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Mechanochemical reactions on copper-based compounds

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Abstract. Mechanochemical reactions of copper and copper oxides with oxygen and carbon dioxide are discussed, as well as decomposition and reduction of copper compounds by mechanical milling under high-vacuum conditions.

Introduction

Mechanical milling and mechanical alloying are known to be able to drive various kinds of mechanochemical reactions. In the first category reactions on gaseous reactants over solid catalysts are driven by mechanical milling [1,2]. The milling serves to create enough vacant surface sites of the catalyst for the reactants and provides the energy required for activation of the reaction. In the second category the solid materials themselves are subject to mechanochemical reactions. Metal oxides can be reduced by mechanical alloying in the presence of a strong reducing element [3,4]. The oxygen is then transferred to the reducing element. In this way CuO is reduced in the presence of Ca. Hydrides, nitrides and oxides are prepared by solid-gas reactions in which the milled material reacts with the atmosphere present in the mill. Hard materials such as TiN can thus be prepared [5-7].

Similarly preparation of catalysts can be performed by various interactions between solids and the gases present in the vial. In this way vanadium containing catalysts [8], CeO₂-based catalysts [9] and Cu/ZnO catalysts used for methanol synthesis [10] are prepared. In the latter case the choice of the surrounding atmosphere appears to be a crucial factor in the ultimate structure and activity of the catalyst. This binary catalyst is slightly different from the customary Al₂O₃ containing ternary catalyst which is used in industry, but has the advantage that the unreduced structure is a homogeneous powder, which is convenient for preparation by ball-milling and leads to a well-defined mixture.

In order to understand the mechanochemical processes which take place during the preparation of a ball-milled binary Cu/ZnO catalyst both Cu and Zn oxides should be investigated independently. This paper deals with various Cu-based precursors.

During mechanical milling contamination is usually expected from the milling tools (vial and balls) as well as from the gas which is present in the vial, notably from oxygen and nitrogen. The oxidation and nitration processes are usually impeded by filling the vial with an inert gas or by continuous pumping. One advantage of continuous pumping is that the resulting partial pressures of these gases is much lower than during milling in an inert atmosphere. This requires a specially designed experimental setup, and can applied with the ball mill which has been used in this paper. For most mills though continuous pumping is not possible. However, an interesting effect which is
usually not accounted for is that under these conditions also decomposition of normally stable compounds can occur during milling.

This paper reports chemical alterations which are inferred by milling under high-vacuum conditions: decomposition of basic copper carbonate in vacuum. Also oxidation of Cu and Cu$_2$O by milling in O$_2$ and carbonate production by milling CuO in the presence of CO$_2$ are considered.

**Experimental**

All samples were milled in a vibratory mill [11] attached to a vacuum pump. Each time the vial was loaded by 2 grams of material. We used Cu powder (40 µm, 99.5% pure, CERAC), Cu$_2$O powder (<74 µm, 99% pure, CERAC), CuO powder (<74 µm, 99.9% pure, CERAC) and CuCO$_3$·Cu(OH)$_2$ powder (Cu-basic-carbonate, Janssen, 54-56% Cu). When milling was performed in vacuum the pressure was lower than 10$^{-6}$ Torr. Milling under synthetic air (20% O$_2$ in N$_2$, 99.999% pure) and carbon dioxide (99.998% pure) took place at a pressure of 2 bar after evacuation, filling with this gas and again evacuation to 10$^{-6}$ Torr. Ambient air was not considered because of climatic variations, e.g. resulting in a variation of water content.

