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Oxidation and reduction in copper/zinc oxides by mechanical milling

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Abstract

When zinc oxide is milled under vacuum or in the presence of oxygen, creation of various types of defects results in an increased amorphous fraction, as well as higher surface area. Mechanochemical reactions occur when copper and copper oxides are milled together with zinc oxide: oxidation of copper and copper oxides takes place in the presence of oxygen, whereas reduction takes place under vacuum. These reactions are promoted by the presence of ZnO. Formation of a Cu₂O-like intermediate is suggested, which is not observed when milled without ZnO. The various resulting copper species reduce at different temperatures in H₂ atmosphere. Both Cu⁰ specific surfaces and BET surfaces are substantially increased for all milled Cu/ZnO samples, making this method an interesting alternative for the preparation of promoted heterogeneous catalysts.

Keywords: Ball-milling; Mechanochemistry; ZnO; Cu/ZnO; Oxidation; Reduction

1. Introduction

Mechanical milling has long been known as a technique for refining particles of solid materials and for the ability to drive mechanochemical reactions. Most effects due to milling can directly or indirectly be attributed to the production of various defects combined with high local temperatures. In pre-alloyed intermetallic compounds, atomic disorder is thus created which can eventually induce phase transformations. Typical effects of mechanochemistry are mixing on a microscopic level and formation of fresh surfaces. The most common mechanochemical reactions include solid-solid and solid-gas reactions. An example of a reaction between solids is the reduction of metal oxides in the presence of a strong reducing element [1,2], such as the reduction of CuO in the presence of Ca. Reactions between solids and a gas include the formation of hydrides, nitrides and oxides [3-6]. Hard materials such as TiN can thus be prepared, as well as catalysts [7,8]. In this paper, the Cu/ZnO catalyst for the synthesis of methanol is investigated.

The Cu/ZnO catalyst is conventionally prepared by coprecipitation of Cu(NO₃)₂ and Zn(NO₃)₂ solutions with subsequent ageing and calcination. In order to achieve high activity a good intimate mixture of Cu and ZnO must be obtained [9,10]. The ultimate structure and activity of the mechanochemically prepared catalyst show a strong dependency on the milling atmosphere [11]. A mixture of Cu and ZnO milled in vacuum was hardly active, whereas this mixture milled in ambient air was as active as a coprecipitated catalyst. Considerable Fe contamination may affect the selectivity towards methanol synthesis, as was shown in [12] with mechanochemically prepared supported Cu/ZnO catalysts using different milling equipment.

As ambient air consists of many components, careful variation of precursors and milling atmosphere is required to determine the exact conditions under which an active catalyst may be prepared. Moreover, the various reactions in this system that can occur during milling deserve

closer investigation. Mechanochemical reactions of Cu and its oxides under several atmospheres have been investigated separately [13]. In the present paper we attempt to further clarify the reduction and oxidation reactions that can occur during preparation of these catalysts by mechanical milling. For that reason milling of ZnO and the mixtures of ZnO with Cu, Cu₂O and CuO is carried out under vacuum and in the presence of oxygen.

2. Experimental

All samples were milled in a vibratory mill [14] attached to a vacuum pump. The vial was typically loaded with 2 grams of material. The standard milling time was 200 hours for all samples. We used Cu powder (40 μ m, 99.5% pure), Cu₂O powder (<74 μ m, 99% pure), CuO powder (<74 μ m, 99.9% pure) and ZnO powder (<74 μ m, 99.995% pure), all purchased from CERAC. For the mixtures, the Cu to Zn atomic ratio was 30:70. Milling under vacuum was carried out below 10⁻⁶ mbar during continuous pumping. Milling in synthetic air (20% O₂ in N₂, 99.999% pure) was performed at a pressure of 2 bar after evacuation, filling with this gas and again evacuation to 10⁻⁶ mbar.

The Cu⁰ specific surface areas of Cu/ZnO samples were determined by N₂O chemisorption according to the method described in [15] using Thermogravimetric Analysis (TGA). Prior to the chemisorption experiments, the samples were pre-treated in Ar and reduced in H₂/Ar (see below). Reduction patterns and oxidation levels were determined by recording the calibrated sample weight loss during catalyst reduction. N₂O chemisorption took place at 363 K, after evacuation at this temperature. The error in Cu⁰ specific surface areas is about 1 m²/g. The total surface area of some samples was determined by the BET-method (N₂-physisorption). Prior to physisorption, the ZnO samples were dried at 383 K under vacuum and the samples containing Cu and Zn were pre-treated in He and reduced in H₂/He. The error in the BET surface areas is in the order of 15 %. Temperature Programmed Reduction (TPR) was performed by H₂-consumption measurements after pre-treatment in He. Reduction was carried out in H₂/Ar at 300 K/hr.

