order to obtain reasonable yields, the reaction must therefore be carried out at relatively high temperatures (> 600°C) and at low pressures; short contact times must be used to minimise coking of the catalysts. The lifetimes achieved with practical catalysts are relatively short and so various different techniques are used to regenerate them. For example, in the OLEFLEX Process (UOP), a catalyst is used which comprises of a platinum-tin-lithium combination supported on γ -alumina and this is regenerated continuously. The STAR Process (Phillips Petroleum) uses an iron-chromium oxide combination, also supported on γ -alumina, and this requires regeneration every eight hours of operation. The CATOFIN Process uses a chromia on γ -alumina catalyst which requires regeneration every fifteen minutes [3]. Typical conversions lie between 20 and 25% and the selectivities quoted are between 90 and 95%.

An alternative to straightforward dehydrogenation is oxidative dehydrogenation, which for propane takes place according to the (exothermic) reaction:

The advantages of carrying out the reaction oxidatively is that there is no equilibrium limitation and so the reaction can be carried out at lower temperatures than those required for the dehydrogenation reaction and there is thus less chance of carbon deposition. A significant disadvantage, however, is that non-selective reactions can also occur, particularly those which produce the oxides of carbon, CO and/or CO₂.

When the work summarised in this paper was started, only limited success had been achieved in obtaining significant yields in oxidative dehydrogenation of simple hydrocarbons ([4]-[7]). For example, we had shown that a magnesium orthovanadate material gave a propane conversion of 7.6% at 600°C with a selectivity to propylene of almost 60%. Our initial results showed that the selective oxidation of propane over the vanadium compounds which we examined depended mainly on the strength of the V-O bond in the structures; there was an optimum behaviour with magnesium, orthovanadate, Mg₃(VO₄)₂, this material having stronger vanadium-oxygen bonding than the other compounds studied. We therefore decided to examine the catalytic properties of the oxides of niobium, the element which lies directly below vanadium in the periodic table, to see if it gave any improvement in the oxidative dehydrogenation behaviour compared to the vanadium compounds; this might be expected as the strength of the niobium-oxygen bond is greater than that of the vanadium-oxygen bond. Having found that niobia did indeed exhibit good catalytic behaviour for the oxidative dehydrogenation reaction, it was decided to test niobia and niobia-containing compounds for other selective oxidation processes. The results are summarised in this short article.

2. NIOBIA AS AN OXIDATIVE-DEHYDROGENATION CATALYST

As is discussed extensively in other papers presented in this symposium, niobia is usually used as catalyst at relatively low temperatures, i.e. at temperatures below those at which Brønsted acidity is lost. It therefore normally functions as a strong acid; there are only a few examples reported in the literature in which niobia is used as a component of a catalyst operating at higher temperatures. A notable exception is the work of Thorsteinson et al. [8] in which it was shown that the addition of relatively small quantities of niobia to a mixture of the oxides of molybdenum and vanadium decreased by more than 250°C the temperature required to give 10% conversion of ethane to ethylene under oxidative conditions: a catalyst having the cationic composition $\text{Mo}_{0.8}\text{V}_{0.2}$ gave a selectivity of 100% with an ethane conversion of 10% at 540°C, while a catalyst with a composition $\text{Mo}_{0.78}\text{V}_{0.19}\text{Nb}_{0.09}$ gave the same selectivity and conversion at 286°C. Another exception is to be found in the work of Oda and his colleagues [9] who, in a search for catalysts for the conversion of isobutene to methacrolein, observed [9] that the addition of niobium oxide to a bismuth molybdenum oxide catalyst gave improved conversions and selectivities to methacrolein.

Our preliminary work on the use of niobia involved a comparison of the oxidative dehydrogenation of propane over a series of oxides, including lanthana, magnesia, zirconia and titania [10]. We found that niobia gave the best performance of the series with a selectivity of 76% to propene and a conversion of propane of 2% at a temperature of 586°C; the next best of the series was titania, which gave a selectivity of 65% at 2% conversion at a temperature of 550°C. The effects of reaction temperature and temperature of calcination of the niobium oxide were thus examined [11,12]. Figure 1 shows typical results for the effect of reaction temperature on the conversion and selectivity of a niobia sample prepared by calcining a commercial sample of hydrated niobia at a temperature of 650°C. It can be seen that this sample had reasonable activity at temperatures of about 500°C; however, although the selectivity was high at low temperatures, it decreased at higher temperatures.