The Cu$^0$ specific surface area was determined by N$_2$ chemisorption according to the method described in [12] and was performed in a Setaram TG 85 thermobalance. Prior to the chemisorption experiments, the samples were calcined in an Ar-flow (99.999% pure at 120 ml/min) after heating at 200 K/hr up to 623 K (for the CuCO$_3$·Cu(OH)$_2$ samples and CuO milled in CO$_2$) or after heating up at 200 K/hr up to 508 K and then at 100 K/hr up to 523 K (all other samples). After cooling in Ar to ambient, reduction of all samples was performed by heating in H$_2$/Ar (at a ratio of 2/1; total flow: 120 ml/min; hydrogen purity: 99.996%) to 523 K using a temperature program identical to the second calcination program. This temperature was held during 5 minutes. Reduction patterns were determined by recording the calibrated sample weight loss during catalyst reduction. N$_2$O chemisorption took place after cooling down to 363 K and subsequent evacuation at this temperature. The TGA was attached to a mass spectrometer, enabling analysis of the molecular weight of the molecules which were released or produced during calcination and reduction.

The total surface area of some of the reduced samples was also determined by the BET-method (N$_2$-physisorption). Prior to the physisorption calcination took place in a He-flow (99.996% pure) at 100 ml/min and reduction in He/H$_2$ (2/1, total flow: 100 ml/min; hydrogen purity: 99.996%) using a temperature program identical to that of the chemisorption experiments.

On some milled CuO samples TPR patterns were also determined by H$_2$ consumption measurements in a conventional home-made TPR set-up with TCD detector after calcination in a He flow (99.996% pure) of 40 ml/min using a temperature program identical to the second one for the chemisorption measurements, but by heating during reduction at 300 K/hr. During reduction a H$_2$/Ar mixture (2/1; total flow: 20 ml/min; Praxair, purity: 99.99%) was used as a feeding gas. XRD patterns were recorded with an Enraf Nonius Curved Position Sensitive 120 (CPS 120) diffractometer.

Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES), using a multichannel Thermo Jarrel Ash ICAP 957 spectrometer, has been performed on all samples to determine the contamination levels of some metals (Fe, Cr, Ni).

**Results and discussion**

**Cu, Cu$_2$O and CuO.** The Cu, Cu$_2$O and CuO precursors were ball-milled during 200 hr under vacuum (except for Cu), synthetic air and carbon dioxide. Compared to the unmilled samples, the XRD patterns (Figs. 1-3) of the samples after milling show a significant broadening of all peaks, indicating a reduction of the crystallite size. Amorphisation is observed for the CuO sample milled
in CO₂. In Table 1 the surface area measurements and reduction data of the samples are summarised. 100% CuO reduction corresponding to the initial oxidation level of CuO, 50% to the oxidation level of Cu₂O. All milled samples show decreased reduction temperatures, which is especially apparent for the Cu₂O samples. This is probably due to roughening of the surface, and by the creation of matrix defects and of O-vacancies [13]. The Cu⁰ specific surface areas of Cu and Cu₂O samples which were milled in synthetic air are slightly increased compared to their unmilled precursors, of all milled CuO samples they are highly increased.

**Oxidation:** For the patterns of the Cu (Fig. 1) and Cu₂O (Fig. 2) samples which were milled in synthetic air, the original peaks almost completely disappeared in favour of an XRD pattern of CuO. Other Cu and Cu₂O samples retain their original XRD peaks, indicating the absence of a chemical reaction during milling. Also from Table 1 complete oxidation of the Cu and Cu₂O samples milled in synthetic air to CuO can be observed.

All CuO samples and the Cu and Cu₂O samples milled in synthetic air have very steep reduction profiles, accompanied by an extra temperature rise of a few degrees. This indicates that the reduction proceeds very quickly and exothermically (the ΔH⁰ for CuO reduction is of the order of -10⁵ J/mol). This could indicate that the Cu⁰ acts as a catalyst for further reduction of the remaining CuO. The other samples have much broader reduction profiles.

**Reduction:** As Cu always possesses some surface oxidation the as-received sample has a non-zero oxidation level. During milling of Cu in CO₂ some reduction of the surface passivation layer has apparently occurred. For the Cu₂O sample milled in CO₂ no such effect is observed from the reduction data. However, during calcination there is a small amount of weight loss at 145 °C, in the order of 0.27% of the total mass after reduction. The reduction data of CuO milled in CO₂ suggest that a small amount of reduction takes place during milling as well.

