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THERMAL REDUCTION AND REOXIDATION OF SPINEL-TYPE $Cu_{1-x}Zn_xAl_2O_4$

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The thermochemical reactivity of the spinel-type quaternary metal oxide $Cu_{1-x}Zn_xAl_2O_4$ has been investigated for different Cu:Zn ratios. In oxygen or inert gas atmospheres no considerable reduction is observed. In molecular hydrogen metal selective reduction of the Cu is found at relatively high temperature. The solid reduction product is made up of sintered, poorly dispersed metallic copper on a Zn–Al–O metal oxide support, a potential catalyst for the methanol synthesis. Owing to the measured high reduction temperature leading to the mentioned sintering of the metallic copper, the activity of this system cannot be high.

Keywords: spinel-type $Cu_{1-x}Zn_xAl_2O_4$, thermal reduction, thermal reoxidation

Introduction

The interest into the preparation as well as the optimization of the activity or selectivity of heterogeneous catalysts exhibiting specific compositions and structures increased strongly during the last years. Therefore the selection of appropriate precursors, which can be transformed thermally or thermochemically into the active species under well-defined experimental conditions, is of decisive importance. In addition, the knowledge of the reactivity of solids including mechanistic and kinetic aspects proves to be useful for the improvement of the mentioned procedures [1].

Mixed metal oxides represent potentially favourable precursor systems, as the products obtained by thermal reduction may be alloys, mixtures of metals on metal oxide supports or alloys on metal oxide supports (see e.g. [2]). The fact that in many cases unusual but nevertheless interesting products may be obtained, can be ascribed to the atomic mixture of the metal cations in the precursor as well as to the usually low reduction temperatures in molecular hydrogen. The reproducible formation of such products, however, can only be guaranteed

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by knowing effects caused by the features of the initial material as well as by the given experimental parameters such as pressure, atmosphere, etc.

For the present investigations $Cu_{1-x}Zn_xAl_2O_4$ has been selected as precursor phase. $Cu_{1-x}Zn_xAl_2O_4$ adopts a partially inverse spinel structure [3–5] where the oxygen anions form a close packed cubic framework and the metal cations occupy half of the octahedral sites and one eighth of the tetrahedral sites. This means that the metal cations are homogeneously distributed on an atomic scale. This quaternary spinel seemed to be an appropriate parent phase for the formation of a catalyst consisting of metallic copper supported on zinc oxide and alumina. This mixture corresponds to the well-known catalyst used for the methanol synthesis according to the ICI low pressure process [6]. The idea was to prepare this catalyst by selective reduction of the copper assuming that the spinel structure would break down simultaneously during the reduction and zinc oxide and alumina would remain.

The main interest of the thermoanalytical studies is focussed on the degradation mechanism of the title compound, i.e. on the type of metal-selective reductions taking place as well as on the specific properties of the products formed in dependence of the Cu:Zn ratio and of the experimental conditions.

Experimental

Samples of $Cu_{1-x}Zn_xAl_2O_4$ were prepared by solid state reaction at 1000°C using mixtures of CuO, ZnO and Al_2O_3 in the desired proportions. These starting materials were of analytical grade purity. They were ground in an agate mortar, pressed into pellets and heated in air for 24 hours, then ground again and heated for further 50 hours. The products with a relatively low copper content are ochre and become darker with increasing copper content.

Structural characterizations were carried out using a Guinier IV camera, a Guinier-Lenné camera and an X-ray powder diffractometer, all of them working with CuK_α radiation.

For the characterization of the thermal reactivity of the title compound measurements in different gas atmospheres were performed using a Mettler TA2000C thermoanalyser.

The micromorphology of the parent spinels as well as their reduction products were investigated by means of scanning electron microscopy using a Philips SEM 515.

Results

$Cu_{1-x}Zn_xAl_2O_4$ spinels with the following compositions have been synthesized an investigated: x=0.75, 0.5, 0.4, 0.35, 0.3, 0.25 and the pure copper-spinel (x=0).