In a further set of experiments summarised in Table 1, it was shown that a calcination temperature above 500°C was necessary to give reasonable selectivity. Below that temperature, the material was amorphous and Brønsted acidity was still present; this gave rise to higher proportions of total oxidation relative to partial oxidation. It should also be noted that the degree of cracking of the propane to a mixture of methane and ethylene increased with increasing calcination temperature, T_c , and that the surface area decreased markedly with increasing T_c .

Table 1

Results of experiments carried out at 550°C with niobia calcined at various temperatures; conditions: 600mg catalyst, 30% propane, 5% oxygen, balance helium.

T_c / °C	Area /m ² g ⁻¹	Phase	Conv- ersion /%	Sel. to C ₃ H ₆ /%	Sel. to CO _x /%	Sel. to cracking /%
300	108.2	Amor.	0.6	53	43	4
500	28.5	TT	1.5	78	16	7
570	18.0	TT/T?	1.1	75	18	7
600	14.3	TT/T?	1.0	82	9	9
650	9.9	T	0.6	85	6	9
700	6.8	T	0.6	83	5	13
750	3.7	T	0.5	79	4	17
850	1.2	T	0.1	76	3	20

It is clear from the results of Table 1 that the conversions obtained with the unselective material under these reaction conditions. It was found that it was not possible to completely mask the surface of the alumina and although it was possible to obtain slightly higher conversions than with the unsupported material, the all-over selectivity was worse due to the exposed alumina surface.

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It was therefore decided to adopt another approach in an attempt to obtain better conversions. This involved the search for promoters for the niobia catalyst itself. Some of the results have previously been presented elsewhere [10] while others are given in more detail in another paper in this volume [13]. A series of oxides including those of vanadium, chromium and molybdenum were mixed with the niobia [10, 13] and then calcined at 530°C before testing for the oxidative dehydrogenation of propane at various temperatures in the range 300° to 600°C. As with the results shown in Fig. 1, the selectivity was high at lower temperatures but it decreased with increasing reaction temperature, in parallel to an increase in the conversion. Some of the results obtained are summarised in Table 2; this compares the temperatures required to give 7% conversion of the propane and the selectivities obtained at those temperatures. For comparison purposes, results are also given for vanadia on MgO and for the unpromoted niobia. It should be noted that the data for the latter sample are given for a conversion of 1%, a temperature of about 600°C being required for 7% conversion; the corresponding selectivity would be about 60%.

Figure 1. Conversion of propane and selectivity to propylene over a sample of Nb_2O_5 calcined at 650°C . Curves 1 and 3 are for 5% O_2 and curves 2 and 4 for 10% O_2

Figure 2. The yield of C₂ products as a function of reaction temperature for the oxidative coupling of methane over doped samples of a Li/MgO catalysts; Δ , undoped sample; $\blacktriangle$, Ge-doped sample; $\blacksquare$, Zr-doped sample; and $\bullet$, Nb-doped sample.

Table 2

Comparison of the behaviours under standard reaction conditions of various promoted niobia samples with a vanadia on magnesia material and unpromoted niobia (from ref.[10]).

Catalyst (Additive content given in mol%)	Surface Area $/\text{m}^2\text{g}^{-1}$	Temperature for 7% conversion of propane $/^\circ\text{C}$	Propylene selectivity at 7% propane conversion /mol%
5% $\text{V}_2\text{O}_5/\text{MgO}$	-	441	57
5% $\text{TiO}_2/\text{Nb}_2\text{O}_5$	28	606	62
5% $\text{P}_2\text{O}_5/\text{Nb}_2\text{O}_5$	36	579	65
5% $\text{Cr}_2\text{O}_3/\text{Nb}_2\text{O}_5$	43	415	67
5% $\text{MoO}_3/\text{Nb}_2\text{O}_5$	16	530	75
5% $\text{V}_2\text{O}_5/\text{Nb}_2\text{O}_5$	11.3	485	85
Nb_2O_5	9.9	540*	85

* Data at temperature required to give 1% conversion.

