Thermochimica Acta, 72 (1984) 111--116
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHARACTERIZATION OF CuO-ZnO-Al_2O_3 METHANOL SYNTHESIS CATALYSTS USING TEMPERATURE PROGRAMMED REDUCTION AND THERMAL STABILITY

E.R.A. MATULEWICZ, M.S. de KEIJSER, J.C. MOL and F. KAPTEIJN
Institute for Chemical Technology, University of Amsterdam,
Plantage Muidergracht 30, 1018 TV Amsterdam (The Netherlands)

ABSTRACT

Temperature Programmed Reduction (TPR), thermal stability experiments and SEM were applied to characterise CuO-ZnO-Al_2O_3 catalysts for the methanol synthesis. TPR studies of the calcined catalyst samples show that at least two kind of oxidic species are present on the catalyst surface. The two species, a crystalline CuO and a dispersed CuO-ZnO phase on alumina could be easily reduced below 520 K. Heat treatment above 570 K in a CO/H_2 atmosphere causes rapid deactivation of the catalyst. X-ray diffraction patterns of these catalysts revealed that the deactivation is accompanied by a shift of the Cu^0 reflections, due to the dissolving of Zn^0 in the Cu^0 crystallites.

INTRODUCTION

The physical and chemical properties of CuO-ZnO catalysts for the low pressure methanol synthesis from CO and H_2 have been extensively investigated (ref.1-3). Herman et al (ref.1) observed that the activity of these catalysts was higher than that of pure CuO and ZnO. They found two maxima for the activity of these catalysts, at CuO:ZnO ratios of 3:7 and 2:1, respectively. A solid solution of Cu^I in the ZnO should be responsible for the methanol synthesis activity of the CuO-ZnO system.

The aim of the present investigation was to study the properties of the CuO-ZnO-Al_2O_3 catalyst system; this system resembles more the commercial catalysts for the methanol synthesis than CuO-ZnO (ref.2-3).

EXPERIMENTAL

Materials

A series of CuO-ZnO-Al_2O_3 catalysts with a final composition of 76 wt % Al_2O_3 and 24 wt % loading, the latter ranging from pure CuO to pure ZnO, was prepared by dry impregnation of γ-Al_2O_3 (Ketjen CK 300, 195 $m^2\ g^{-1}$ N_2 BET, 70-100 μm) with aqueous solutions of copper nitrate and zinc nitrate. After drying, a subsequent calcination in O_2 took place at 600 K for about 2 h.

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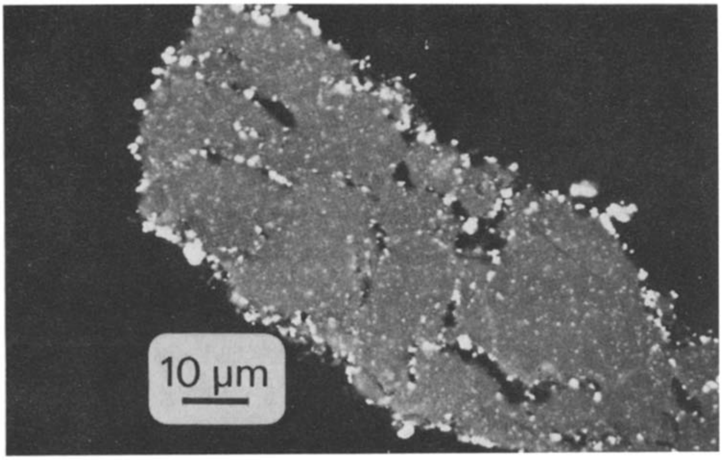


Fig. 1. Photograph of the CZA 12-12-76 catalyst using material contrast in SEM.

Activity measurements

The reaction between CO (>99.5) and H_2 (>99.995) in a ratio of 1:2 (obtained from BOC) was carried out in a micro-catalytic fixed-bed flow reactor, first at 0.35 MPa for 20 h at 543 K; thereafter the activity was measured after 20 h at the standard conditions of 0.35 MPa and 473 K. The products were analyzed by a gas chromotograph on a 1/8" x 3 m Porapak Q column (flame ionization detector).

