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Methanol synthesis over Cu/ZnO catalysts prepared by ball milling

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Cu/ZnO catalysts (with a Cu/Zn atomic ratio of 30/70) have been prepared by high intensity mechanical mixing of copper and zinc oxide powder in air and under vacuum. During milling in vacuum gradual amorphisation of the constituents occurs, as evidenced by broadening of the Cu⁰ and ZnO diffraction peaks in XRD, but the two original phases remain. The result of such treatment is a catalyst with low BET area and low Cu metal surface area. Consequently, the activity of the vacuum milled samples in batch methanol production from synthesis gas (CO/CO₂/H₂ = 20/5/75) at 50 bar and 250°C is low. Milling in air leads to oxidation of the copper metal phase and much higher BET surface area and, after reduction, Cu metal surface area. Prolonged milling times in air result in more than 90% Cu²⁺ formation as evidenced by TPR. Activity in methanol synthesis for the air milled samples is comparable to a conventional Cu/ZnO catalyst prepared by coprecipitation. It is concluded that high intensity ball milling at ambient conditions is a promising method to prepare mixed oxide catalysts or catalyst precursors.

Keywords: copper–zinc oxide, ball milling, methanol synthesis, XRD, N₂O chemisorption, TPR

1. Introduction

Copper containing catalysts are widely used in industry for the hydrogenation and dehydrogenation of organic functional groups. The main applications include methanol production from synthesis gas, oxo-alcohol manufacture from hydroformylation processes and fatty alcohol synthesis by ester hydrogenolysis. Due to the ever increasing importance of the first mentioned application, considerable research efforts continue to be directed towards the methanol synthesis catalyst. From a scientific point of view, copper catalysis is actively studied because of the controversy that still exists about the active site for methanol synthesis [1–3]. The consensus reached in the literature is that a good intimate mixture of Cu and ZnO (or Cu–Zn–Al/Cr) must be obtained during catalyst preparation in order to achieve high activity [1,4,5]. For the commercial type Cu–Zn catalyst this is achieved by coprecipitation of Cu(NO₃)₂ and Zn(NO₃)₂ solutions with subsequent ageing and calcination [4,5]. In this paper high intensity mechanical mixing of copper powder and zinc oxide without high temperature treatment is studied as a novel approach to obtain such well-mixed systems.

Obviously, ball milling has long been known as a tech-

nique for refining particles of a large variety of solid materials. Formation of amorphous alloys by mixing on an atomic scale of elemental metallic powders and uniform dispersions of oxide particles in metal alloys (mechanical alloying) or amorphisation of pre-alloyed intermetallic compounds (mechanical milling) and formation of solid solutions by high intensity mechanical mixing have also been reported (for a review, see ref. [6]). Recently, mechanical milling has been applied in the preparation of various catalysts such as ion-exchanged montmorillonite clays [7], mixed VPO/Bi₂O₃ and VPO/BiPO₄ oxidation catalysts [8] and binary solid solutions of CeO₂ with Zr, Hf or Tb [9].

In this paper we investigated the influence of the gas phase and milling time on the activity of mechanically mixed Cu–ZnO catalysts in the methanol synthesis reaction from a H₂/CO/CO₂ feed mixture. The high intensity ball milling process is analysed by X-ray diffraction (XRD), nitrogen physisorption, N₂O chemisorption and temperature programmed reduction (TPR).

2. Experimental

Two series of catalysts were prepared by ball milling with Cu (30 at%; 40 μm, 99.5% pure, CERAC, USA) and ZnO (70 at% of Zn; 70 μm, 99.995% pure, CERAC) in a vibratory ball mill described earlier [6]. The series 1 catalysts were prepared by milling in vacuum

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(10^{-6} Torr) for different intervals. The series 2 catalysts by milling in ambient air. The structural changes of the catalysts during the milling process were examined by X-ray diffraction. It should be noted that the process of ball milling is sensitive to the intensity of the milling action, which in turn is influenced by experimental parameters that cannot always be fully controlled. In particular, the milling intensity varies between different ball mills and depends on the weight of the sample that is subjected to milling. Thus, the milling time is only a qualitative measure of the progress of milling and not a quantitative one. For reference, a coprecipitated Cu–ZnO catalyst was prepared in the same atomic ratio as indicated above, according to ref. [4].

The total surface area of the catalysts was determined by the BET method (N_2 physisorption) and the Cu specific surface area by N_2O chemisorption according to the method described in ref. [10]. For chemisorption measurements the samples were calcined for 12 h in situ in an Ar-flow (99.999% pure at 120 ml/min) after heating up at 200 K/h to 508 K; at 100 K/h to 523 K; cooling in Ar to ambient and subsequently reduced for 1 h in Ar/ H_2 (at a ratio of 33/66; total flow: 120 ml/min; hydrogen purity: 99.996%) with an identical temperature programme.

