DEVELOPMENT AND SCREENING OF SELECTIVE CATALYSTS FOR THE SYNTHESIS OF CLEAN LIQUID FUELS

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SUMMARY

This article is a compilation of the research carried out under EEC contract EN3V-0400-D at the Institut für Energieverfahrenstechnik in Jülich and at the Faculty of Chemical Technology and Materials Science, Delft, concerning the development and screening of copper/cobalt-based catalysts for the synthesis of alcohol mixtures from syngas. Analogous work, based on copper/zinc oxide/alumina catalysts, has been performed at the Faculty of Chemical Technology in Twente University at Enschede. This work is described in a companion paper. Comparative tests of several catalysts in a pressure micropulse reactor and in a plug flow tubular reactor, carried out at the Institut für Technische Chemie, TU Braunschweig, are presented in a second companion paper.

In the discussion section of the present article the results obtained by the joint groups are compared with the initial objectives of the programme.

INTRODUCTION

Synthetic alcohols and mixed alcohols are expected to become predecessors of hydrogen as important fuels for the near future [1, 2]. Examples of such alcohols, called energy alcohols in Germany, are methanol, biologically produced ethanol and mixtures of methanol and higher alcohols.

These alcohols and mixed alcohols may especially become important in countries with abundant natural gas and coal resources. They can be used for energy storage, as domestic and industrial fuels and as a substitute for, or admixture to, gasoline and diesel. The synthesis gas (CO/CO₂/H₂ mixtures) needed for the production of energy alcohols can relatively easily be obtained from fossil fuels like coal and brown coal and also by steam reforming of natural gas.

Admixture of energy alcohols to engine fuels is fully in line with the present trend to improve their environmental quality. Indeed, since 1989, the oil industry has introduced the so-called ‘reformulated fuels’, modifying the fuel specifications as follows: fewer low-boiling hydrocarbons, fewer aromatic compounds (benzene), reduction of the carbon content in the fuel by omitting higher-boiling hydrocarbons, diminishing the proportion of hydrocarbons with high photochemical reactivity (the higher olefins) and adding more alcohols and ethers in order to enhance the octane number and the anti-knock properties of the fuel over Cu-based catalysts [3, 4]. Higher alcohols can be formed by changing the reaction temperature and/or the composition of the feed (less hydrogen). Addition of alkali causes a further increase of the percentage of higher alcohols. Typical of such a catalyst is the presence of isoalcohols in the product mix.
Copper-cobalt-based catalysts differ essentially from the type discussed above. Examples of copper-cobalt catalysts can be found, for instance, in patents granted to IFP [5, 6]. We are dealing here with copper/cobalt crystallites supported by, for instance, zinc oxide/alumina and promoted by alkali. Apart from an excess of methanol, a Schulz–Flory distribution of mainly straight-chain higher alcohols is produced. Typical reaction conditions are a reaction temperature ranging from 270 to 320°C, a total pressure of about 60 atm, a gas-hour space velocity of 6000 h⁻¹ and a \( \text{H}_2/(2\text{CO} + 3\text{CO}_2) \) ratio of one.

**Catalyst preparation**

All catalysts for the synthesis of mixed alcohols are prepared by the coprecipitation method. By way of example, we here describe the preparation of two copper/cobalt catalysts applied in the project and designated as the Delft-1 and Delft-2 catalysts.

Preparation of the catalyst precursors involved coprecipitation from two aqueous solutions, one of which contained the metal nitrates and the other sodium carbonate. All reagents were of analytical grade. The first solution had a 1 M total metal-ion concentration, and the ratios of the metal ions was chosen so that the final catalyst composition corresponded to 0.6 mole of copper, 0.4 mole of cobalt, 0.9 mole of zinc and 1.2 mole of aluminium. The second solution was 1 M in sodium carbonate. The two solutions were mixed in a metal reaction vessel containing 0.5 litres of demineralized water at 70°C. The solutions were injected below the surface of the water, which was rapidly stirred, and the flow rates were adjusted to maintain the pH at 7.0.