TPR measurements

In the TPR apparatus a mixure of Ar (>99.998) and H_2 (>99.999) in a ratio of 1:2 (Matheson) was passed successively through the reference cell of a standard thermal conductivity detector, a quartz tube with the catalyst sample (placed in a temperature programmable oven), columns with molecular sieves 4A and 6A, respectively (to remove the H_2O), the sample cell of the detector (to measure the hydrogen consumption) and finally a flame ionization detector (to control if methane was formed during the experiment). In a typical experiment a catalyst sample of 50 mg, contained between two beds of quartz wool, was used. This sample was heated in a flow of Ar/H_2 (20 cc STP min^{-1}) at a heating rate of 1 K min^{-1} to a temperature of 1150 K, while the H_2 consumption was continuously monitored.

RESULTS

By Scanning Electron Microscopy (SEM) not only the outsite of the catalyst can be studied but after enbedding catalyst particles in a polyester resin and subsequently cutting and polishing, cross sections of the catalyst particles can also be studied. Fig. 1 shows the cross section of the CZA 12-12-76 (12 wt %

TABLE 1

H_2 consumption in TPR experiments and activity of the catalysts.

Catalyst[a]	Catalyst loading CuO[b]	ZnO[b]	total[b]	Consumed H_2[c]	Activity[d] MeOH[e]	DME[f]
CZA 00-24-76	-	147	147	59	0.034	0.002
CZA 03-21-76	19	129	148	65	0.034	0.005
CZA 06-18-76	38	111	149	81	0.058	0.009
CZA 10-14-76	63	86	149	111	0.037	0.007
CZA 12-12-76	76	74	150	155	0.040	0.006
CZA 15-09-76	94	55	149	101	0.046	0.008
CZA 18-06-76	113	37	150	135	0.012	0.019
CZA 22-02-76	138	12	150	135	0.003	0.022
CZA 24-00-76	151	-	151	141	0.005	0.024

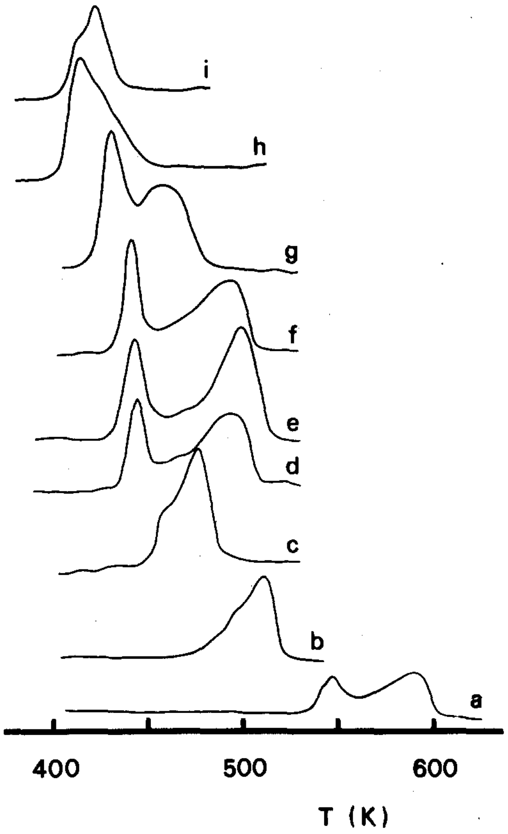
[a] CZA 00-24-76 = 0 wt % CuO, 24 wt % ZnO and 76 wt % Al_2O_3.
[b] µmol present on 50 mg catalyst (calculated quantities from wt %).
[c] µmol consumed for 50 mg catalyst (calculated quantities from TPR peak area).
[d] reaction rate (mol kg^{-1} h^{-1}).
[e] MeOH = methanol.
[f] DME = dimethylether.

