The synthesis of alcohols using Cu/ZnO/Al₂O₃ + (Ce or Mn) catalysts

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Cu/ZnO/Al₂O₃ catalysts modified by compounds of manganese or cerium were prepared by coprecipitation or by impregnation and were tested for the synthesis of alcohol mixtures from synthesis gas at pressures of up to 70 bar. They were also examined by XPS both before and after the reaction. With both the impregnated and the coprecipitated catalysts, manganese increased the selectivity to higher alcohols (mainly isobutanol). However, in the case of cerium, the location of the cerium ions appeared to determine the selectivity; it shifted towards alkanes and CO₂ when cerium was present at the surface of the catalyst (probably as CeO₂), but to isobutanol when the cerium ions were present in the bulk. Changes were found in the selectivities of the catalyst doped with cerium with time on stream and these could be explained by a segregation of the cerium ions to the surface. Some of the mechanistic steps in the formation of higher alcohols as proposed in the literature were confirmed.

Keywords: alcohols; methanol; Cu/ZnO/Al₂O₃; promoters; mechanism

1. Introduction

The combustion of fuels by cars is a significant source of environmental pollution, and research on modifications or even on alternative fuels is therefore very important. As a possible alternative to petrol, a mixture of petrol with methanol and higher alcohols has been considered [1–3]. The main goal of our study was the development of a catalyst which produces such an alcohol mixture. In order to achieve this, it was thought to be helpful to have some more insight in the reaction mechanism. This again may also be useful for the syntheses of specific alcohols, such as methanol and isobutanol (e.g. for the synthesis of methyl tert-butyl ether, MTBE).

It is well known that a mixture of methanol and higher alcohols can be produced from synthesis gas (CO + H₂) over a modified Cu/ZnO/Al₂O₃ catalyst [4–6]. Alkali metals, such as K or Cs, are most commonly used as additives to such a cat-

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alyst. However, more stable catalysts may be obtained by the addition of ions which can be incorporated in the copper lattice. In this paper, compounds of manganese and cerium were used. The addition of these compounds to Cu/ZnO/Al₂O₃ catalysts has been described in the patent literature; however, these additions have always been accompanied by the addition of (many) other elements [6]. In this study, these components were added individually either by coprecipitation or by impregnation; in the former case, the ions were found to be present throughout the catalyst material, whereas in the latter, they were found only at the surface.

In order to explain the behaviour of the different catalysts, two analysis techniques were used to study the surface of the catalyst both before and after reaction. The metal surface area was measured by reactive N₂O adsorption and the surface composition was studied with XPS. To gain more information on the reaction mechanism, especially with respect to the formation of products directly from methanol, methanol was added to the feed gas stream of the reactor in a number of the experiments.

2. Experimental

Cu/ZnO/Al₂O₃ catalysts with a Cu : Zn : Al ratio of 9 : 9 : 2 were prepared by coprecipitation from a solution of the dissolved metal nitrates with a potassium carbonate solution. A detailed description of this preparation technique has been given elsewhere [7,8]. The materials were washed, dried and then calcined at 350°C. Prior to the reaction, they were reduced in a 1% H₂/N₂ mixture (heating rate 1°C/min, maximum temperature 240°C). In the same way, series of cerium-containing and of manganese-containing catalysts were prepared by adding the appropriate metal salts to the nitrate solution. Another series of doped catalysts was prepared by impregnation of the calcined CuO/ZnO/Al₂O₃ material with various amounts of cerium or manganese nitrates. The amounts of the additives used varied from 0 to 8 mol% with respect to the metal ions.

