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Thermochimica Acta 282/283 (1996) 61–68

thermochimica
acta

Thermoprogrammed reduction and thermoprogrammed hydrogen desorption of and from Cu and Cr oxides supported on alumina and alumosilica[1]

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Abstract

Following our research concerning thermoprogrammed reduction (TPR) and thermoprogrammed desorption (TPD) of and from bimetallic oxides, this paper deals with the Cu–Cr system. The TPR curves give information concerning surface reconstruction induced by the interaction of the catalysts with hydrogen. The hydrogen consumption depends on the method of catalyst preparation, as well as on the nature of the support. The TPD curves evidenced strongly bonded forms of hydrogen chemosorption which are desorbed at high temperatures.

Keywords: Adsorption; Supported catalysts; Surface reconstruction; Thermoprogrammed desorption; Thermoprogrammed reduction

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1. Introduction

Bimetallic oxides of Cu–Cr type are widely used as catalysts for the oxidation of CO from exhaust gases [1–4], hydrogenation of CO [5], total oxidation of some hydrocarbons [6,7], methanol hydrogenation [8], conversion of ethanol to acetaldehyde [7], etc.

This work reports an investigation of the Cu–Cr oxidic unsupported catalyst and that supported on alumina and alumosilica using TPR and TPD techniques. The active

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[1] Dedicated to Takeo Ozawa on the Occasion of his 65th Birthday.

SSDI 0040-6031(96)02821-3

phase was prepared by the thermal decomposition of coordination compounds as precursors.

2. Experimental

2.1. Catalyst samples

The active material of the catalyst was prepared by precipitation of a mixture of $Cu(NO_3).3H_2O$ and $Cr(NO_3)_3.9H_2O$ in the metallic ratio 4:1, in a solution of ethanol and aqueous ammonium hydroxide (10%) in the ratio 1:1 with tartaric acid. The precipitate was filtered and then dried in vacuum at 90°C. The corroboration of the results concerning chemical analysis, IR-spectra and magnetic measurements led to the following formula for the precursor coordination compound: $[CrCu_4Ta_6]\ 5\,H_2O$, where Ta is the tartaric anion.

The unsupported catalysts were prepared by calcining the precursor for 12 h at 750°C.

The supported catalysts were prepared using two procedures:

1. The deposition of the precursor by impregnation on two kinds of supports, namely tabletted alumina (sample A_1) and granulated alumosilica (sample A_2). The supported precursors were dried in vacuum at 90°C for 24 h and then calcined at 750°C for 12 h.
2. The synthesis of the precursor on the support. The mixture of nitrates and tartaric acid solution was deposited by successive impregnation of the two previously mentioned supports. Subsequent drying and calcination as in procedure 1 led to the catalyst samples A_3 (on alumina) and A_4 (on alumosilica).

The surface area of the catalyst samples is listed in Table 1. The metallic content of the supported samples was 8.5–10%.

In order to identify the oxidic phases, X-ray diffraction analysis with copper Kα radiation was applied.

2.2. The experimental device and the operating procedure

TPR measurements were carried out with the thermal conductivity cell previously described [9], by determining the hydrogen consumption from a flowing gas mixture of argon with 10% hydrogen. The TPD measurements were performed using the same cell

Table 1
Surface area of the catalyst samples

Sample	A_1	A_2	A_3	A_4	$\gamma-Al_2O_3$	$\gamma-Al_2O_3+SiO_2$
Surface area/($m^2\,g^{-1}$)	167	124	122	123	161	153

recording the hydrogen evolved in argon which was used as a carrier gas. The gas flow rate was kept at 6 $cm^3 s^{-1}$.

A linear heating program of increasing the temperature in the range 20–500°C with a rate of 10 K min^{-1} was applied. Catalyst sample of 0.11g were introduced in a metallic reactor.

The catalyst samples were pretreated in flowing argon at 500°C for 4 h. After cooling them in flowing argon to room temperature, the carrier gas was switched to the mixture Ar + 10% H_2 and the baseline was stabilised; the system was then heated at 10 K min^{-1} to 500°C while the hydrogen consumption from the carrier gas was recorded (curve HCRI, heating cycle record). The sample was kept at 500°C until the baseline was stable and then cooled in argon to room temperature. After switching on the gas mixture and baseline stabilisation, the heating program was again applied and the curve HCR2 was recorded.