The coprecipitates formed were aged in the mother liquor at 70°C for 1 h. During the period of aging the pH increased slowly to ca. 8.5. The coprecipitates (catalyst precursors) were filtered, washed carefully in distilled water and dried overnight at 80°C.

The Delft-1 catalyst was calcined in a stream of nitrogen at 200°C for 2 h and next at 450°C for 3 h. The calcined powder, particle diameter between 0.2 and 0.8 mm, was pelletized to 3 mm pellets after addition of 2 wt% of graphite as a lubricant.

The Delft-2 catalyst was prepared starting from the Delft-1 catalyst in its calcined form by dry impregnation with an aqueous potassium hydroxide solution. After drying at 80°C and addition of 2 wt% of graphite, the powder was pelletized to 3 mm pellets. The pellets were stabilized by heating in a stream of nitrogen at 100°C for 2 h, followed by heating at 350°C for 2 h. The potassium oxide content was 2 wt%.

**Catalyst characterization**

The composition of the precursors was analytically controlled by application of ICP-AES (Inductive Coupled Plasma Atomic Emission Spectroscopy). For three preparations of Delft-1 the maximum deviations of the weight percentages in elemental composition appeared to be only 0.3 to 0.6 wt%. Notwithstanding the careful washing procedure, the Delft-1 catalyst still contained 2.8 atomic% of sodium only. The Delft-2 catalyst contained 3.0 atomic% of sodium and 3.0 atomic% of potassium.

Powder X-ray diffraction patterns were obtained for both the precursors and the calcined samples. It is important to note that the precursors from three different preparations all appeared to be monophasic; they all showed a hydroxalcite diffraction pattern. Hydroxalcites are built up of brucite-like double layers of densely packed hydroxyl ions, accommodating both divalent and trivalent cations. The double layers alternate with interlayers comprising water molecules and carbonate ions. The latter are intercalated to compensate for the positive net charge of the brucite layers, caused by the partial substitution of the divalent cations by trivalent ones [7]. In our case, the cations in the brucite double layers are copper, zinc, aluminium and cobalt ions.

The precursor structure described above ensures an optimal homogeneous mixing of all catalyst components on an atomic scale. This is advantageous to the formation of small copper/cobalt alloy particles in the final catalyst, and also to the formation of strong interaction between the alloy crystallites and the zinc oxide/alumina support. The fresh Delft-1 catalyst appears to be X-ray amorphous, while the fresh Delft-2 catalyst showed the presence of crystalline CuO [8, 9].

Differential Thermal Analysis (DTA) spectra of three different coprecipitates (Figure 1) were measured by heating the samples in a stream of clean air at a heating rate of 12 K/min. The spectra are typical of the
decomposition of a hydrotalcite. The peaks around 200°C correspond to the evolution of carbon dioxide and water, and the peaks around 300°C correspond to the decomposition of carbonates.

The surface areas and pore-volume distributions of the catalysts were determined from the physical adsorption of nitrogen at −196°C (BET method) and from the capillary condensation of nitrogen at that temperature. Before measurement, the samples were calcined in air up to 150°C and reduced up to 450°C in a nitrogen stream containing 10% hydrogen.

Free-metal surface areas \( S\text{(met.)} \) were determined gravimetrically from the adsorptive decomposition of nitrous oxide [10]: The results are presented in Table 1.

It may be seen, that the potassium-doped Delft-2 catalyst has nearly the same BET surface area as the Delft-1 sample. However, the free-metal surface area has been strongly reduced by the potassium impregnation. Apparently the potassium oxide is widely spread out over the metallic part of the catalyst surface.

The relatively high free-metal surface area of the Delft-1 catalyst (about 30% of the total surface area) corresponds to a free-metal surface area of 92 m² per gram of metal. Assuming the surface of the metal crystallites to be reduced by 50% due to incapsulation in the zinc oxide/alumina support, a metallic dispersion of 0.28 is calculated. This number corresponds to a mean volume-surface diameter of the crystallites of about 3.5 nm. From electron microscopy, the largest metal particles were found to be about 5 nm in diameter, whereas most of these particles had diameters lower than 2.2 nm. Hence, data from electron microscopy is in reasonable accordance with our estimation of the metallic dispersion from the free-metal surface area, if we make the above assumption regarding encapsulation.
Transmission Electron Microscopy (TEM) combined with Energy Dispersive Spectroscopy (EDS) was carried out with the coprecipitates, the calcined and the reduced samples. In all cases it was found that zinc, aluminium and cobalt were homogeneously distributed over the surface and bulk of the samples. Copper distributions cannot be reliably measured by means of EDS.