Thermal reduction

The mentioned $Cu_{1-x}Zn_xAl_2O_4$ samples were heated in a microbalance under molecular hydrogen with a heating rate of 10 deg·min^{-1}. The thermogravimetric measurements of the reduction (Fig. 1) give evidence for a strong dependence of the thermochemical reactivity from the Cu:Zn ratio:

– The temperature onset of the reduction increases with increasing zinc content.

– Only in the copper-rich phases with x=0.25 and 0.3 a selective reduction of the copper takes place. The onset temperatures of these process are 390°C for x=0, 480°C for x=0.25 and 500°C for x=0.3. Compared with the thermochemical reactivity of the corresponding binary oxides i.e. in particular CuO these temperatures are surprisingly high.

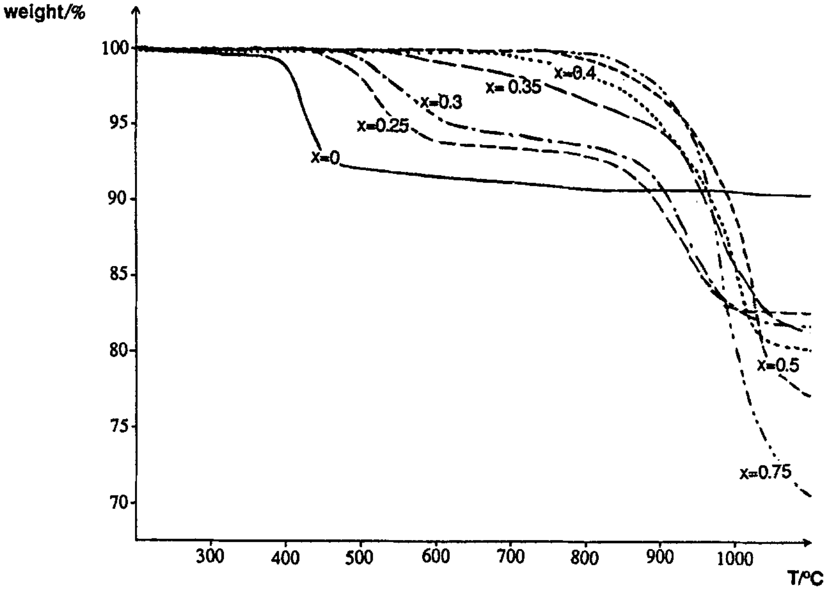

Fig. 1 Thermogravimetric measurements of the reduction of $Cu_{1-x}Zn_xAl_2O_4$ with x=0, 0.25, 0.3, 0.35, 0.4, 0.5, 0.75 in molecular hydrogen at ambient pressure (heating rate: 10 deg/min; H_2 gas flow: 30 ml/min; ambient pressure)

The reduction of the Zn(II) starts at 870°C. If one assumes only the reduction of the zinc to the metal the weight loss of this second step is much too high compared with the weight loss of the first. Obviously a second process takes place: at these temperatures a substantial part of the zinc metal evaporates (melting point: 419.6°C, boiling point: 907°C).

– When the zinc content is higher than x=0.35, no well defined reaction steps can be derived from thermogravimetric measurements, i.e. there is no indication for a primary copper-selective reduction and the formation of copper can no more be separated from the reduction of the zinc and its evaporation. The starting temperature of the reduction increases from 550°C for x=0.35 to 810°C for x=0.75.

The solid reduction products were characterized by X-ray diffraction. For the pure Cu–Al-spinel metallic copper and γ-Al_2O_3 is found. The formation of the γ-phase of alumina seems to be reasonable, as this phase adopts a defect spinel structure.

The reduction of samples with higher copper content (x=0.25 and 0.3) leads to metallic copper and an Al-rich Zn–Al–O-spinel phase. This has not been expected, but there are some more examples where aluminum spinels can solve a large amount of Al_2O_3 and thus form defect spinels. X-ray powder diffraction patterns show, that the spinel-phase exists at least up to temperatures around 750°C.