After cooling the sample at room temperature in the flowing gas mixture in order to saturate it with hydrogen, the carrier gas was switched to argon. After stabilising the signal, the sample was linearly heated to 500°C and the TPD curve was recorded.

3. Results

Fig. 1 shows the HCR1 and HCR2 curves for alumina and alumosilica.

As one can see from inspection of the curves, the two supports exhibit identical behaviour, being characterized by practically identical reducibilities. One can notice two peaks at temperatures higher than 360°C on the HCR1 curve. The HCR2 curve exhibits only the low temperature peak located at 370°C.

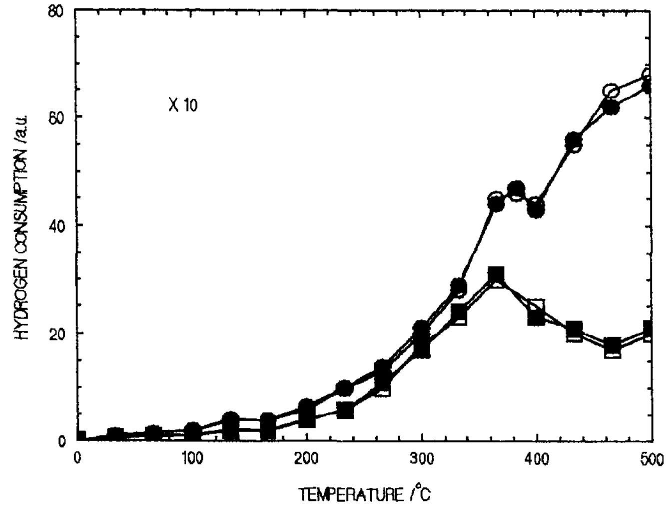

Fig. 1. The heating cycle record HCR1 for alumina (○) and alumosilica (●), and HCR2 for alumina (□) and alumosilica (■).

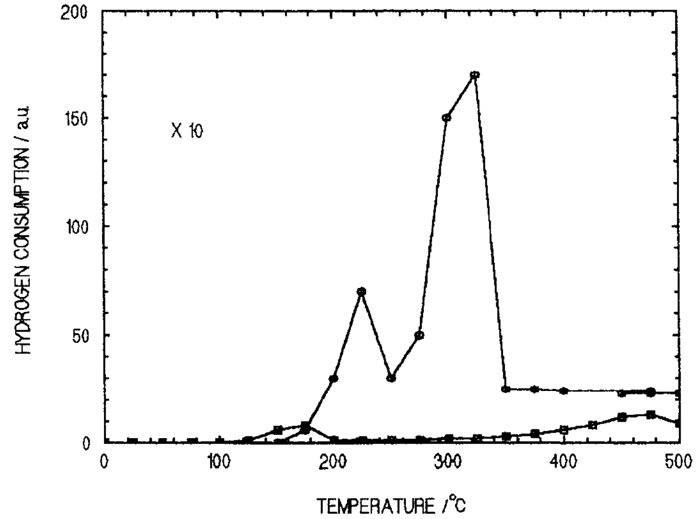

Fig. 2. HCR 1 (●) and HCR 2 (■) for the unsupported catalyst.

Fig. 2 shows the HCR1 and HCR2 curves for the unsupported calcined precursor. These curves show that: the hydrogen consumption in HCR1 is 25 times higher than the corresponding consumption in HCR2; the HCR1 curve, as well as the HCR2 curve, exhibits two peaks located at temperatures in the range 180–400°C.

For A_1 and A_2 supported samples, the HCR1 and HCR2 curves are given in Figs. 3 and 4 which show that the highest hydrogen consumption at lower temperatures is due

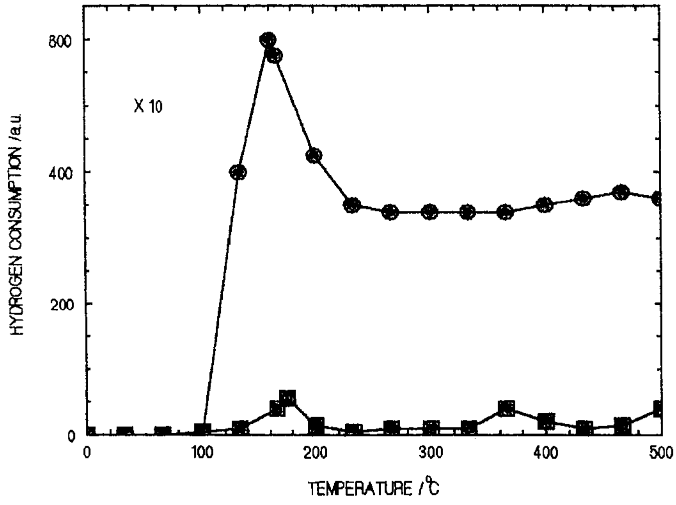

Fig. 3. HCR 1 (●) and HCR 2 (■) for the sample A_1.