**REDUCTION OF CALCINED CATALYSTS**

An extensive study has been made of the Temperature Programmed Reduction (TPR) of the calcined samples \([8,9]\). Owing to space limitations, we only mention the main results. From the hydrogen consumption as a function of the reduction temperature (heating rate 10 K/min; hydrogen/argon mixture 2:1) it was found that the reduction takes place in at least three stages, and reduction peaks are found with maxima around 223, 318 (broad peaks) and 600°C. This is in accordance with results published by Baker et al. \([11]\). The total hydrogen consumption, up to a reduction temperature of 800°C, is higher than would be expected on the basis of the copper and cobalt oxide contents of the calcined samples. This is due to the fact that part of the carbonate in the hydrotalcite decomposes only above 600°C. It is likely that the carbon dioxide that is set free reacts with the hydrogen to give methane. Furthermore, part of the zinc oxide may be reduced at higher temperatures to give zinc which then forms small amounts of brass by alloying with cobalt and/or copper \([9]\).

The TPR results were in good accordance with data obtained from X-ray Photoelectron Spectroscopy (XPS) combined with Auger Electron Spectroscopy (AES). For catalysts reduced in 2% hydrogen in nitrogen, followed by full reduction in 100% hydrogen at different temperatures (20, 200 and 450°C), the spectra showed that copper reduction in the catalyst takes place up to 200°C and that cobalt is reduced in a number of stages in the range of temperatures from 200 to 450°C. Zinc oxide is also partly reduced in this temperature range \([9]\), and the formation of small amounts of brass could be detected \([12]\).

**BENCH-SCALE EXAMINATION OF PERFORMANCE OF CATALYSTS**

*Comparison of performance of copper/cobalt catalyst in a Berty reactor and in a DSC*

For careful kinetic studies, it is desirable to work with a differential reactor, one in which the gas and solid composition, pressure and temperature are essentially uniform throughout the reactor. A representative design is the Berty reactor, in which the catalyst pellets are stationary and the gases are internally recycled. The Berty reactor used in our study contained 10 g of catalyst in all experiments. Inevitably, the gas flow entering the catalyst bed contained product fractions, 0.5 to 1.5 mole% in our case. The gas composition could be changed by variation of the gas flow from 30 to 200 l(STP)/h. Liquid products were condensed out of the gas flow leaving the reactor and were analysed off-line by gas chromatography. Gaseous products were analysed online in a second gas chromatograph.

A Differential Scanning Calorimeter (DSC), equipped with an online gas chromatograph, was also used. The catalyst was a single pellet (25 mg), and the gas flow was varied from 6 to 12 litre/h (STP). Owing to the small product fractions in the off-gas, only methanol, ethanol, propanol and methane could be analysed. The additional measuring signal obtained is the evolved heat of reaction.

Figure 2 shows the reaction rates measured at 280°C, a total pressure of 50 atm. and a hydrogen/carbon monoxide ratio of 2, both in the Berty reactor and the DSC, for methanol, ethanol and propanol, as a function of the partial methanol pressure, respectively the methanol content. In both systems, the reductive pretreatment of the catalyst was the same (details are given in the following paragraph) and the maximum reduction temperature was 450°C. Figure 2 demonstrates that the reaction rates measured in the Berty reactor are influenced by the methanol partial pressure and the volume flow. For methanol contents below 0.5 mol%, the Berty results are in good agreement with the results measured in the DSC.

