

## SURFACE REDOX STRENGTH AND CATALYTIC ACTIVITY OF THE CuO/ZnO SYSTEM

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*Dedicated to Dr Miloš Kraus on the occasion of his 65th birthday.*

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Information about the reduction properties and reactivity of surface hydroxyl groups has been obtained from the interaction of iodine with a series of CuO/ZnO samples in wide range of concentrations. The maximum capacity of iodine reduction and maximum catalytic activity in water gas shift reaction were observed with the sample containing 20 wt.% CuO. The correlation found gives evidence in favour of the associative mechanism of the reaction.

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The most active and widely applied catalysts in the water gas shift reaction (WGSR)<sup>1,2</sup> and methanol synthesis<sup>3</sup> are based on the CuO/ZnO system. Despite of numerous investigations carried out by now, the knowledge of the active site structure is still unsatisfactory. Since both reactions mentioned above can be referred to as redox reactions with great reliability, the question arises about redox properties of the surface of the catalyst. Investigations by Flockhart et al.<sup>4</sup> show that the reduction of iodine on the metal oxide surface provides valuable information about redox properties of the surface and the reactivity of surface hydroxyl groups.

In the present study, this method has been applied to a series of CuO/ZnO samples with the aim to compare the results with the catalytic activity of the samples in WGSR and obtain thus information about active sites and mechanism of the reaction.

### EXPERIMENTAL

A series of CuO/ZnO samples containing the following CuO contents (wt.%) was investigated: 5, 15, 20, 25, 30, 40 and 70 wt.% CuO, the pure CuO and the pure ZnO, designated as follows: 5 CuO, 15 CuO, 20 CuO, 25 CuO, 30 CuO, 40 CuO, 70 CuO, 100 CuO and 100 ZnO. The samples were obtained in an automatic laboratory reactor Contalab (Contraves, Switzerland) ensuring perfect reproducibility of preparation conditions (pH, temperature, the introduction of reagents, stirring intensity, etc.). The starting salts were  $\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$  and  $\text{Zn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$  (Merck, analytical grade). The investigated samples were prepared by co-precipitation of aqueous mixed metal nitrates solution with aqueous  $\text{Na}_2\text{CO}_3$  at 80 °C and pH

7.25. The obtained precipitates aged for one hour at the same temperature. After filtration and careful washing the samples were dried at 110 °C and then calcined at 400 °C for 2 h. Their physical and structure characteristics were studied in detail elsewhere<sup>5,6</sup>.

The catalytic activity (*A*) of the samples was measured in a flow reactor at a pressure of 2 MPa at 200 °C, using gaseous mixture containing 4.0 vol.% CO. The reaction rate was determined at water vapour/gas ratio 0.66 and a flow rate of 60 000 h<sup>-1</sup>. The catalytic activity was expressed by the productivity, i.e. by moles of CO converted per unit CuO area in 1 h (mol<sub>CO</sub> h<sup>-1</sup> m<sup>-2</sup> g<sub>CuO</sub><sup>-1</sup>).

The reduction strength (*RS*) of the surface was expressed by the amount of iodine which reacted with the unit CuO surface area (mmol<sub>I<sub>2</sub></sub> m<sup>-2</sup> g<sub>CuO</sub><sup>-1</sup>). According to the method described<sup>4</sup>, the reduction of iodine proceeds in solution of an organic solvent (hexane) at room temperature in a dry-box argon atmosphere which is carefully freed of oxygen (≤ 3 ppm) and moisture (≤ 3 – 4 ppm). An amount of 0.5 ± 0.0001 g sample was introduced into flasks provided with ground-glass stoppers. All the samples were exposed to dry-box argon atmosphere for 24 h until oxygen and moisture content fell below 3 – 4 ppm. A definite amount of 0.005M iodine-hexane solution was then added to each sample and the samples were left for 24 h to complete their reduction. Since the samples were coloured, they were filtered and carefully washed by hexane after the reaction, the free iodine thus leaving with the filtrate. After that, 10 ml aqueous potassium iodide was added to each sample. The free iodine moved into the water layer where it was determined by titration with sodium thiosulfate solution, using starch as an indicator.