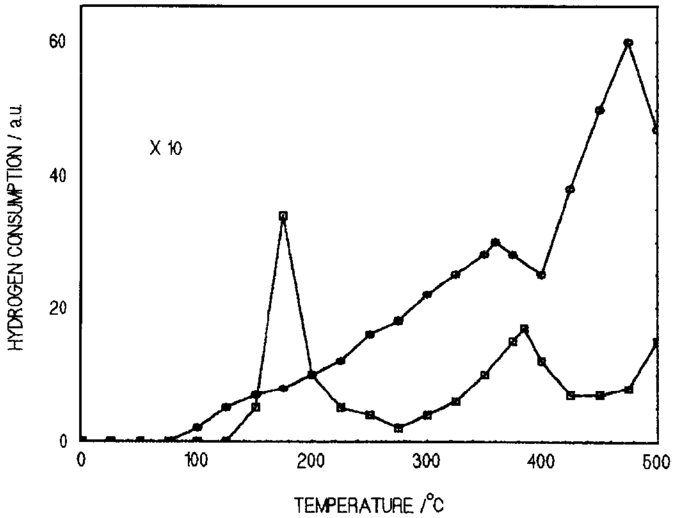

Fig. 4. HCR1 (●) and HCR2 (■) for the sample A_2.

to sample A_1. From the same figures one can see that sample A_2 exhibits the low temperature peak only in the HCR2 curve. The TPR curves shown in Figs. 5 and 6 correspond to samples A_3 and A_4.

As seen from Fig. 5, sample A_3 exhibits a significant peak only at low temperatures, on the HCR1 as well as the HCR2 curves. The slight increase in the hydrogen consumption at temperatures higher than 300°C can be assigned to adsorption on the

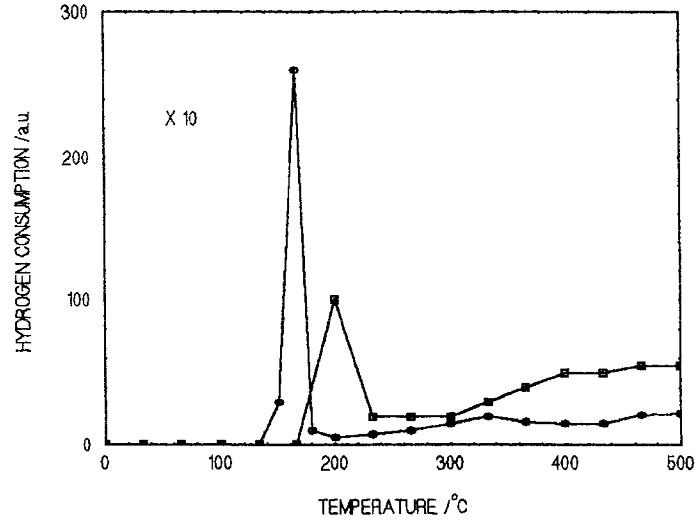

Fig. 5. HCR1 (●) and HCR2 (■) for the sample A_3.

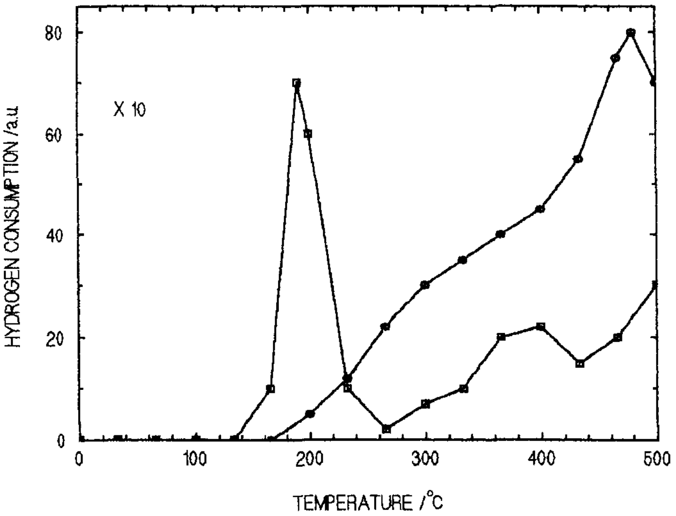

Fig. 6. HCR1 (●) and HCR2 (■) for the sample A_4.

support. Fig. 6 shows that, as in sample A_2, the HCR1 curve for sample A_4 does not exhibit the low temperature peak which appears only in the HCR2 curve.