TPR was performed in a Setaram TG 85 thermobalance prior to the N_2O chemisorption measurements by recording the calibrated sample weight loss during catalyst reduction (i.e. after calcination). The conditions are indicated directly above.

XRD spectra were recorded with a Philips PW 1050 diffractometer, using Cu $K\alpha$ radiation. The diffractometer was equipped with an Anton Paar HTK-10 high temperature device.

The methanol activity for all samples was tested in an isothermic gold-coated stainless steel batch reactor with a volume of 7 ml, at 523 K and 50 bar pressure. The reactant gas consisted of a $CO/CO_2/H_2$ mixture of 99.99% pure gases in a 20 : 5 : 75 ratio. Catalyst reduction was performed in situ at reaction conditions, i.e. by the reactant gas phase. Prereduction of the 142 h air-milled catalyst in H_2 at 523 K gave exactly the same results as reduction by the synthesis gas and therefore was omitted for all other samples. The products were analysed using a Hewlett Packard 5890 gas chromatograph. Besides methanol small amounts of higher alcohols and hydrocarbons were found, possibly due to residual Fischer–Tropsch type activity of the catalyst.

3. Results and discussion

The XRD pattern of the physically mixed catalyst (i.e. 0 h milled catalyst) is the sum of the patterns of Cu^0 and ZnO. After milling for 24 h under vacuum (series 1), all the peaks of the catalyst become broader, indicating a size reduction of the Cu and ZnO crystal domains during

ball milling under vacuum. The XRD pattern changes continuously for milling times up to 48 h; thereafter, the XRD pattern remains constant and the peaks attributed to Cu and ZnO lattices remain visible in the XRD spectra. From this we conclude that the catalyst milled in vacuo largely consists of Cu and ZnO as two separate phases.

A quite different effect has been observed for the air-milled catalysts from (series 2, figure 1). For this series it is observed that the Cu^0 peaks ($2\theta = 43.8, 50.5, 74.2^\circ$) gradually disappear from the XRD spectrum with increased milling times. This implies that Cu is either substantially made amorphous or dissolves in the ZnO lattice; i.e. upon oxidation of the Cu powder the mixed oxide of CuO and ZnO is formed. After a milling time of 56 h, no Cu or CuO peaks could be detected.

From TPR measurements it could be concluded that during ball milling in vacuo no Cu oxidation occurred as no significant hydrogen uptake could be measured. The sample milled in air for 56 h showed a single reduction peak in TPR with a maximum at 390 K corresponding to reduction of 65% (up to 523 K) of the copper present if an initial valency of 2+ is assumed. This means that part of the copper has not been fully oxidised during milling and hence still is in the metallic or 1+ state or that not all copper ions are reducible below 523 K. From figure 1 it is clear that some of the copper of the 56 h air-milled sample is still in the metallic state, as e.g. the Cu^0 reflection at $2\theta = 43.8^\circ$ has not disappeared completely yet. Hence, the first explanation is most likely. The XRD pattern, however, cannot be interpreted quantitatively to check the amount of metallic copper derived from TPR as the previously mentioned amorphisation of crystallites by the milling treatment causes considerable line broadening for all samples investigated. The sample milled in air for 142 h gave rise to a peak at 398 K corresponding to reduction of 92% of all copper present. Again, from figure 1 it could already be concluded that oxidation of the copper has progressed further for the

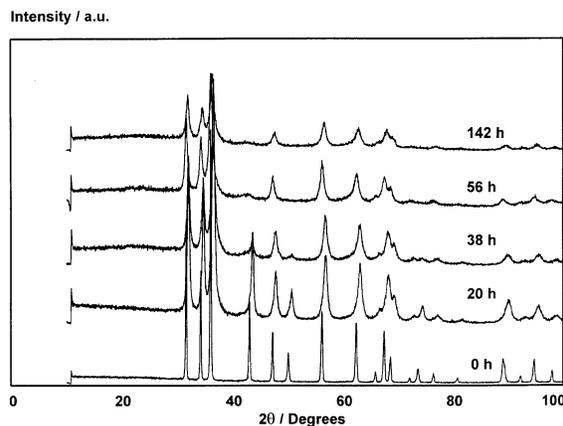


Figure 1. XRD spectra of catalyst series 2 at increasing milling times in air.

142 h air-milled sample compared to a milling time of 56 h. The observed shift of the peak maximum to higher temperature is indicative of a more intimate contact of the CuO with ZnO [11,12], although shifts to lower temperature upon admixing increasing amounts of ZnO to CuO in coprecipitated catalysts have also been reported [13]. An alternative explanation, which seems less likely, could be that the higher amount of residual metallic copper in the 56 h air-milled sample more effectively catalyses CuO reduction compared to the 142 h milled catalyst.