## RESULTS AND DISCUSSION

The dependence of the amount of iodine reduced by the surface and of the catalytic activity of the samples in WGS on the CuO content in the sample is shown in Fig. 1. One can see a very close correlation between them: a sharp maximum in the iodine reduction is observed at about 20 wt.% CuO, which coincides with maximum catalytic activity. Pure CuO and ZnO show significantly lower (by about one order of magnitude) reduction activity. This is in accordance with their very low catalytic activity. One can attempt at explaining the observed correlation as follows. According to Flockhart et al.<sup>4</sup>, the iodine reduction on solid oxide systems in the presence of an organic solvent can be caused mainly by the surface oxide OH groups, obeying an interaction mechanism analogical to that in aqueous alkaline solutions:

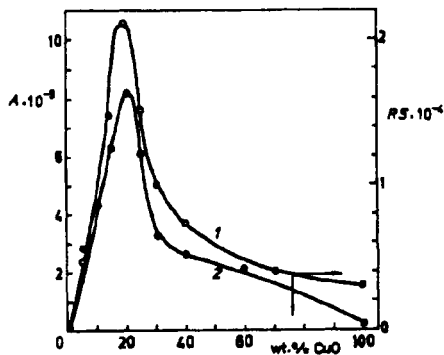
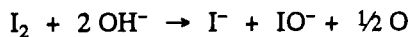
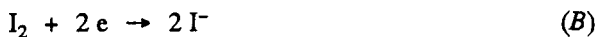


FIG. 1  
Dependence of 1 the amount of reduced iodine (*RS* in mmol<sub>I<sub>2</sub></sub> m<sup>-2</sup> g<sub>CuO</sub><sup>-1</sup>) and 2 the catalytic activity in WGS (*A* in mol<sub>CO</sub> h<sup>-1</sup> g<sub>CuO</sub><sup>-1</sup>) on CuO content



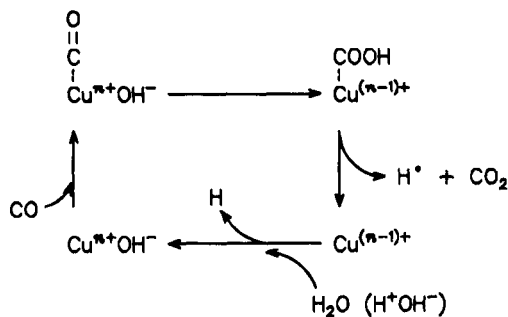
However, the iodine reduction can occur at any place of the surface capable of giving an electron by the following mechanism:



Such places can be the defects in the crystal lattice like F-centers, the metal atoms ( $\text{Cu}^0$ ,  $\text{Zn}^0$ ) in the lattice, the partially reduced ions, etc. In our case, as the dehydration was performed at 400 °C in air for 2 h, the presence of the reduced species is improbable. A special experiment with a pre-reduced sample was performed which showed that the activity towards iodine increases within one order of magnitude. The low calcination temperature suggests that the main reduction sites are surface OH groups and only to the lower degree also crystal lattice defects.

Experimental results<sup>4</sup> for aluminium oxide and silica-alumina demonstrate clearly that the reduction ability of the surface is greater at the lower dehydration temperatures and is mainly due to the presence of surface OH groups. Providing that the main amount of the reduced iodine arises from interaction with the surface hydroxyl groups, there is still one unanswered question: Why these groups show maxima both in their amount and in their reactivity at definite CuO concentrations?

The detailed investigation of physical properties of the samples<sup>5,6</sup> gave the following basic results. The maximum catalytic activity in WGS is exhibited by clustered copper ions in a solid solution with zinc oxide as well as by the highly dispersed and defective copper oxide phase. The appearance of maximum catalytic performance of the active oxide phases at about 20 wt.% CuO is due to the special chemical properties of the CuO/ZnO system and the procedure of its synthesis. According to the modern concepts<sup>2</sup> of the associative mechanism of WGS over the CuO/ZnO system, two features are essential (Scheme 1),



SCHEME 1

the high activity of hydroxyl groups during the formate complex formation and the enhanced electron transfer in the change of copper valence state (redox transfer). On the basis of these considerations one can explain the close correlation between the maximum catalytic activity and maximum amount of reactive hydroxyl groups (the maximum reduction ability) at about 20 wt.% CuO content in the CuO/ZnO system.

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