After the second step of the degradation, i.e. the reduction of zinc, a Zn–Al–O-phase is found together with metallic copper and γ-Al_2O_3. This finding is in agreement with the fact that the weight loss due to the reduction and evaporation of the zinc does not correspond to the loss of hundred percent. The obtained phase is related to $Zn_3Al_{94}O_{144}$ [7]. This oxide adopts a monoclinic structure, which is related to a distorted spinel. It has been obtained by heating non-stoichiometric Zn–Al–spinel phases above 850°C or by reduction of $ZnAl_2O_4$ at temperatures around 1150°C [8].

The reductions of the samples with higher zinc content, i.e. x=0.35, 0.4, 0.5 and 0.75 lead to the same products as the reductions of the aforementioned samples, i.e. they are made up of metallic copper, γ-Al_2O_3 and $Zn_3Al_{94}O_{144}$.

Comparative scanning electron microscopic investigations of agglomerates of parent crystals (Fig. 2a), partly reduced material (Fig. 2b) and final products (Fig. 2c) give evidence for an increasing roughening of the crystal surface, but no pronounced textural changes.

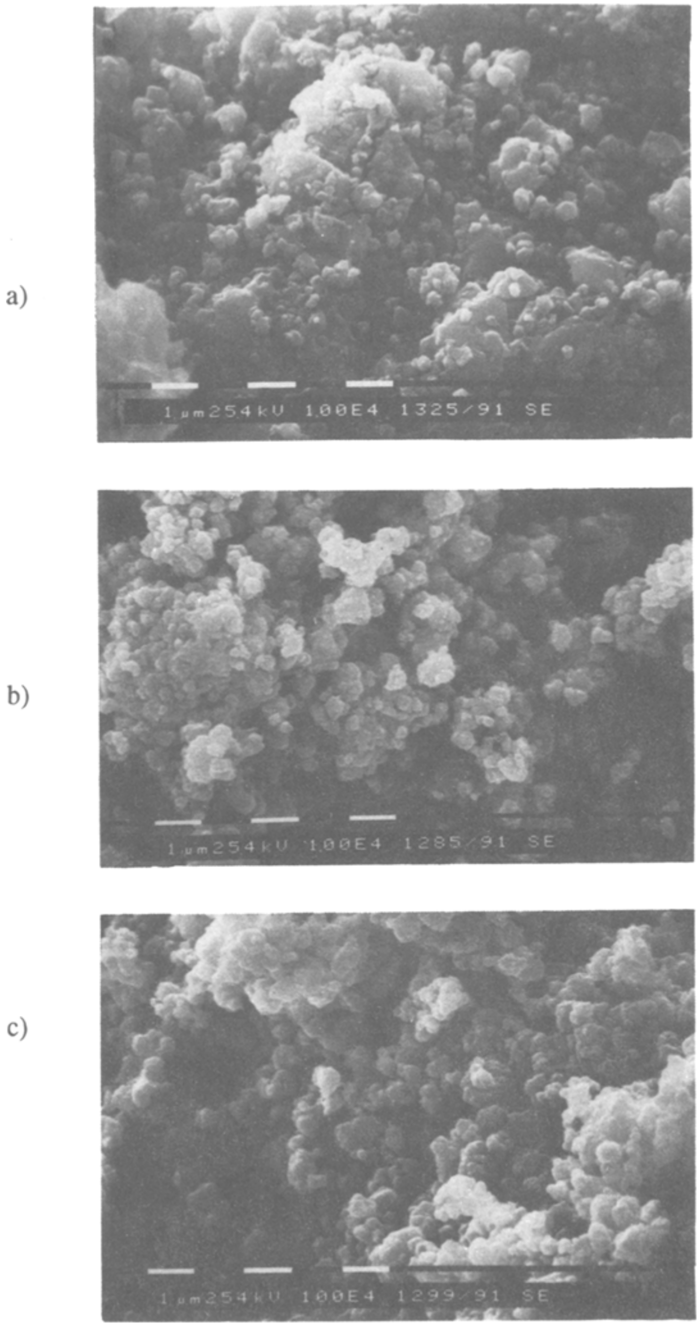

Fig. 2 Scanning electron micrographs showing agglomerated $Cu_{1-x}Zn_xAl_2O_4$ crystals with x=0.3 (Fig. 2a), partly reduced material obtained at ~600°C (Fig. 2b) and the final reduction product made up of $Cu^o/\gamma\text{-}Al_2O_3/Zn_3Al_{94}O_{144}$ obtained at ~1000°C (Fig. 2c)

Thermal reoxidation

Measurements of the reoxidations have been carried out for the reduction products of the $Cu_{1-x}Zn_xAl_2O_4$ spinels with the following compositions: x=0.25, x=0.5 and x=0.75. The samples were heated in molecular oxygen with a heating rate of 10 deg·min^{-1} (Fig. 3). The reoxidations were performed immediately after the reduction, without taking the sample out of the reaction cell.