Pre-treatment was carried out by heating in a flow of Ar or He at 200 K/hr from 298 K to 508 K, then at 100 K/hr to 523 K. Subsequently, the samples were cooled to 298 K. Reduction was carried out in a flow of H₂/Ar or H₂/He (2/1) with a similar thermal treatment (except for TPR); the temperature of 523 K was held during 5 minutes.

X-ray diffraction XRD patterns were recorded using CuK α radiation. Relative amorphous fractions were determined by comparison of the ratio between the intensities of background and diffraction peaks with this ratio in the unmilled materials, and are given in arbitrary units. Some samples were analysed with Transmission Electron Microscopy (TEM) at 100 kV.

Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP–AES) was performed on all samples to determine the contamination levels due to the milling equipment (Fe, Cr, Ni). The total contamination of the samples containing Cu and Zn mainly consisted of Fe and was always below 0.65 at.% of the metallic fraction, and on average 0.37 %. Differential dissolution was used for determination of the stoichiometry of separate phases according to [16].

3. Results and discussion

3.1. ZnO

After milling of ZnO under vacuum and synthetic air (s.a.), the white colour of ZnO changes to olive-green and yellow-green respectively. The XRD patterns of the samples do not reveal a shift in peak position, indicating that the lattice parameters of all milled ZnO samples remain unchanged

after milling. No new peaks could be observed, but a reduction of the crystallite size, typical of milling, occurred as the peaks were significantly broadened. An increase of the amount of amorphous ZnO was observed as can be seen in Table 1; also BET surface areas and contamination levels are given here for both milled and unmilled samples. BET areas increase after milling, but are limited to a factor of 2 for ZnO milled in synthetic air. The contamination by the milling equipment clearly remains within acceptable limits, and can not be held solely responsible for the dramatic changes in colour. These changes are probably due to the formation of colour centres and have been observed by others [17] in milled ZnO as well. They can also be formed by irradiation [18] but are commonly found after a thermal treatment at around 1500 K and are generally explained to be oxygen vacancies. The number of oxygen vacancies is significantly higher after a thermal treatment in N₂ than in O₂ [19]. Milling under vacuum will probably also result in the formation of oxygen vacancies and will give a higher number than milling in synthetic air. Alternatively, milling in synthetic air could also result in a limited amount of interstitial oxygen. The defects probably partially destroy the crystalline structure and hence explain the increased amount of amorphous ZnO. As the error in the ICP measurements is around 2%, the exact defect concentration is too small to be detected by ICP. No meso- or macroporosity could be detected. Some microporosity can be attributed to increased surface roughness due to milling.

3.2. *Cu/ZnO, Cu₂O/ZnO and CuO/ZnO milled in vacuum or synthetic air*

In Table 2, surface area measurements and H₂-reduction data of samples milled under vacuum or in synthetic air are compared to the unmilled mixtures. For these samples, 100% of CuO reduction corresponds to the oxidation level of CuO and 50% to the oxidation level of Cu₂O. ZnO is assumed to remain unreduced under H₂ at the applied conditions. Both oxidation and reduction during milling can be observed so that in synthetic air Cu/ZnO and Cu₂O/ZnO are almost entirely oxidised to the level of CuO/ZnO, whereas by milling under vacuum the oxidation levels of Cu₂O/ZnO and CuO/ZnO decrease. The TGA oxidation levels are well reproducible within approximately 3%; the TPR errors are about 5%.

XRD patterns (Fig. 1) also indicate the occurrence of mechanochemical reactions, but in a more complex way. All patterns show broadened diffraction peaks, typical of milling, and an increased amorphous fraction. The diffraction pattern of ZnO can be clearly identified for all samples. Also, some diffraction peaks of Cu, Cu₂O and CuO can be observed.