It can be seen from Table 2 that the most active catalyst obtained was that containing Cr_2O_3 , which gave a selectivity of 67% at 415°C ; this represents a considerable improvement over the magnesia-supported sample which only gave 57% selectivity at 441°C , a result similar to that for the magnesium orthovanadate sample discussed above. However, the samples containing MoO_3 and V_2O_5 gave much improved selectivities, 75% and 85% respectively, compared with approximately 60% for the unpromoted sample at the same conversion (see above). A range of other promoters were also tested [10] but none of these gave such good results. Our subsequent work has therefore concentrated on the addition of vanadia to the catalysts, although it is our intention also to do further work on the effects of the additions of the oxides of molybdenum and chromium. The results obtained for the effect of the vanadium content of the $\text{V}_2\text{O}_5/\text{Nb}_2\text{O}_5$ samples are given elsewhere in this issue [13]; in summary, increasing vanadia content increases the catalyst activity but it appears that there is an optimum vanadia content of about 1 wt%, beyond which the selectivity at equivalent conversions drops somewhat with increasing vanadia content. It would appear that the active catalyst depends on some sort of synergy between the vanadia and the niobia and that the niobia does not only provide a support function to the vanadia; there is some evidence that the formation of a surface mixed-oxide phase contributes to the improved behaviour of these samples. Further work is in progress in an attempt to clarify the nature of these catalysts.

3. NIOBIA AS AN ADDITIVE TO METHANE-COUPPLING CATALYSTS

The oxidative coupling of methane to form C_2 compounds has attracted much interest over the last decade or so and much work has been carried out in an attempt to find active, selective and stable catalysts for use in a process to produce ethylene in an economic way [14]. Part of our own work on the subject has been concerned with the development of modified Li/MgO catalysts; we have shown that promotion of Li/MgO materials by the addition of oxides such as SnO_2 gives a significant increase in activity without substantial loss in selectivity [15]. Experiments were therefore carried out in which a variety of other oxides including niobia were added to a Li/MgO material to see whether these additives had any effect on the activity and selectivity of the basic material. Fig. 2 shows some typical results; the yields of C_2 products (both ethane and ethylene) are shown as a function of the reaction temperature for an unpromoted Li/MgO material and also for Li/MgO promoted by the oxides of Ge, Zr and Nb [16]. Germanium oxide had a detrimental effect on the behaviour of the catalyst but both zirconium and niobium oxides gave slight improvements; the main effect was on activity, the selectivities remaining almost constant. As is shown in another paper in this meeting in which the behaviour of niobium-promoted Li/MgO for the oxidative coupling reaction is compared with that for the oxidative dehydrogenation of ethane [17], the improved behaviour was probably due to the formation of a $LiNbO_3$ phase; however, the niobium-promoted materials were unstable, this instability being found to be at its greatest at a temperature above the melting point of a separate Li_2CO_3 phase.

4. VANADIA-PROMOTED NIOBIA AS A CATALYST FOR THE OXIDATIVE DEHYDROGENATION OF METHANOL

Previous work from our laboratory was concerned with the selective oxidation of methanol and other molecules such as toluene and o-xylene over supported vanadia catalysts [17]. As a part of a study of the effect of the support material on the selectivities of vanadia-supported catalysts [18], we have examined the behaviour in methanol oxidation of the vanadia-promoted niobia whose development was described in Part 2 above. It was found that whereas a titania-supported vanadia catalyst gave a selectivity towards formaldehyde of about 55%, the $5\%V_2O_5-Nb_2O_5$ material gave a selectivity to formaldehyde of approximately 80%, with a methanol conversion of 80%, at a temperature of about $240^\circ C$; the minor products were methyl formate and dimethoxymethylene. For comparison purposes, a vanadia-niobia catalyst supported on zirconia was tested; this gave predominantly methyl formate at lower temperatures but the main products were CO and CO_2 when the conversion of methanol approached 100% at about $300^\circ C$.

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