Atomic absorption spectroscopy (AAS), X-ray fluorescence spectroscopy (XRF) and X-ray diffraction (XRD, Philips PW1710, Cu K α radiation) were used for analysis of the bulk of the catalyst. The copper surface area was measured by N₂O decomposition, as described by Chinchén and co-workers [9] and the composition of the surface was studied using X-ray photoelectron spectroscopy (XPS, Kratos XSAM-800, Al K $\alpha_{1,2}$ radiation: 1487 eV). Steady-state charging was corrected for by fixing the C 1s line (graphite) at 285.1 eV. Prior to the XPS study, the fresh samples were pretreated by reduction in a mixture of 10% H₂/Ar using a heating rate of 1°C/min, the temperature being raised from 120 to 240°C, and were then oxidised mildly by exposing them to N₂O at 60°C. The samples studied after an activity test were transferred from the reactor after flushing with nitrogen and then very slowly admitting air to the system at room temperature.

The catalysts were tested for their activity in the synthesis of alcohols using a high pressure reactor system. The total pressure was varied from 30 to 70 bar; a temperature range of 240–300°C was covered; H_2/CO ratios between 0.5 and 2.0 were used. The amount of catalyst used was 1.0 g, and the flow rate was either 1.92 or 3.84 $\ell(\text{STP})\text{ h}^{-1}$. Products were analyzed using a Varian gas chromatograph equipped with Hayesep R column.

3. Results

Almost all the catalysts tested deactivated during the first 20 h of operation; the activity stabilized at a level about 30% lower than the initial value. However, the catalyst coprecipitated with 4% Ce showed a very interesting behaviour. Fig. 1 shows the formation of several products during the first 170 h of the reaction. Only the experiments carried out under exactly the same conditions (used as “reference measurements”) are included in the figure. In between these points both the temperature and the flow rates were varied, so that the figure does not show exactly which conditions caused the changes in the activity and selectivity. Fig. 1a demonstrates that the activity for the formation of alcohols and other oxygenated products drops dramatically with time. The scatter found for the production rate of isobutanol around 30 h might even suggest a very strong deactivation for this component at this temperature, since, during the first 30 h, the catalyst was only exposed to lower temperatures. On the other hand, fig. 1b shows that the production of alkanes and CO_2 is more or less constant over this period. Thus, there are at least two groups of products which seem to be formed independently. Of these products, only values for the major representatives are given in the figures and tables; it should be noted that minor amounts of other products were formed, such as propanol, ethane, methyl formate and methyl acetate. In spite of the large number of products analysed, the C balance was usually correct within 5% and the O balance within 10%. It is possible that higher alkanes and alcohols were also formed, but could not be analysed; this is likely as the C balance was lower than the O balance.

Table 1 gives the selectivity (percent of C converted into each individual product) of the coprecipitated catalyst containing various amounts of Ce. There are several effects of the addition of Ce by coprecipitation. At low concentrations of Ce (2%), the selectivity shifted from methanol to isobutanol; the selectivities to ethanol, methane and CO_2 were hardly affected. At higher Ce concentrations (4%), however, the selectivity to higher alcohols decreased and the selectivities to methane and CO_2 increased. The catalyst with 4% Ce also had a lower activity than the other catalysts. Thus small amounts of Ce are favourable for the synthesis of higher alcohols whereas larger amounts are unfavourable.

The effect of the addition of Mn by coprecipitation is shown in the figs. 2a–2c. Fig. 2a shows that the selectivity to methanol increased with the amount of Mn

Fig. 1. Deactivation behaviour of coprecipitated $\text{Cu/ZnO/Al}_2\text{O}_3$ catalysts containing 4 mol% Ce. (a) Production of oxygenates with time. (b) Production of methane, ethane and CO_2 with time. 1.0 g of catalyst; flow rate = 3.84 l h^{-1} ; $P = 40 \text{ bar}$; $T = 280^\circ\text{C}$; $\text{H}_2/\text{CO} = 1$.

present in the catalyst; the selectivity to ethanol decreased with Mn-content but that to isobutanol increased slightly. Fig. 2b gives the selectivity to CO_2 , which decreased with increasing concentration of Mn, and that to methane, which increased slightly. It is of interest to see if the effect of Mn-content on the isobutanol concentration could be enhanced by raising the temperature (which would thermodynamically favour the formation of higher alcohols over the formation of methanol); fig. 2c demonstrates that the selectivity to isobutanol was increased to about 10% C, but only at low concentrations of Mn ($< 2\%$) did an increase in the Mn-content have an effect on this selectivity.