It can be concluded from TPR and the XRD patterns, that in catalyst series 1, Cu cannot dissolve in the ZnO lattice as no CuO is generated in vacuum pre-empting formation of the mixed oxide with ZnO. The situation is different in catalyst series 2. In this case Cu is oxidised and may dissolve as CuO – at least to some extent – in ZnO or vice versa (see, e.g., ref. [14]). Moreover, ball-milling may considerably extend the range of solubility of two components [6]. XRD patterns measured using LaB₆ as a reference show a shift towards slightly higher 2θ values of the main ZnO diffraction peak as a function of milling time in air. Such an (extremely small) effect has been reported as indicative of solid solution of copper cations into the ZnO structure [15]. In our case, however, the shift is in the same order of magnitude of the accuracy of the measurement ($2\theta = 0.03^\circ$). This does not necessarily imply the absence of solid solution, but rather reflects the small change in the lattice parameter due to the similar ionic radii of Cu²⁺ and Zn²⁺ (73 and 74 pm respectively).

In table 1 the surface area measurements and catalyst activity data are summarised. It is clear from this table that the BET surface area and the Cu specific surface area of series 2 are much larger than those of series 1. The fact that a Cu specific surface area of 16.4 m²/g-cat is found for the 142 h air-milled catalyst of series 2, suggests a high degree of Cu dispersion (64.2 m²/g-Cu). The

higher BET surface area for the series 2 catalysts compared to series 1 reflects the same phenomenon. From table 1 it can be seen that the particle size of air-milled samples grows somewhat after prolonged milling times resulting in a lower BET surface area for the 142 h milled catalyst compared to the 56 h treated sample, in contrast to the observed monotonous increase in Cu dispersion as a function of milling time. Confirmation of this phenomenon was obtained by analysing two different batches of the air-milled oxides, and measuring the areas twice per batch. In conclusion, we can state that the catalyst series 2 exhibits a much better dispersion of Cu particles after reduction than series 1.

The methanol activity profiles for all the tested catalysts as a function of run time are qualitatively very similar. Figure 2 shows the methanol activity of the sample of series 2 milled for 142 h. During the first 15 min, the catalyst is reduced by the reactant gases resulting in an activity increase. Subsequently a gradual deactivation takes place. The activity decline could for instance be due to sintering of the copper metal particles. For the sample milled for 142 h in air, XRD showed a copper crystallite diameter increase of approximately 15% only (initial diameter 6.5 nm, calculated using the Scherrer formula), both in pure hydrogen and synthesis gas at 250°C. When after 2.5 h reaction time the synthesis gas was refreshed, initial activity was fully restored. This could be repeated several times. Consequently sintering can be ruled out as the deactivation mechanism. Since conversion is far removed from thermodynamic equilibrium, depletion of the feed gases is not substantial and also not the cause for the observed phenomena. Hence, the inhibition must be linked to product (water and/or methanol) formation. A confirmation of this conclusion was obtained by preliminary flow experiments, showing constant catalyst activity for the full 20 h of these experiments for ball-milled samples.

From figure 2 and table 1 we see that the maximum

Table 1
Cu specific surface area, BET surface area and activity in methanol synthesis for various Cu/ZnO catalysts

Sample (milling time/atm)	BET surf. area (m ² /g)	Cu area (m ² /g-cat)	Max. rate ^a ($\mu\text{mol}/(\text{g-cat s})$)	TOF ^b (molec./ (Cu-site s))	Cum. yield ^c (mmol/g-cat)	TON ^c (molec./site)
pure Cu	0 ^e	–	4.3×10^{-3} ^d	–	2.3×10^{-3}	–
pure ZnO	2.4	–	0.025	–	0.089	–
phys. mix.	0 ^e	0.8	0.028 ^d	1.5×10^{-3}	0.084	4.4
24 h/vac.	1.1	0.1	0.20	0.08	0.76	315
48 h/vac.	–	0.5	0.48	0.04	1.65	136
96 h/vac.	1.7	0.4	0.33	0.034	1.3	134
56 h/air	43	12.5	5.9	0.020	27.3	91
142 h/air	32	16.4	11.5	0.029	37.8	95
coprecip.	39	20.3	7.5	0.016	44.5	90

^a Maximum rate at 15 min run time.

^b Assuming 1.46×10^{19} Cu surface atoms per m².

^c At $t = 2$ h.

^d At $t = 3$ min.

^e Below detection limit.