It was shown by Mausbeck \([12]\) that the test conditions were the same in both reactors; the residence times were 37 and 35 s and the space velocities were 286,000 and 222,000 h⁻¹ in the DSC and Berty reactor, respectively. The apparent activation energies for the formation of ethanol were 103 and 105 kJ/mol in DSC.
and Berty reactor, respectively, whereas, for the formation of propanol values of 120 and 102 kJ/mol, respectively, were calculated. As the production of the higher alcohols follows a Schulz-Flory distribution (constant growth probability of the carbon chains), the apparent activation energies for ethanol and propanol should be equal, and this was indeed found within the accuracy of the experimentation. The formation of methanol seems via another reaction mechanism than that for the formation of the higher alcohols [13]; the apparent activation energies for methanol formation, 82 kJ/mol (DSC) and 65 kJ/mol (Berty), are in line with this.

Influence of method of reduction on performance

The method of reduction of the catalysts strongly influences their performance and also their final composition. In order to study this phenomenon, the Delft-1 catalyst was reduced according to a fixed programme at a pressure of 4 atm, starting with a mild reduction in a stream of 2% hydrogen in nitrogen, followed by a more rigorous reduction in pure hydrogen. The only variation was the choice of the maximum final temperature of reduction, both in the mild and rigorous part of the programme. The procedure starting with a mild reduction has the advantage that sintering of the copper due to the high exothermicity of the copper oxide reduction is circumvented [12]. The experiments were performed in the DSC.

The results are presented in Figures 3 and 4; the rates of reaction and the selectivities are plotted as a function of the maximum temperature of reduction. These figures clearly demonstrate that the choice of a maximum reduction temperature of about 500°C leads to the highest yield of alcohols combined with a relatively low methane production. This complies with the objectives of the project.

Running-in procedure

In accordance with the well known adage 'the environment makes the catalyst' [14] it was found that the performance, and in particular the selectivities of the catalyst, change strongly in the presence of the reacting gases during the running-in time (see Figure 5). It takes about 90 h before a steady state is reached.

The increase of the methanol selectivity is due to a gradual partial oxidation of the copper surface by carbon dioxide. This is in line with the present insight into the reaction mechanism [15] according to which
methanol synthesis occurs via Cu(O) sites for the dissociative chemisorption of hydrogen, combined with Cu(I) sites for the formation of surface formates from carbon monoxide; surface reduction of the formates leads to methanol.

The gradual decrease of the rate of methane formation is likely to be due to a gradual poisoning of the most active cobalt sites through oxidation by carbon dioxide. These sites are able to chemisorb carbon monoxide dissociatively, which is a prerequisite for methane formation.
The practical consequence of the running-in behaviour of the catalyst is that a comparative study of different types of catalyst is significant only provided the typical running-in time of the catalyst in question is completed.

Choice of optimal reaction temperature

Figure 6 shows the ratio of higher alcohols to methanol in the liquid product as a function of temperature (Berty reactor, Delft-1 catalyst). In the temperature range from 250 to 300 °C, the fraction of higher alcohols in the liquid product increases with rising temperature. There are two reasons for this. On the one hand, the activation energy for the formation of higher alcohols is higher than that for methanol, and hence, by increasing the temperature, the formation of higher alcohols is enhanced more strongly. On the other hand, owing to the increase of the partial pressure of methanol, its formation is suppressed by shifting of the equilibrium \( \text{CO} + 2\text{H}_2 = \text{CH}_3\text{OH} \) to the left.

Temperatures between 280 and 300 °C should thus be selected to meet the objectives of the project.

Influence of hydrogen/carbon monoxide ratio in feed on catalytic performance

The influence of changing the hydrogen/carbon-monoxide ratio on the rate of production of the alcohols is demonstrated by the results plotted in Figure 7. Whereas the rate of methanol production decreases with increasing \( \text{H}_2/\text{CO} \) ratio, the rate of production of the higher alcohols slightly increases. In view of the objectives of the project a \( \text{H}_2/\text{CO} \) ratio between 2 and 2.5 is most attractive.

