Hydrogenolysis of Dimethyl Maleate on Cu/ZnO/Al₂O₃ Catalysts

By M. Mokhtar, C. Ohlinger, J. H. Schlander and T. Turek

The gas-phase hydrogenolysis of dimethyl maleate at 10 bar and 513 K was investigated over a series of co-precipitated Cu/ZnO/Al₂O₃ catalysts. High copper surface areas were obtained with a molar Al content of 5% in the catalysts. Upon variation of composition at fixed alumina content, copper surface areas increased until the molar ratio exceeded Cu/Zn = 2:1. At the given reaction conditions, dimethyl maleate was completely converted to dimethyl succinate, which further reacted to methanol, γ-butyrolactone, tetrahydrofuran, and water over all catalysts. Initial deactivation of catalysts was mainly caused by a loss of copper surface area. The catalyst with a molar Cu/Zn ratio of 1:2 was found to be most active and stable under reaction conditions.

1 Introduction

1,4-butanediol (BDO) and its derivatives γ-butyrolactone (GBL) and tetrahydrofuran (THF) are important intermediates in industrial organic chemistry. BDO is being used for the production of polybutylene terephthalate and polyurethanes. GBL is mainly converted to different pyrrolidones, while THF is primarily transformed to polytetramethylene ether glycol that is starting material for a variety of polymers such as polyurethanes and spandex fibers. Both GBL and THF also find widespread use as solvents [1]. While the main part of these components is still produced via the classical Reppe process using acetylene and formaldehyde as feedstock, newly announced expansions are predominantly based on maleic anhydride [2]. Processes developed by Davy McKee, Kvaerner and Eurodil employing the hydrogenolysis of maleic diesters appear to be especially advantageous due to mild reaction conditions and the possibility of co-producing BDO, GBL and THF [3, 4, 5, 6]. Reaction of dialkyl maleates at 180 to 240 °C and pressures below 70 bar gives rise to almost complete conversion to valuable products, with low temperatures and high pressures clearly favouring BDO formation.

Previous studies of the hydrogenolysis of dialkyl maleates or succinates have mainly employed copper-based catalysts, that are generally used in the catalytic hydrogenolysis of esters to alcohols [7]. Trimm and coworkers used Raney copper for the hydrogenolysis of dimethyl succinate in the gas phase [8, 9]. Copper chromite, the classical catalyst for hydrogenolysis of esters, was also used for production of BDO, GBL and THF from maleic esters [10, 11]. In a study comparing different catalysts, the rate of dimethyl succinate hydrogenolysis could be enhanced by addition of zinc oxide to copper [12]. The promoting effect of ZnO was also found during other related reactions such as the direct hydrogenation of maleic anhydride in the gas phase [13] and in the liquid phase [14], as well as the hydrogenolysis of maleic acid [15, 16].

In an earlier paper, we used Cu/ZnO catalysts for the gas-phase hydrogenolysis of dimethyl maleate [17]. The addition of alumina as further component to copper/zinc oxide should increase copper surface areas and thus catalytic activities. Such catalysts have been successfully used by Zhang et al. for the hydrogenolysis of diethyl maleate [18]. In the present contribution we report data obtained during the reaction of dimethyl maleate with hydrogen over a series of Cu/ZnO/Al₂O₃ catalysts with special emphasis on the relationship between activity and copper surface area.

2 Experimental Setup

2.1 Catalysts

The precipitated Cu/ZnO/Al₂O₃ catalysts were obtained by mixing of 1 M aqueous Na₂CO₃ solution with 1 M solution of copper, zinc, and aluminium nitrates under vigorous stirring at 359 K and a constant pH of 7. The suspension was allowed to cool for 1 h and the precipitate was filtered, washed thoroughly with deionized water, and dried overnight at 353 K. Calcination was carried out in air by heating the precursors within 2 h to 623 K, maintaining this temperature for 1 h. The resulting oxide powders were pressed to tablets, crushed, and sieved to a fraction between 315 and 500 μm. X-ray diffraction (XRD) was carried out by means of a Siemens diffractometer using Cu-Ko radiation. BET surface areas were determined using a Micromeritics ASAP 2010 analyzer with N₂ adsorption. Catalyst compositions are expressed as mole fractions

\[
x_i = \frac{n_i}{n_{Cu} + n_{Zn} + n_{Al}}
\]

or as molar Cu/Zn ratios.