For all CO₂ milled samples the reduction peak is located at a relatively low temperature, also compared to other milled samples. Apparently the presence of CO₂ during milling facilitates the reduction, which is also indicated by the lower oxidation levels of the Cu and CuO samples after milling.

Some reduction has also occurred during milling of CuO in vacuum, which follows from both TGA and TPR data. It has to be remarked that the measurements in Table 1 have been performed on a sample which had a contamination of metallic Fe and Cr of around 9% due to a different pretreatment of the milling vial. In Table 1 these contamination effects have been corrected for by subtraction of the contribution of contamination to the total weight. The TPR peak maxima follow the TGA peak maxima. The decreased reduction temperature for the vacuum milled sample is probably also due to a larger amount of O-vacancies (and thus the presence of Cu⁰).

**Carbonate formation:** For the CuO milled in CO₂ decomposition takes place around 316 °C to CuO and CO₂. The amount of CuCO₃ is then 65.4%, the balance CuO. As calcination did not exceed 250 °C, and thus decomposition was not complete, the level of H₂ consumption (which is even slightly lower than for unmilled CuO) indicates that a watergas shift reaction (CuCO₃ + 2H₂ → Cu⁰ + CO + 2H₂O) does not occur during reduction.

**Accuracy and contamination:** The TGA oxidation levels are well reproducible, within approx. 1%. The TPR errors are larger, about 4%. The error in Cu⁰ specific surface areas is about 1m²/g, in the BET surface areas it is about 15%. Changing the temperature program in favour of longer times or higher temperatures during calcination results in a slight decrease of the Cu⁰ area, in the order of 10% for 100 °C higher calcination temperature or 30 minutes longer calcination at 250 °C. Except for the CuO sample milled in vacuum for all samples the Fe contamination levels are around or well below 1%, the Cr and Ni contamination levels are even lower.
The factor between the Cu\textsuperscript{0} specific surface areas and the BET surface areas for the reduced CuO samples has probably to do with a different orientation of the N\textsubscript{2} molecules on the Cu\textsuperscript{0} surface than expected from the model. This is currently being investigated.

Table 1. Reduction data and surface areas of milled and unmilled Cu, Cu\textsubscript{2}O and CuO samples.

<table>
<thead>
<tr>
<th>Sample/atm</th>
<th>Reduction peak max [°C]</th>
<th>% CuO reduced (TGA)</th>
<th>% CuO reduced (TPR)</th>
<th>Cu\textsuperscript{0} area [m\textsuperscript{2}/g]</th>
<th>BET surf. area [m\textsuperscript{2}/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>unmilled Cu</td>
<td>129</td>
<td>5.4</td>
<td>-</td>
<td>0.6</td>
<td>-</td>
</tr>
<tr>
<td>Cu/synth. air</td>
<td>135</td>
<td>99.6</td>
<td>-</td>
<td>2.1</td>
<td>-</td>
</tr>
<tr>
<td>Cu/CO\textsubscript{2}</td>
<td>95</td>
<td>1.2</td>
<td>-</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>unmilled Cu\textsubscript{2}O</td>
<td>242</td>
<td>50.1</td>
<td>-</td>
<td>0.4</td>
<td>-</td>
</tr>
<tr>
<td>Cu\textsubscript{2}O/vac</td>
<td>135</td>
<td>52.2</td>
<td>-</td>
<td>2.1</td>
<td>-</td>
</tr>
<tr>
<td>Cu\textsubscript{2}O/synth. air</td>
<td>133</td>
<td>108.3</td>
<td>-</td>
<td>1.9</td>
<td>-</td>
</tr>
<tr>
<td>Cu\textsubscript{2}O/CO\textsubscript{2}</td>
<td>124</td>
<td>49.9</td>
<td>-</td>
<td>0.4</td>
<td>-</td>
</tr>
<tr>
<td>unmilled CuO</td>
<td>141</td>
<td>101.2</td>
<td>100</td>
<td>2.2</td>
<td>4.9</td>
</tr>
<tr>
<td>CuO/vac (\textsuperscript{*})</td>
<td>131</td>
<td>95.4</td>
<td>85</td>
<td>15.4</td>
<td>28</td>
</tr>
<tr>
<td>CuO/synth. air</td>
<td>137</td>
<td>103.6</td>
<td>-</td>
<td>19.2</td>
<td>31</td>
</tr>
<tr>
<td>CuO/CO\textsubscript{2}</td>
<td>134</td>
<td>97.2</td>
<td>98</td>
<td>10.0</td>
<td>17</td>
</tr>
</tbody>
</table>