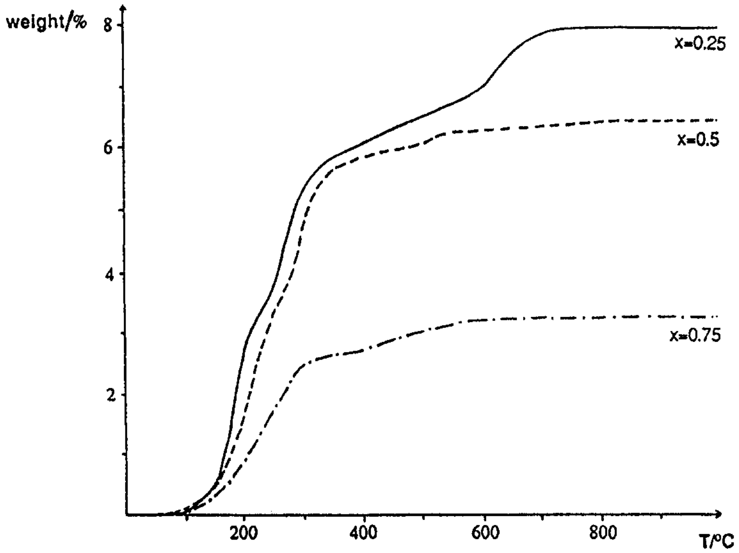

Fig. 3 Thermogravimetric measurements of the reoxidation in oxygen of the products obtained by the reduction of $Cu_{1-x}Zn_xAl_2O_4$ with x=0.25, 0.5 and 0.75 (heating rate: 10 deg/min; O_2 gas flow: 30 ml/min; ambient pressure)

The reoxidation behaviour of the three samples shows no pronounced differences. The weight gains during reoxidation are as expected, i.e. corresponding to the different content of metallic copper.

The curve resulting from the reoxidation of the quaternary sample with the highest copper content (x=0.25) showns three steps. The total weight gain corresponds to the oxidation of the metallic copper to Cu(II). The first step – corresponding roughly to 50% of the over-all weight gain – can be related to the oxidation of metallic copper to copper(I) oxide. Temperature-dependent X-ray diffraction by means of the Guinier-Lenné camera give evidence for the formation of (intermediate) Cu_2O in the temperature range from 140° to 250°C. The formation of copper(II) oxide starts at 240°C. In order to explain this unexpected three-step reoxidation mechanism an attempt was made to determine the products after the second step. The X-ray diffraction pattern shows only very weak and broadened reflections indicating microcrystalline phases. Only CuO and γ-Al_2O_3 could be identified. From Guinier-Lenné measurements the existence of CuO, γ-Al_2O_3 and $Zn_3Al_{94}O_{144}$ is determined, moreover there was found a phase in a temperature range from 400° to 600°C, which could not be identified. At 750°C the formation of a spinel-phase begins.