Table 1

Coprecipitated Cu/ZnO/Al₂O₃ catalysts with CeO₂: selectivities at 280°C. Catalyst weight = 1.0 g, flow rate = 1.92 l h⁻¹, H₂/CO = 1

Product	Cu/ZnO/Al ₂ O ₃	2% Ce	4% Ce
methanol	57.4	52.1	55.2
ethanol	5.6	4.7	2.8
isobutanol	1.8	7.1	3.8
methane	1.3	1.3	2.3
CO ₂	21.5	21.2	25.6
activity (mmol g ⁻¹ h ⁻¹)	9.2	9.1	8.1

In order to investigate the hypothesis that the exact location of the added ions, either in the bulk of the catalyst material or at its surface, would be of importance in determining the selectivities found, catalysts impregnated with either Ce or Mn compounds were also studied. Table 2 gives the results for the catalysts impregnated with various amounts of cerium nitrate. The selectivities to alcohols, methane and CO₂ remained (within experimental error) constant when the amount of cerium was increased; further, the activity did not vary with the amount of Ce added. Comparison of the data in table 2 with those in table 1 shows that the catalysts impregnated with Ce gave much lower selectivities to methanol than did the corresponding coprecipitated ones, and that the selectivities to methane and CO₂ were significantly higher for the impregnated catalysts. Thus, the location of the cerium ions does determine the selectivity of the catalyst.

Table 3 shows the effect of the addition of Mn by impregnation. Although there was no effect of the Mn on the selectivities to ethanol and methane and only a slight decrease in that to methanol, the selectivity to CO₂ increased significantly and that to isobutanol more than doubled when 4% Mn was present. Comparison with the results given in fig. 2 shows some difference between results for the impregnated catalysts and those for the coprecipitated ones, though the difference is much smaller with Mn than with Ce. Thus, there is also a small effect with Mn of the location at which the added ions are present.

The analysis techniques used may shed some light on the location of the various ions in the catalyst materials. The formation of separate crystalline phases was studied using X-ray diffraction (XRD), a bulk analysis technique. The addition of cerium ions appeared to have no effect at all on the structure; this either means that there was no separate crystalline phase formed or that the particles formed were too small to be detected by XRD. The catalysts to which Mn-ions had been added by coprecipitation showed a separate phase if the concentration of Mn was above 4 at% Mn; this phase was probably Mn₂O₃.

The copper surface areas of the coprecipitated catalysts, determined by the N₂O decomposition method, varied from 23 to 28 m² Cu g_{cat}⁻¹. There was no great

Fig. 2. Selectivities of Cu/ZnO/Al₂O₃ catalysts containing Mn. (a) Selectivity to alcohols as a function of Mn-content at 280°C. (b) Selectivity to methane and CO₂ at 280°C. (c) Selectivities to isobutanol at two different temperatures. 1.0 g of catalyst; flow rate = 1.92 l h⁻¹; P = 40 bar; T = 280°C; H₂/CO = 1.

Table 2

Impregnated Cu/ZnO/Al₂O₃ catalysts with CeO₂: selectivities at 280°C. Catalyst weight = 1.0 g, flow rate = 1.92 l h⁻¹, H₂/CO = 1

Product	0.35% Ce	3.46% Ce	6.92% Ce
methanol	42.2	45.1	42.2
ethanol	4.0	3.8	3.0
isobutanol	3.9	2.0	4.1
methane	3.5	3.6	3.3
CO ₂	32.1	30.4	29.1
activity (mmol g ⁻¹ h ⁻¹)	9.5	9.3	10.0

effect of the addition of Ce or Mn in these catalysts. Impregnation using Ce or Mn nitrate, however, decreased the copper area by up to 20%. Apparently, some of the copper metal was covered by cerium or manganese compounds in these catalysts.