In Cu/ZnO/s.a.(synthetic air) and in Cu₂O/ZnO/s.a. some CuO can be observed indicating oxidation, but especially Cu₂O diffraction peaks can be clearly identified. These Cu₂O peaks are unusually large relative to the ZnO peaks as compared to unmilled Cu₂O/ZnO. The presence of Cu₂O is remarkable, as almost complete oxidation to the level of CuO has occurred, so only a small fraction of Cu₂O is to be expected. One explanation may be a specific orientation of Cu₂O crystals, but as both the (200) and the (220) peaks of the cubic crystal are well represented this is not very probable. It is more likely that Cu₂O is well dispersed, which is also indicated by the broad diffraction peaks, and well attached to the ZnO surface as an intermediate state. This intermediate state may even partially consist of ZnO and is probably the configuration in which further oxidation to CuO occurs. According to Klier [20] Cu⁺ may dissolve substantially in the ZnO lattice, in contrast to Cu²⁺. In Cu₂O/ZnO/s.a. the Cu₂O peaks eventually disappear after more than 400 hours of milling, indicating total oxidation to CuO.

The opposite is the case for CuO/ZnO/vac, where both Cu₂O and a shoulder of CuO are visible. Here reduction occurs to Cu₂O probably through an intermediate state. In Cu₂O/ZnO/vac not only Cu₂O, but also Cu and a small shoulder of CuO can be seen. At shorter milling times, CuO is more clearly visible, but Cu can not be observed. Apparently, here the intermediate state first leads to the formation of some CuO attached to ZnO, which may subsequently reduce to Cu. This would be in

agreement with [13] where reduction of pure CuO under vacuum has been observed but no reduction of pure Cu₂O [13], making this mechanism more probable than direct reduction of Cu₂O to Cu.

As can be expected, in the XRD pattern of CuO/ZnO/s.a. only ZnO and (shoulders of) CuO are visible. This clearly indicates that no reduction or oxidation has taken place in this sample.

It seems as if ZnO serves as a support on which an intermediate Cu oxide can be stabilised, as the Cu₂O-like intermediate has not been observed in similar experiments on Cu and its oxides without ZnO. The direction of the net reaction is dependent on the amount of oxygen present in the sample and the O₂-partial pressure in the milling vial. An influence is also to be expected on the structure of ZnO and the amount of defects. It may be noted that ZnO is an n-type semiconductor that can easily form an excess of interstitial Zn²⁺ and e⁻, while Cu₂O is a p-type forming a deficit of Cu⁺ and Cu²⁺. Oxygen ions may then be built into the Cu₂O matrix, being compensated in charge by Zn²⁺. Although speculative, this mechanism would explain both the high intensity of the (200) Cu₂O peak and the oxidation and reduction reactions.

After H₂-reduction, the XRD patterns show relatively narrow diffraction peaks of metallic Cu and ZnO and a decreased amorphous fraction as compared to the as-milled samples, indicating a larger crystalline fraction as well as larger crystallites.

The Cu/ZnO/s.a. sample has been subjected to differential dissolution. As Cu and Zn dissolve simultaneously at constant stoichiometry, very good contact between Cu and Zn exists. About 20% dissolve after a longer time but have the same stoichiometry. Although no evidence of the character of the structure has been found, this harder soluble phase could well be crystalline material, as the XRD patterns indicate that the amorphous to crystalline ratio is much larger than 1. An alternative option is that this may be the intermediate Cu₂O on ZnO.

TEM measurements performed on CuO/ZnO/vac confirm the XRD data (Figure 2). Diffuse rings in the electron-diffraction pattern can be observed, indicating the presence of amorphous or nanocrystalline material. Small crystallites (<10 nm) can be observed on the edge of the particle. After reduction and passivation with N₂O, the size of the crystallites is larger (10-20 nm).

3.2.1. Reduction temperature

Due to milling, roughening of the surface and creation of matrix defects and of O-vacancies may occur, giving rise to decreased reduction temperatures [21]. This indeed occurs in all samples as compared to their unmilled precursors. Cu/ZnO/s.a. and Cu₂O/ZnO/s.a. are special cases here as CuO, a different oxide, is formed.

Reduction profiles of all samples are shown in Figure 3. The first reduction peak of Cu₂O/ZnO/s.a. and the reduction profiles of all CuO/ZnO samples, indicated with an asterisk in Table 2, are very steep and positioned at relatively low temperature. Reduction is accompanied by an extra temperature rise of a few degrees, indicating that the reduction proceeds very quickly and exothermically (the ΔH^0 for CuO reduction is of the order of -10^5 J/mol). In these samples the presence of a CuO species is assumed that is easily reducible where Cu⁰ acts as a catalyst for further reduction of the remaining CuO [22]. The second reduction peak of Cu₂O/ZnO/s.a. and the reduction profile of Cu/ZnO/s.a. are much broader and positioned at a higher temperature. Probably this CuO species is more closely in contact with ZnO. The TPR hydrogen consumption patterns are broader than the TGA patterns, but the maxima are in accordance with the TGA maxima. However, in case of CuO/ZnO/vac a second peak can be discerned. Moreover, its maximum is about 10K higher than that in Cu/ZnO/s.a.