The specific copper surface areas of the catalysts were measured after reduction with hydrogen using the decomposition of N₂O at atmospheric pressure. Reduction of catalyst precursors was carried out with 3% H₂ in He temperature-ramped from 413 to 513 K at 20 K/h, after which the diluted hydrogen stream was replaced by pure H₂. After cooling to 333 K in pure He, the flow was switched to 0.1% N₂O in He. The copper surface areas were determined from the consumed amount of nitrous oxide according to Chinchen et al. [19]. Copper surface areas of used catalysts were determined ex situ. Preliminary experiments have revealed that contact with air only slightly decreases the measured copper surface areas of reduced Cu/ZnO/Al₂O₃ catalysts.

1) List of symbols at the end of the paper.

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Temperature-programmed oxidation of used catalysts was carried out with 1 % O₂ in He while the temperature was increased from ambient temperature to 773 K at 10 K/min. The carbon content was then calculated from the formed amounts of carbon oxides measured with infrared analyzers.

2.2 Catalytic Measurements

The catalyst (2.0 g) was diluted with the same volume of an inert glass sieve fraction (500 to 630 μm) and placed in a stainless steel tubular reactor of 13 mm inner diameter and 200 mm length. The catalysts were reduced at atmospheric pressure as described above before the pressure was increased. Vaporized dimethyl maleate and hydrogen were then introduced into the reactor at a molar ratio of 1:45, a hydrogen flow rate of 500 cm³/min (STP), a temperature of 513 K, and a pressure of 10 bar. A detailed description of the experimental set-up can be found in [17]. On-line analysis was carried out after pressure release and addition of an internal standard (N₂) by gas chromatography (Hewlett-Packard, 5890 II series with TCD detector).

3 Results and Discussion

XRD analysis of catalyst precursors after drying revealed that the samples with a molar Al content of 0.05 and Cu/Zn ratios below 1:1 mainly consist of hydrozincite and aurichalcite phases, whereas at higher Cu/Zn ratios only malachite could be observed. This is in good agreement with results obtained by Fujita et al. [20, 21]. In calcined samples, only CuO and ZnO could be identified with catalysts becoming more amorphous at increasing alumina content.

Fig. 1 depicts BET and copper surface areas for catalysts with equimolar amounts of copper and zinc as a function of the molar aluminium content. It can be seen that aluminium-free samples exhibit low values of copper and total surface area, that are in good agreement with earlier reported data [17]. The BET surface area continuously increases with increasing Al content, whereas a maximum copper surface area is observed at 5 % Al.

In Fig. 2 the relationship between BET and copper surface area and catalyst composition at a fixed aluminium content of 5 % is shown. With increasing copper contents, the BET surface area remains constant at around 70 m²/g, while the copper surface area continues to increase until Cu/Zn = 2:1. Both total and copper surface area sharply decrease at even higher copper content.

During the catalytic tests, complete conversion of the starting material dimethyl maleate to dimethyl succinate was observed in all experiments. Therefore the conversion of dimethyl succinate to subsequent products was used as a measure for the catalytic activity. The product composition was found to be independent of the catalyst composition within the experimental accuracy (± 2 %). Selectivities were calculated based on the conversion of dimethyl succinate using mole fractions, with the amount of excess hydrogen not being taken into account. Average selectivities for the series of catalysts used were found to be 64.3 % methanol, 28.4 % γ-butyrolactone, 4.0 % tetrahydrofuran, 2.3 % water together with traces of 1,4-butanediol, butanol, and carbon dioxide. These values are in good agreement with earlier results obtained over Cu/ZnO catalysts [17]. Thus it appears that alumina does not alter the product selectivities.

After contacting with reactants for the first time, the catalysts showed a significant decrease of activity before a steady state was attained. Fig. 3 shows, as examples, the conversion of dimethyl succinate versus time over the catalysts with Cu/Zn = 1:1 and Cu/Zn = 2:1.