Influence of carbon dioxide fraction in synthesis gas

This variable was studied in the DSC with the Delft-1 catalyst. For carbon dioxide fractions of less than or equal to 0.1 mol%, the selectivity for methane was found to be very high, whereas the selectivity for methanol was very low. Attractive selectivities (19.1% methane, 67.6% methanol, 11.5% ethanol and 1.3% propanol) were arrived at between 1 and 2.5 mol% of \( \text{CO}_2 \), with an optimum around 1.6 mol%.
Figure 6. Ratio of higher alcohols to methanol against temperature.

Figure 7. Reaction rate against hydrogen/carbon-monoxide ratio.
Effect of total pressure on reaction rates and selectivities

In Figure 8, the rates of formation of methane and of the alcohols, methanol, ethanol and propanol, are plotted as a function of the total pressure. Notwithstanding the fact that the system is not in equilibrium, Le Chatelier's principle appears to be effective; alcohol formation involves a greater volume reduction than methane formation, and hence the selectivities to the alcohols increase with rising pressure whereas the selectivity to methane is hardly influenced by it.

The important practical consequence of this result is that the formation of methanol and the higher alcohols can be enhanced strongly by working at higher pressure ($p > 50$ atm). As can be seen from Figure 8, the ratio of the alcohol concentrations remains almost unchanged on increasing the pressure.

Stability of catalysts

Stability (or life) of a catalyst is an important technical and industrial factor. We therefore tested the stability of the Delft-1 catalyst in the Berty reactor for a period of six months. The results are represented in Figure 9. A large percentage of the decrease in activity appears to occur during the first 1000 h; thereafter the deactivation elapses more slowly. The experimental conditions are Berty reactor. $T = 280^\circ$C, flow rate $501 (\text{STP}) \cdot h^{-1}$, $\text{H}_2/\text{CO} = 2$, total pressure 50 atm. Fraction CO$_2$ in the feed 1-6 mol%. After six months the decrease in activity is about 20% for methanol, 50% for the higher alcohols and 60% for methane.

The gradual decrease in activity might be caused by contaminations in the feed to the reactor. However, before entering the reactor, the syngas was dried over active carbon, deoxygenated over reduced copper and desulphurized over zinc oxide. Hence, gradual poisoning from an external source is not very plausible.

Deactivation as a result of gradual sintering of the copper/cobalt crystallites is equally unlikely. As methanol formation takes place over the copper part of the catalyst surface and the decrease in activity for methanol in six months is only 20%, it follows that the copper hardly sinters. This, in turn, makes cobalt sintering improbable because the Tamman temperature of cobalt (the temperature at which the lattice begins to be appreciably mobile) amounts to 603 °C, whereas the Tamman temperature of copper is 405 °C.

![Figure 8. Effect of total pressure on reaction rates.](image-url)
For the time being, we ascribe the deactivation to the deposition of coke formed from the reactants and the products. Furthermore, separation of cobalt from the originally homogeneously distributed cobalt and copper phases as well as loss of active species (in particular of cobalt in the form of volatile cobalt carbonyl) may take place; a further possibility is the formation of surface carbides \[S, 91\]. These conclusions are in accordance with those of Courty et al. [16] and Szymanski et al. [17].

An interim reduction treatment of the catalyst after three months of testing (see point a in Figure 9) did not result in an appreciable change of the activity and the selectivities. Such a treatment is obviously not sufficient to remove the coke from the cobalt or to decompose the cobalt carbide.

Table 2. Activity of Delft-1 and Delft-2 catalysts, compared with literature values.

<table>
<thead>
<tr>
<th>Type of catalyst</th>
<th>H₂/CO ratio</th>
<th>Space time ( W/F )</th>
<th>Fractional conversion of CO</th>
<th>Rate of CO conversion mmol CO ( \cdot g^{-1} \cdot h^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Courty et al. [16]</td>
<td>(a) 1</td>
<td>100</td>
<td>0.70</td>
<td>5.0 to 9.0</td>
</tr>
<tr>
<td>Pan et al. [18]</td>
<td>(b) 1</td>
<td>20</td>
<td>0.08</td>
<td>6.0</td>
</tr>
<tr>
<td>Pan et al. [18]</td>
<td>(c) 2</td>
<td>15</td>
<td>0.05</td>
<td>4.5</td>
</tr>
<tr>
<td>Delft-1</td>
<td>(d) 2</td>
<td>22.4</td>
<td>0.06</td>
<td>3.7</td>
</tr>
<tr>
<td>Delft-2</td>
<td>(e) 1</td>
<td>8.9</td>
<td>0.03</td>
<td>3.1</td>
</tr>
</tbody>
</table>