Probably, the species that reduces at a higher temperature is associated with the intermediate Cu₂O-like oxide, and is more closely attached to ZnO. A milled copper oxide species reducing at a higher temperature has not been observed for copper samples milled without ZnO. This delaying

effect of ZnO on the reduction of CuO has also been found to be accompanied by the existence of stable intermediate Cu₂O by others [23].

The low reduction temperature of Cu₂O/ZnO/vac indicates the presence of a significant amount of Cu⁰ catalysing the reduction of mainly Cu₂O.

3.2.2. Surface area

A Cu/ZnO sample milled in vacuum had been investigated previously [11], showing both low Cu metal area and low BET surface area. The Cu⁰ specific surface areas of all milled samples discussed here are increased by more than one order of magnitude compared to their unmilled precursors. The increase in Cu⁰ specific surface area per gram of Cu is even larger than in the absence of ZnO, as has been described in [13]. This could indicate a larger Cu dispersion due to the presence of or interaction with ZnO during milling, but also stabilisation of dispersed Cu⁰ by ZnO after reduction. Also the BET surface areas of the milled Cu/ZnO samples are further increased compared to what would be expected when the contributions of the milled components are considered separately.

4. Conclusions

High-intensity milling of ZnO results in an increased fraction of amorphous ZnO and in a higher surface area, probably due to surface roughening or an increased dispersion. Milling of mixtures of Cu, Cu₂O or CuO and ZnO results in oxidation of the Cu precursors when milling occurs in synthetic air and reduction when milling occurs under vacuum. These mechanochemical reactions are promoted by the presence of ZnO. The formation of a Cu₂O-like intermediate closely attached to ZnO has been observed, as well as several copper oxide species reducing at different temperatures. Milled samples possess much higher surface areas than both the unmilled mixtures and mixtures of the separately milled components.

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Table 1. Analytical data of milled and unmilled ZnO samples.

Milling conditions	Relative amorphous fraction [a.u.]	BET surface area [m ² /g]	% metallic contamination
unmilled	1.0	3.0	0.05
vacuum	2.5	4.2	1.2
synthetic air	2.2	6.0	0.5

Table 2. Reduction data and surface area of milled and unmilled samples containing Cu, Cu₂O or CuO, and ZnO. For * see text.

Sample	Milling conditions	Reduction max [K]	% reduced CuO (TGA)	% reduced CuO (TPR)	Cu ⁰ area [m ² /g]	BET surf. area [m ² /g]
Cu/ZnO	unmilled	402	5.4	-	0.2	-
Cu/ZnO	s.a.	432	104.9	-	6.5	-
Cu ₂ O/ZnO	unmilled	515	50.1	-	0.1	-
Cu ₂ O/ZnO	vacuum	383	43.7	-	5.3	-
Cu ₂ O/ZnO	s.a.	414* and 442	94.4	-	5.6	-
CuO/ZnO	unmilled	414*	101.2	100	0.6	3.5
CuO/ZnO	vacuum	412*	91.0	95	9.1	29
CuO/ZnO	s.a.	409*	105.7	101	9.3	24

Figure 1: XRD patterns of milled Cu/ZnO/s.a. (a), Cu₂O/ZnO/vac (b), Cu₂O/ZnO/s.a.(c), CuO/ZnO/vac (d) and CuO/ZnO/s.a. (e). The patterns are plotted on a logarithmic scale. ZnO peaks are represented by ◆.

Figure 2: TE micrograph of CuO/ZnO/vac and the corresponding diffraction pattern (inset).

Figure 3: TGA reduction profiles of unmilled Cu/ZnO (a), Cu/ZnO/s.a. (b), unmilled Cu₂O/ZnO (c), Cu₂O/ZnO/vac (d), Cu₂O/ZnO/s.a. (e), unmilled CuO/ZnO (f), CuO/ZnO/vac (g) and CuO/ZnO/s.a. (h).