Fig. 3 shows XPS results for the coprecipitated catalysts containing Ce. The top spectrum was measured for pure CeO₂. The other spectra show the Ce 3d region for the catalysts with various cerium contents. The concentrations of cerium found with XPS (a surface sensitive technique) increased with the amounts of cerium added, although cerium was hardly detectable in the sample containing 2% Ce. Table 4 gives some ratios of integrated peak areas (in counts s⁻¹). The ratio of the Cu 2p and the Zn 2p peak areas were constant, within experimental error, but the cerium to copper and zinc ratios increased with the amount of Ce present in the catalyst and the cerium ions apparently had no significant preference in covering either the copper or zinc ions. The numbers in this table give the opportunity to compare the concentrations at the surface of both the coprecipitated and the impregnated catalysts. For instance, the concentration of cerium at the surface of the coprecipitated catalyst containing 2 mol% Ce was equal to that of the catalyst impregnated with 3.46 wt% cerium nitrate. This table also gives the XPS results of

Table 3

Impregnated Cu/ZnO/Al₂O₃ catalysts with Mn-oxide: selectivities at 280°C. Catalyst weight = 1.0 g, flow rate = 1.92 l h⁻¹, H₂/CO = 1

Product	Cu/ZnO/Al ₂ O ₃	0.2% Mn	4% Mn
methanol	57.4	49.0	53.0
ethanol	5.6	5.5	5.3
isobutanol	1.8	2.5	3.9
methane	1.3	1.1	1.1
CO ₂	21.5	25.4	25.0
activity (mmol g ⁻¹ h ⁻¹)	9.2	9.0	8.5

Fig. 3. XPS spectra of Cu/ZnO/Al₂O₃ catalysts containing different mole percentages (as indicated) of Ce. "100" gives the spectrum of CeO₂ (different scale).

two coprecipitated catalysts after having been used in the alcohol synthesis reaction. The concentration of cerium at the surface of these catalysts had increased significantly; in the case of the catalyst with 2 mol% Ce, the increase was by a factor of four. The used catalysts had a surface concentration of cerium of more than double that of the catalyst impregnated with 6.92 wt% cerium nitrate.

Table 4

Ratios of integrated XPS peak areas

Cu/ZnO/Al ₂ O ₃ +	Ce 3d/Cu 2p (area/area)	Ce 3d/Zn 2p (area/area)	Cu 2p/Zn 2p (area/area)
0.35 wt% Ce nitrate	0.17	0.04	0.25
3.46 wt% Ce nitrate	0.44	0.14	0.33
6.92 wt% Ce nitrate	0.69	0.23	0.33
2 mol% Ce coprec.	0.46	0.14	0.31
4 mol% Ce coprec.	1.14	0.42	0.37
8 mol% Ce coprec.	3.36	0.99	0.29
2 mol% Ce, used	1.82	0.51	0.28
4 mol% Ce, used	1.37	0.51	0.37

In order to study the formation of products directly from methanol, some experiments were carried out in which methanol was added to the feed gas of the reactor. Table 5 shows the results for the major products, which again fall into two groups. On the one hand, the addition of methanol caused a decrease in the formation of methanol by roughly the number of moles added, and there was also a significant decrease in the production of ethanol. On the other hand, the amounts of methane, ethane and CO_2 formed increased, showing a maximum when 500 μmol methanol was added.

4. Discussion and conclusions

The results presented show that doped $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalysts can be prepared in which the added ions are either present throughout the material (coprecipitates) or at the surface of the catalyst (impregnated catalysts). When the additives were present at the surface, they were shown to cover part of the copper metal and also part of the zinc oxide. In the coprecipitated catalysts the additives were present throughout the material; after use in the alcohol synthesis reaction, however, the surfaces of these cerium-promoted catalysts were found to be enriched with the additive. We do not believe that this enrichment is caused by a different pretreatment, as the pretreatments were very similar for both the fresh and the used samples. Furthermore, the surface enrichment appeared to be accompanied by a change in activity and selectivity.