Samples with lower copper content (x=0.5) show a similar behavior, but the third step is much less pronounced. The thermogravimetric measurement of the third sample (x=0.75) gives no evidence for the formation of Cu_2O.

As final products of all three reoxidations again spinel phases are obtained. This can be explained by the fact that aluminum defect spinels can also be formed with copper.

Discussion and conclusions

The experimental results give evidence, that metal selective reductions in mixed metal oxides strongly depend on the metal cations accommodated in the given structural framework. In the spinel structure, i.e. the close packing of oxygen anions with partially filled octahedral and tetrahedral sites, the presence of metal cations such as Zn or Al being difficult to undergo reduction obviously hinder the potentially easy reduction of metal cations such as Cu. This fact can be explained by 'shielding effects': the CuO_6 octahedral fragment in the spinel structure is generally surrounded or edge-linked by other MO_x polyhedral fragments, which in turn do not undergo reduction at low temperatures. For the reduction of the spinel, Cu cations have to diffuse to the surface. This process obviously takes place at higher temperatures than the temperature onset of the reduction of binary CuO. Consequently, the metallic copper sinters and is not finely dispersed on the metal oxide by-product as one would need it for an active catalyst. In structural frameworks of mixed metal oxides adopting no close oxygen packing and/or an anisotropic structural framework this 'shielding effect' is not as efficient. As example the reduction of perovskite-type $SrRu_xTi_{1-x}O_3$ may be mentioned, where the reduction of Ru is observed at a relative low temperature [9].

As preliminary studies show [10], for spinel systems containing only such metal cations which undergo reduction at low temperatures, the initially defined approach of preparing finely dispersed metals or even alloys (see e.g. [2]) can certainly be realized, i.e. metal selective reduction of mixed metal oxides can be used for the generation of interesting product phases.

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References

1 H. R. Oswald and A. Reller, Ber. Bunsenges. Phys. Chem., 90 (1986) 671.
2 H. R. Oswald, P. Kuhn and A. Reller, Solid State Ionics, 32/33 (1989) 528.
3 A. Galasso, Structure and Properties of Inorganic Solids, International Series of Monographs in Solid State Physics, Vol. 7, Pergamon Press, Oxford 1970, p. 217 ff.
4 R. J. Hill, J. R. Craig and G. V. Gibbs, Phys. Chem. Minerals, 4 (1979) 317.
5 C. Otero Arean, J. S. Diez Vinuela, J. M. Rubio Gonzalez and A. Mata Arjona, Materials Chemistry, 6 (1981) 165.
6 G. C. Chinchen, M. Mansfield and M. S. Spencer, Chemtech., 20 (1990) 692.
7 F. Colin, Rev. Int. Hautes Temp. Refract., 5 (1968) 267.
8 F. Colin and J. Théry, Rev. Chim. Min., 3 (1966) 121.
9 S. Casagrande, H. R. Oswald and A. Reller, Workbook ESTAC5, Nice 1991.
10 R. Kernke, Ph. D. Thesis, University of Zürich, in progress.

Zusammenfassung — Für verschiedene Cu:Zn-Verhältnisse wurde die thermochemische Reaktivität des quartären Metalloxides $Cu_{1-x}Zn_xAl_2O_4$ vom Spinelltyp untersucht. In Sauerstoff oder in inerten Gasen wird keine nennenswerte Reduktion beobachtet. In molekularem Wasserstoff keine bei relativ hohen Temperaturen eine selektive Metallreduktion von Cu beobachtet werden. Das feste Reaktionsprodukt besteht aus gesintertem, schwach dispersem metallischem Kupfer auf einem Zn-Al-O-Metalloxidträgermaterial: ein potentieller Katalysator für die Methanolsynthese. Wegen der gemessenen hohen Reduktionstemperaturen, die zur Sinterung des Kupfers führen, kann die Aktivität dieses Systemes nicht allzu hoch sein.