\textsuperscript{*} This sample has been corrected for a moderate amount of contamination.

Cu\textsubscript{2}O\textsubscript{3}•Cu(OH)\textsubscript{2}. Ball-milling of Cu\textsubscript{2}O\textsubscript{3}•Cu(OH)\textsubscript{2} (malachite, the predominant compound resulting from basic deposition of Cu salts) was performed under vacuum (approx. 10\textsuperscript{-5} Torr) for various milling times. From the TGA data (Table 2) it can be seen that upon prolonged milling both the decomposition temperatures and the reduction temperature decrease. This is probably due to an increased amount of vacancies. Also the amounts of CO\textsubscript{2}\textsuperscript{-} and OH\textsuperscript{-} that are left decrease, assuming that they decompose to H\textsubscript{2}O, CO\textsubscript{2} and CuO. The Cu\textsuperscript{0} specific area increases, again probably due to vacancies and therefore a rougher surface. The XRD patterns (Fig. 4) show a less continuous order of events. First the diffraction lines broaden because of crystallite size reduction, then the material becomes amorphous, and finally the pattern begins to resemble that of CuO. Moreover, the amorphous pattern is also what we found when milling CuO in CO\textsubscript{2}, which suggests that this is an intermediate state between CuO and Cu\textsubscript{2}O\textsubscript{3}.

Table 2. Calcination and reduction data and surface areas of milled and unmilled Cu\textsubscript{2}O\textsubscript{3}•Cu(OH)\textsubscript{2}.

<table>
<thead>
<tr>
<th>Milling time</th>
<th>Calcination peak max [°C]</th>
<th>Reduction peak max [°C]</th>
<th>% decomposed</th>
<th>Cu\textsuperscript{0} area [m\textsuperscript{2}/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 h</td>
<td>265</td>
<td>164</td>
<td>0</td>
<td>3.3</td>
</tr>
<tr>
<td>50 h</td>
<td>241</td>
<td>144</td>
<td>47.9</td>
<td>4.2</td>
</tr>
<tr>
<td>150 h</td>
<td>237</td>
<td>141</td>
<td>58.4</td>
<td>5.5</td>
</tr>
<tr>
<td>200 h</td>
<td>233</td>
<td>141</td>
<td>66.3</td>
<td>8.5</td>
</tr>
</tbody>
</table>
Figure 1. XRD patterns of Cu, from top to bottom: as-received, milled in synthetic air and in CO₂.

Figure 2. XRD patterns of Cu₂O, from top to bottom: as-received, milled in vacuum, in synthetic air and in CO₂.

Figure 3. XRD patterns of CuO, from top to bottom: as-received, milled in vacuum, in synthetic air and in CO₂.
Figure 4. XRD patterns of CuCO₃-Cu(OH)₂, from top to bottom: as-received, milled for 50, 150 and 200 h in vacuum

Conclusions

High intensity milling of Cu and Cu₂O results in oxidation to CuO when milling occurs in synthetic air. Milling of CuO results in partial reduction when milling is performed in vacuum and carbonate formation when milling takes place in CO₂. No carbonates are formed from Cu₂O nor does any reduction take place. Bivalent Cu seems to be necessary when CO₂ is to be built in a copper oxide matrix or for creating oxygen vacancies. CuCO₃-Cu(OH)₂ decomposes during prolonged milling at vacuum conditions to CuO. Milled samples possess higher surface areas than unmilled samples. Reduction of milled samples takes place at lower temperature, indicating a larger number of defects.

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References