(a) Total pressure 60 atm. (b) No CO₂ added; 20 Cu/20 Co/20 ZnO/40 Al₂O₃/0.5 K₂O. (c) Calculated from Figure 3; DSC; 16 mol% CO₂. (d) Calculated from Figure 2; Berty reactor. (e) Calculated from Figure 7; Berty reactor.

\( W \) is the weight of catalyst in grammes and \( F \) is in moles per hour of inlet carbon monoxide.
Notwithstanding the fact that the compositions of the catalysts are mutually divergent, the rates of carbon monoxide conversion are not very different.

In Table 2, a comparison of the activities of our catalysts to those in the literature is made. It is important to note that Pan et al. [18] found that the rate of carbon monoxide conversion is approximately constant when the fractional carbon monoxide conversion changes from 0.08 to 80%. This means that the rates of reaction are hardly influenced by the space time (and hence by the space velocity chosen). Pan et al. also found that the selectivities to the higher alcohols are perfectly constant in the range of W/F values from 20 to 120. However, the rate of methanol formation saturates at higher W/F values. It follows that at higher W/F values (at much lower space velocities than applied in our research) the selectivity to the higher alcohols (about 20%) will increase appreciably, up to values (at a rough estimate) of about 60 to 70%.

GENERAL CONCLUSIONS AND RECOMMENDATIONS

Copper-cobalt-based catalysts

The method of preparation of these catalysts, as already described, leads to a reproducible catalytic performance. The several methods of characterization described can be used in technical practice to assess the qualities of fresh and spent catalysts.

The overall activity of the Delft-1 and Delft-2 catalyst meets the requirements formulated in the introduction. The activity can be increased further by increasing the total pressure to above 50 atm (see Figure 8).

The optimum reduction temperature is 500 °C, and the reduction of the catalysts has to be performed very carefully, as described earlier. The optimum reaction parameters are reaction temperatures from 280 to 300 °C, total pressure above 50 atm, hydrogen/carbon monoxide ratios from 2 to 2.5, and a carbon dioxide content of 1 to 2.5 mol% in the feed. A relatively long running-in time should be taken into consideration.

The selectivity for higher alcohols amounts to 20% of the liquid alcohol product under the conditions of our experiments (low space time). Indications are found in the literature [18] that the higher-alcohol
selectivity can be further increased by working at much higher space time in an integral flow reactor, while retaining the ratio of higher alcohols reported in our study. It is likely that the selectivity to methanol can be further suppressed by making use of catalysts with a copper/cobalt molar ratio of 1 to 1, instead of 1.5 to 1 as was the case in our research [18].

The stability (life) of the Delft catalysts is at least six months; further improvement is desirable. If this cannot be achieved, improvement of the regenerability should be studied further. Addition of small amounts of group VIII metals to the catalyst is a possible remedy.

Copper/zinc oxide/alumina catalysts

An alternative group of catalysts are those based on the well-known copper methanol synthesis catalyst, modified by the addition of alkali and other promoters. The performance of these catalysts is discussed in a companion paper.

These catalysts show the advantage of a substantial higher activity per gramme of catalyst (a factor of about 7 to 10), combined with the formation of isoalcohols besides linear alcohols. Isoalcohols are attractive components in fuels, as they increase the octane number.

The maximum higher alcohols selectivity which can be achieved is lower than that found for the cobalt-copper catalysts (about 30%). Stability studies have not yet been performed by us, but the stability is likely to be of the same order as is valid for common methanol copper-catalysts, namely 2 to 3 years.

Experiments to provide comparative studies in a pressure micropulse reactor and in a plug flow turbular reactor are described in a companion paper.

REFERENCES

14 Schmidt, L. D., quoted from lecture at 7th Roermond Conference on Catalysis, Rolduc, Kerkrade, June 1990.