CuO, 12 wt % ZnO and 76 wt % Al_2O_3) catalyst, using material contrast in SEM. The presence of two phases is observed: the small white spots and the grey bulk. EDAX analysis in SEM confirmed these two phases: the white spots contain crystalline copper (more than 98 %) and the bulk contains a homogeneously dispersed copper-zinc species on alumina in a ratio of 1:2. The copper particles are built up from copper needles (10^{-7}-10^{-6} m), and are situated on the outside and in the macro pores of the catalyst particles. EDAX analysis and material contrast did not reveal differences in the catalyst structure before and after the activity test.

TPR results are presented in Fig. 2 and Table 1. Pure ZnO on alumina yields two peaks in the TPR spectrum, indicating that two structures on the alumina can be reduced; this ZnO on alumina has only been partially reduced (see Table 1). Addition of a small amount of CuO to the catalyst (CZA 03-21-76 and CZA 06-18-76) causes a shift to lower reduction temperatures and only a broad peak is left. At higher copper contents again two peaks appear, one at about 460-490 K and one at about 410-440 K. At copper contents of 22 wt % and more only the latter peak still exists.

The methanol activity of the catalysts (Table 1) shows two maxima at CuO:ZnO ratios of 1:3 and 5:3, respectively, while the dimethylether activity increases with increasing copper content and stabilizes at copper contents from 18 wt %.

For the determination of the thermal stability of the catalyst, the following procedure was pursued. After activation of the CZA 12-12-76 catalyst sample at 543 K (at which temperature the activity remains constant for at least a week),



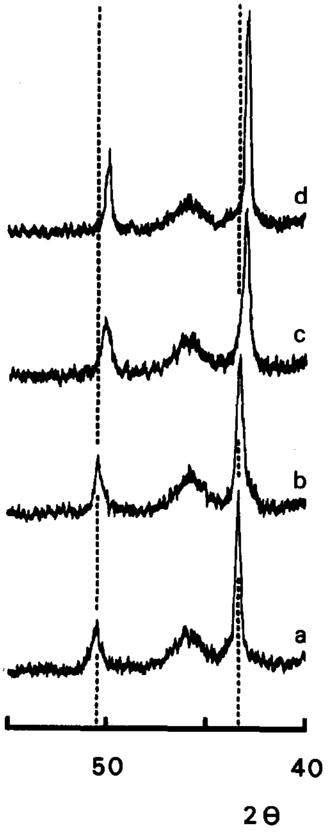


Fig. 2. (left) TPR spectra, H_2 consumption as a function of the temperature for the catalyst samples: 61.0 mg CZA 00-24-76 (a); 58.2 mg CZA 03-21-76 (b); 60.1 mg CZA 06-18-76 (c); 61.8 mg CZA 10-14-76 (d); 56.6 mg CZA 12-12-76 (e); 58.5 mg CZA 15-09-76 (f); 59.2 mg CZA 18-06-76 (g); 41.6 mg CZA 22-02-76 (h); 22.0 mg CZA 24-00-76 (i), all with a heating rate of 1 K min^{-1}.

Fig. 3. (right) X-ray diffraction patterns of the CZA 12-12-76 catalyst samples tested for their thermal stability under CO/H_2 atmosphere at different temperatures: 543 K (a); 573 K (b); 623 K (c); 773 K (d).

the temperature was raised for 3 h at different temperatures above 543 K. Subsequently, the activity for the formation of methanol and dimethylether was measured at standard conditions. Fig. 4 shows that the methanol activity decreases drastically above 543 K, whereas the dimethylether activity increases up to 623 K, but at higher temperatures decreases too. Fig. 3 shows the X-ray diffraction patterns of the samples after the thermal stability tests. The sample treated at 543 K shows the normal Cu^0 reflections, whereas for the