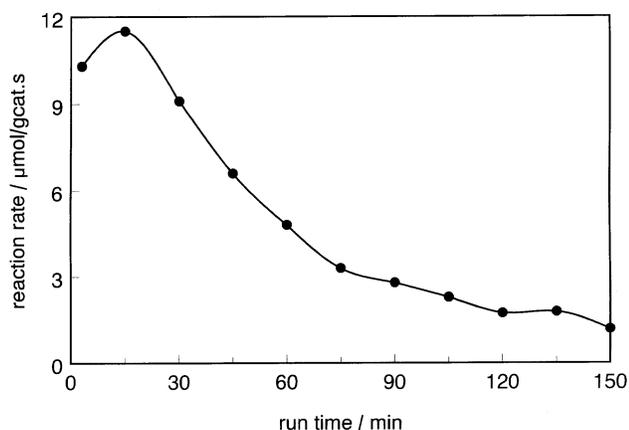


Figure 2. Methanol rate as a function of time for the catalyst milled for 142 h in air.

methanol activity for the 142 h air-milled catalyst is $11.5 \mu\text{mol}/(\text{g-cat s})$ and the cumulative yield after 2 h reaction time is $37.8 \text{ mmol}/\text{g-cat}$. This activity is of the same order as found for the catalyst prepared by coprecipitation ($7.5 \mu\text{mol}/(\text{g-cat s})$; $44.5 \text{ mmol}/\text{g-cat}$, see table 1). It can be concluded that the Cu/ZnO catalyst prepared by simple ball milling in air shows a comparable activity to the catalyst prepared by conventional coprecipitation of Cu and Zn salts.

The activities of the two series of samples as a function of milling time are shown in figure 3. It is obvious from figure 3 that the catalysts of series 2 have a much higher methanol activity than those of series 1 (please note the difference between the scales of the left- and right-hand axes). In series 2 the methanol activity increases with the milling time, whereas in series 1 the methanol activity increases until a milling time of 48 h and subsequently decreases after prolonged treatment. This may be due to an increase in copper particle size during milling under vacuum. It was found that after

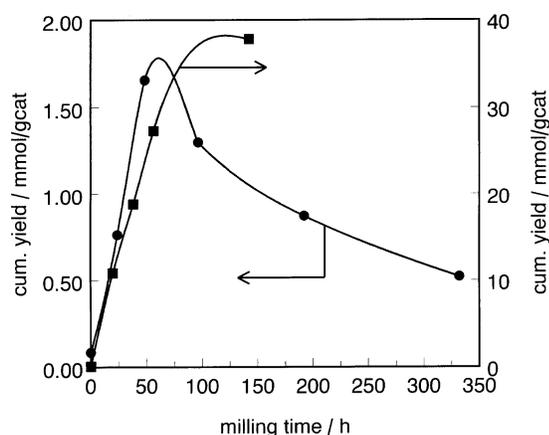


Figure 3. Cumulative methanol yield after 2 h reaction time for all catalysts prepared by ball milling as a function of milling time. (●) Series 1, (■) series 2.

milling in vacuum for 20 h, due to the ductile nature of the copper material some agglomerated flat fragments with a diameter of 1.5–2.5 mm were formed by cold welding from the original $44 \mu\text{m}$ particles

As mentioned above, the reduced samples in series 2 show much higher Cu specific surface areas most likely due to the better Cu dispersion in the ZnO lattice caused by the oxidative atmosphere during milling. The longer the catalyst is milled under air, the more Cu interacts with the ZnO and the less metallic Cu exists (see figure 1 and the TPR results mentioned above) which causes the higher Cu dispersion when it is reduced under synthesis gas, resulting in higher methanol activity as shown in table 1. In fact, in all aspects the 56 and 142 h air-milled samples are quite similar to the coprecipitated catalyst. It is also clear from the table that pure Cu, pure ZnO and the physical mixture of the two components are not very active. The occurrence of a simple correlation between methanol activity and the specific copper surface area via comparison of the turnover frequencies or turnover numbers of the catalysts cannot be given due to the inaccuracy of the lower values of the copper surface areas given in table 1, which are close to the detection limit of the chemisorption technique.

It is the intention of the authors to further investigate the effects of various gas-phase components and different precursor materials on the structure and performance of promoted copper catalysts prepared by high intensity ball milling. This will provide valuable information on the nature and prerequisites of the copper promoter interaction.

4. Conclusions

High intensity mechanical mixing of Cu powder and ZnO in vacuo results in amorphisation of the components, but separate Cu^0 and ZnO phase remain. Consequently Cu dispersion is not enhanced and low BET and copper metal surface areas result. The activity in synthesis gas conversion towards methanol is low for such catalysts.

In contrast, ball milling of Cu and ZnO in air results in (partial) oxidation of the copper and improved interaction of CuO with ZnO. High BET and copper metal areas result. The activity of the latter catalysts after in situ reduction by the synthesis gas mixture for methanol production is comparable to coprecipitated Cu–ZnO catalysts.

High intensity ball milling at ambient conditions is a promising method for the preparation of mixed oxidic catalysts or catalyst precursors.

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