The TPD curve for sample A_1 is given in Fig. 7. The other samples give similar TPD curves characterized by a continuous increase in hydrogen presence at temperatures higher than 300°C.

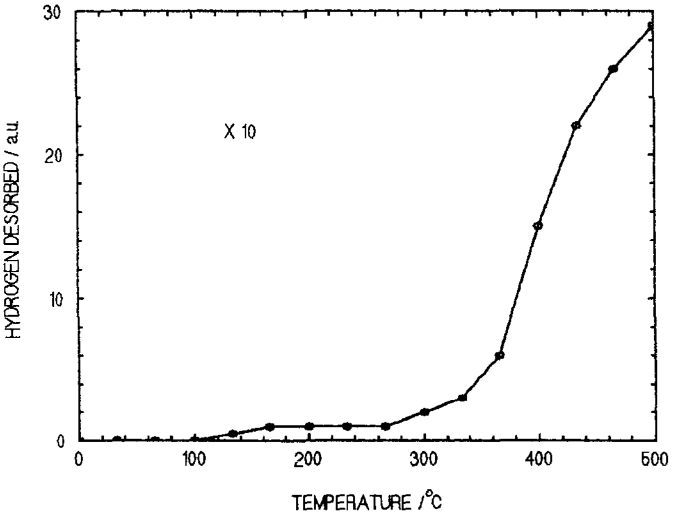

Fig. 7. The TPD for the sample A_1.

4. Discussion

According to the literature data [10,11], the TPR curves for the CuO/alumina catalysts exhibit a single peak located in the temperature range 280–367°C.

The temperature of the peak depends on the procedure used to prepare the sample and the experimental conditions (hydrogen concentration, flow rate and heating rate). For the CuO/alumosilica catalysts, the TPR records exhibit either three peaks [12] or a peak and a shoulder [13] depending of the procedure of preparation as well as on the character of the interaction between the support and the Cu^{2+}ions.

The peaks are located in the temperature range 300–800°C and have been assigned to the changes

$$Cu^{2+} \longrightarrow Cu^{2+} \longrightarrow Cu$$

For the chromium oxide supported on alumina or alimosilica [14], the TPR records exhibit two or more peaks at temperatures higher than 360°C.

Analysis of X-ray diffractograms of the samples showed that the unsupported oxidic sample contains CuO as well as $CuCr_2O_4$ and $Cu_2Cr_2O_4$. In the supported samples, no crystalline oxidic phase except that of the support was detected.

The TPR curves of the supports (Fig. 1) show a low hydrogen consumption only at high temperatures, which can be assigned to the adsorption on alumina taking into account that alumosilica exhibits similar TPR curves. The low temperature peak on the TPR curve for the unsupported samples (Fig. 2) can be assigned to the reduction of CuO.

The high temperature peak on the HCR1 curve is probably due to the transformation $CuCr_2O_4 \rightarrow Cu_2Cr_2O_4$. As shown on the HCR2 curve, the sample has been restructured, not completely reduced, and, consequently, one still records two forms of hydrogen consumption. The low-temperature form can be assigned either to hydrogen adsorption on metallic copper after the first reduction, or to the reduction of the residual forms of CuO.

For the samples supported on alumina (A_1 and A_3), their TPR curves exhibit only one low-temperature peak which can be assigned to the reduction of CuO.

The TPR curves of samples A_2 and A_4 supported on alumosilica show a quite unusual behaviour, in that the high-temperature peak appears only after a previous reduction. This shows once more that the samples undergo reconstruction.

Concerning the TPD curves, these show only hydrogen forms which desorb at high temperatures, i.e. strongly bonded. The weakly bonded forms can be desorbed in the gas flow at room temperature.

5. Conclusions

The presented data concerning the TPR and TPD of hydrogen of and from copper and chromium oxides unsupported and supported on alumina and alumosilica showed that the reduction is generally accompanied by surface reconstruction.

Acknowledgements

The authors express their gratitude to Mrs. Valeria Pocol and Dr. Luminita Patron for generous help in the preparation of the coordination compounds.

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