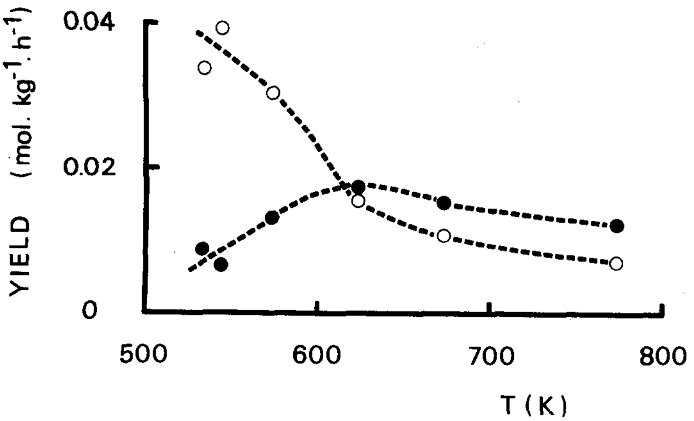


Fig. 4. Activity of CZA 12-12-76 catalyst samples at standard conditions after a thermal stability test under CO/H_2 at different temperatures (o = methanol and ● = dimethylether).

samples treated at higher temperatures the Cu^0reflections are shifted.

DISCUSSION

The EDAX analysis in SEM indicates that two different species are present at the catalyst (CZA 12-12-76) surface after calcination. In the TPR spectrum of this catalyst two species are observed too. X-ray diffraction studies of the catalysts (ref. 4) shows that only above 10 wt % CuO, CuO crystallites are present. From a comparison with the TPR patterns it is concluded that the peak at about 410-440 K corresponds to these CuO crystallites. Subsequently, the peak at about 460-490 K corresponds to the dispersed CuO-ZnO species.

The low temperature peak being pure CuO, the CuO:ZnO ratio of the CuO-ZnO species is calculated from the H_2 consumption to be 1:2 (fig. 2 and Table 1), identical to the EDAX results. When it is assumed that all the CuO present in the CZA 03-21-76 catalyst is reduced during the TPR experiment, the recorded peak represents a CuO-ZnO species with a ratio of 1:2.5, which is, of course, an upper limit. In the same way the ratio of the CZA 06-18-76 catalyst is calculated to be 1:1 and this ratio is about 1:1 for the CZA 18-06-24 catalyst too. In conclusion, the dispersed CuO-ZnO phase becomes easier reducible with increasing copper content of this phase, which is reflected in a shift of the TPR peak to a lower temperature.

Apparently, higher CuO:ZnO ratios of the dispersed phase can not be achieved due to the formation of crystallites CuO. Comparison of the TPR results with those of the activity tests indicate that this dispersed phase must be responsible for the methanol formation. Moreover, the highest activity for methanol formation corresponds to the highest (1:1) CuO:ZnO ratio of the dispersed phase.

Although the CuO-ZnO phase is completely reduced in the TPR experiments below 520 K, it is possible that during the activity tests in CO/H_2 atmosphere these surface structures are partially reoxidized by CO_2 or H_2O formed during the reaction. This is supported by results obtained with a $CuO-ZnO-SiO_2$ system: FTIR measurements indicate that under reaction conditions copper is not present as Cu^0 but has a higher oxidation state instead(ref.5). For $CuO-SiO_2$, a copper species with a more metallic character has been proposed.

X-ray diffraction patterns of the catalyst samples after the activity tests showed that the CuO crystallites had been reduced to Cu^0 crystallites under our reaction conditions. It is obvious that the presence of this Cu^0 species coincides with the formation of dimethylether.

The shift of Cu^0 reflections in X-ray diffraction of samples treated at temperatures above 543 K (see fig. 3) is caused by partial dissolving of Zn^0 (up to 12 %) in the Cu^0 crystallites. The decrease in peakwidth of these reflections indicate crystallite growth. Thus thermal treatment at above 543 K results in sintering of the active dispersed phase, consequently the methanol activity decreases.

We conclude that a dispersed copper-zinc species, probably partially reoxidized at our methanol synthesis conditions, is active for the methanol synthesis, with an optimal copper:zinc ratio of about 1:1. This corresponds with the lowest reduction temperature of this phase in TPR.

ACKNOWLEGMENTS

Thanks due to W. Molleman and Dr. B. Koch (Department of X-ray Spectrometry and Diffractometry) for help in the recording and interpretation of the X-ray diffractograms, and to Ir. H.J.W. Elzerman and Dr. R.L. de Groot (AKZO Research Laboratories Arnhem) for the recording and interpretation of the SEM photographs.

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