The observed decrease of catalytic activity during the first hours on stream is accompanied by a decrease of copper
surface areas. An interesting result of the measurements for determination of copper surface area is depicted in Fig. 4. It can be seen that the shape of the N$_2$O breakthrough curve using the fresh, reduced catalyst is very similar to the corresponding curve obtained with the oxidized catalyst. In this case, values of the consumed amount of nitrous oxide calculated from the differences in breakthrough times

\[
n_{N_2O} = \frac{V_p}{R \cdot T} \cdot \int_{t_{ox}}^{t_{red}} x_{N_2O,ox} dt - \int_{t_{red}}^{t_{red}} x_{N_2O,red} dt
\]  

are only slightly lower than the data determined by accurate integration of the concentration curves as shown in Fig. 5:

\[
S_{Cu} = \frac{m_{cat}}{m_{cat}}
\]

Copper surface areas are then calculated according to reference [19]. The relative error in copper surface area of the fresh catalysts is less than 10 % if only breakthrough times are considered, which is in good agreement with observations by Soerensen and Cant [22].

On the other hand, considerable tailing of the nitrous oxide concentration is observed over the used catalyst, where the surface area must obviously be calculated by integration. The reason for the occurrence of a strong tailing over the use catalysts is not yet clear. A possibility is the inhibiting effect of carbonaceous deposits formed during the hydrogenolysis reaction on the oxidation of copper by N$_2$O. Temperature-programmed oxidation of the used catalyst with Cu/Al = 1:1 and integration of the formed amounts of CO and CO$_2$ yielded a carbon content of 2.5 wt. %. Similar carbon uptakes were reported by Cheng et al. after decomposition of methanol over copper-based catalysts [23].

The copper surface areas of the fresh catalysts steadily increase until a molar Cu/Zn ratio of 2:1 is reached, whereas a constant Cu surface area of around 22 m$^2$/g for catalysts between Cu/Zn = 1:2 and 2:1 was observed for the used samples (Fig. 5). The catalysts lost between 20 and 35 % of the copper surface area during the first hours of reaction with Cu/Zn = 1:2 exhibiting the highest stability.

In Fig. 6 steady-state conversions of dimethyl succinate to further products are depicted for the series of catalysts used. It can be seen that the catalyst with Cu/Zn = 1:2 is most active. It has been shown earlier that the hydrogenolysis of dimethyl maleate can be described with a simple first-order kinetics [24]. The conversions were thus used to calculate first-order rate constants. If the rate of reaction is related to the active copper surface area ($S_{Cu} \cdot m_{cat}$), one obtains for constant number of moles in an integral reactor with plug-flow behaviour:
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4 Conclusions

It was found that a molar Al content of 0.05 in Cu/ZnO/Al₂O₃ catalysts used for the hydrogenolysis of dimethyl maleate gives rise to high values of copper surface area. Variation of the copper content revealed that the Cu surface areas of the fresh catalysts are only slightly higher than the corresponding deactivation was observed during the gas-phase reaction of dimethyl maleate. Overall it appears that copper is the active species for the reaction under investigation. The most active catalyst, that also exhibits the most stable Cu surface area under reaction conditions, has a molar ratio of Cu/Zn = 1:2.

Symbols used

<table>
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<tr>
<th>Symbol</th>
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<tbody>
<tr>
<td>k_Cu</td>
<td>first-order rate constant</td>
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<tr>
<td>m_cat</td>
<td>catalyst mass</td>
</tr>
<tr>
<td>n</td>
<td>amount of substance</td>
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<tr>
<td>p</td>
<td>pressure</td>
</tr>
<tr>
<td>R</td>
<td>ideal gas constant</td>
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<tr>
<td>S</td>
<td>specific surface area</td>
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<tr>
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<td>time</td>
</tr>
<tr>
<td>T</td>
<td>temperature</td>
</tr>
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<td>volume flow rate</td>
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<tr>
<td>x</td>
<td>mole fraction</td>
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<tr>
<td>X_DMS</td>
<td>dimethyl succinate conversion</td>
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Abbreviations

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<tr>
<th>Symbol</th>
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<tbody>
<tr>
<td>Al</td>
<td>aluminium</td>
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<tr>
<td>Cu</td>
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<tr>
<td>red</td>
<td>reduced</td>
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</tbody>
</table>

References


Fig. 6. Conversion of dimethyl succinate (closed symbols) and first-order rate constant related to copper surface area after reaction (open symbols) for catalysts with different copper contents. Open squares denote values determined with initial conversion and surface area of the fresh catalysts. Molar Al content = 0.05, reaction conditions as indicated in Fig. 3.

$$k_{Cu} = \frac{V}{S_{Cu} m_{cat}} \ln \left( \frac{1}{1 - X_{DMS}} \right)$$  (4)