The behaviour during the first 170 h in the reactor of the coprecipitated catalysts containing cerium showed that there were two groups of products formed: oxygenates and alkanes. The production of the oxygenates decreased with time, whereas that of the alkanes and CO_2 was constant with time. This behaviour coincides with the segregation of cerium ions at the surface. There is, therefore, a correlation to be expected between the location of the cerium ions and the selectivity: cerium ions in the bulk of the catalyst produce mainly oxygenates but cerium oxide present on the surface enhances the production of alkanes and CO_2 . The results found for the impregnated catalysts compared to the coprecipitated ones confirm this explanation: the impregnated materials produced far more alkanes and CO_2

Table 5

The effect on the rate of formation of various products of the addition of methanol to the feed gas consisting of H_2 and CO . Flow rate = 3.84 l h^{-1} , catalyst weight = 1.0 g, $T = 280^\circ\text{C}$. $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst with 4 mol% Ce added

MeOH added ($\mu\text{mol g}^{-1} \text{ h}^{-1}$)	Methanol ($\mu\text{mol g}^{-1} \text{ h}^{-1}$)	Ethanol ($\mu\text{mol g}^{-1} \text{ h}^{-1}$)	Methane ($\mu\text{mol g}^{-1} \text{ h}^{-1}$)	Ethane ($\mu\text{mol g}^{-1} \text{ h}^{-1}$)	CO_2 ($\mu\text{mol g}^{-1} \text{ h}^{-1}$)
0	8215	314	176	84	2521
526	7469	203	267	105	2743
978	7132	195	221	94	2658

than did the comparable coprecipitates. Since it is not likely that separate ions in the structure of the catalyst have a direct effect on the selectivity, it is concluded that separate ions close to, or in very low coverages on the catalyst surface are important for the synthesis of oxygenates. As we discussed previously [6], several authors [10,11] have proposed reaction mechanisms for the formation of oxygenates in which positive ions on the surface stabilize the reaction intermediates leading to higher oxygenates. The cerium and manganese ions could play such a role in our catalysts.

The reaction network apparently falls into two parts: (i) the formation of alcohols, and (ii) the formation of alkanes, both routes being accompanied by the formation of CO_2 . The formation of alkanes in addition to alcohols is not, as far as we know, described in the literature. In this paper, we have shown that the addition of methanol to the feed gas initially causes an increase in the production of alkanes and CO_2 . Methanol may thus adsorb on the catalyst surface and react to give alkanes, or, alternatively, gaseous methanol may react with surface species present and form alkanes. The latter possibility seems to be contradicted by the infrared experiments reported elsewhere which showed that methanol readily adsorbs on $\text{Cu/ZnO/Al}_2\text{O}_3$ catalysts [8]. On the other hand, the addition of methanol to the feed gas caused a decrease not only in the production of methanol (which may be explained in terms of an adsorption equilibrium), but also in the formation of ethanol. As discussed above, ethanol is commonly believed to be formed from methanol; the present results seem to indicate that there are two types of "methanol-like" intermediate: one formed from synthesis gas (and leading to the formation of etha-

Fig. 4. Schematic drawing of proposed formation routes to several products.

nol) and one formed from methanol (and leading to alkanes). In fig. 4, we give a tentative schematic reaction network in which we try to account for the formation of both oxygenates and alkanes. In this scheme, the term "MeOH-precursor" should be seen as representing the two types of intermediate species described above. The ions present on the catalyst influence the number and type of intermediate formed, and therefore affect the consecutive step: oxygenates are formed when Cu, Zn and Ce/Mn ions are present, but alkanes and CO₂ are produced when CeO₂ is present. Not only the location of the added ions but also the nature of the ions added determines the selectivity. The results show that Mn ions enhance the production of methanol whereas cerium ions increase the selectivity to isobutanol. The presence of cerium oxide at the surface also has a much stronger effect than does the segregated manganese compound. This may be due to a difference in the intrinsic activity of cerium oxide and manganese oxide for the different reactions in the proposed reaction network. The main conclusion which can be drawn is that the addition of manganese compounds shifts the selectivity to methanol and that the addition of cerium ions increases the selectivity to isobutanol, as long as the surface coverage of these ions can be kept low.

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