ELSEVIER

Thermochimica Acta 274 (1996) 307–313

thermochimica
acta

Thermoprogrammed reduction and thermoprogrammed desorption studies of Co and Cr bimetallic oxides

M. Teodorescu [a], V. Georgescu [a], I. Sitaru [a], M.I. Vass [a], E. Segal [b,*]

[a] *Institute of Physical Chemistry "I.G. Murgulescu", Romanian Academy, Spl. Independentei 202, Bucharest, Romania*
[b] *University of Bucharest, Faculty of Chemistry, Department of Physical Chemistry, Bd. Republicii 13, Bucharest, Romania*

Received 18 April 1995; accepted 5 August 1995

Abstract

Bulk (unsupported) bimetallic oxide catalysts and those supported on alumina and alumosilica (type 4Co-1Cr) have been investigated by thermoprogrammed reduction (TPR) and thermoprogrammed desorption (TPD) techniques. Influences of the support and the preparation method on the heating cycle records are demonstrated.

Keywords: Bimetallic oxide catalysts; $CoCr_2O_4$; Co_3O_4; TPD; TPR

---

1. Introduction

Oxidic catalysts of type Co-Cr are frequently used in heterogeneous oxidation and reduction, depollution and synthesis of organic compounds (methanol or higher alcohols, etc.) [1, 2].

The investigation of these catalysts requires the determination of the active element and/or phase, as well as the influence of various factors on the active phase generation. Among these, an important role is played by the preparation method (the precursors, the conditions of calcination, etc.), the nature of the support as well as its interaction with various components, the extent of reduction, etc. Unlike monometallic oxide catalysts, the bimetallic oxidic catalysts exhibit at least two phases and their behavior is different with respect to the individual oxides.

---

[*] Corresponding author.

SSDI 0040-6031(95)02702-5

TPR has proved useful for the investigation of oxidic catalysts.

The supported catalysts prepared by the two above-mentioned procedures (C_1, C_2, C_3, C_4) were dried for 24 h at 90°C and calcinated at 750°C for 12 h.

2. Experimental

2.1. *The catalysts*

The catalysts consist of mixtures of Co_3O_4 and $CoCr_2O_4$ obtained through the thermal decomposition of the double tartrate of cobalt and chromium.

The precursors were obtained by precipitation at pH 7 of a mixture of aqueous solutions of cobalt and chromium nitrates with tartaric acid in a solution of ethanol and ammonium hydroxide in the ratio of 1:1.

After precipitation, the compound obtained was dried in vacuum at 90°C and subsequently submitted to chemical analysis, IR spectrometry, and magnetic and thermoanalytical measurements. All the results obtained gave the formula $[CrCo_4Ta_6].5H_2O$ for the precursor where Ta indicates tartaric anion, with octahedral coordination of the metallic ions.

The unsupported catalyst was obtained by drying the precursor for 24 h at 90°C and subsequently 12 h calcination at 750°C.

In order to prepare the supported catalyst two procedures were used. The first was the synthesis of the precursor on the support through successive impregnations of the solution of tartaric acid and of the solution of the nitrate mixture, for the catalysts denoted C_1 and C_2. The second was the synthesis of the precursor, its dissolution in water and its deposition on the support by impregnation, for the catalysts denoted C_3 and C_4.

Tablets of 6 mm size of γ-Al_2O_3 with 161 $m^2\,g^{-1}$ surface area for the catalysts C_1 and C_3, and grains of 3–5 mm of γ-Al_2O_3 + 20% SiO_2 with 153 $m^2\,g^{-1}$ surface area for the catalysts C_2 and C_4 were used as supports. The metallic content all the catalysts was 8.5–10% by weight.

2.2. *The experimental device*

TPR measurements were carried out by a REACROM Chromatograph, with a thermal conductivity cell as previously described [3], by measuring the hydrogen consumption from a gaseous mixture of argon with 10% hydrogen.

TPD measurements were carried out using the same chromatograph, recording the hydrogen evolved in argon, which was used as the carrier gas.

The gas flow rate was kept at 80cm^3 min^{-1}. A linear programme of increasing temperature with time at a heating rate of 9 K min^{-1} was applied.

The sample mass was 0.11 g. The catalyst was placed in a metallic reactor and put in a furnace that can work either at constant temperature or with the temperature increasing linearly at the above-mentioned heating rate.

2.3. The operating procedures

The catalyst samples were pretreated in flowing argon at 480°C for 4 h. After cooling them in the argon flow to room temperature, the carrier gas was switched to the mixture argon–10% hydrogen. After the baseline was stable, the system was heated at 9 K min^{-1} to 500°C while the hydrogen consumption from the carrier gas was recorded (HCR 1) (HCR being heating cycle record). After this hydrogen consumption cycle, 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 stabilization, the temperature programme was again applied and the TPR curve corresponding to the second heating cycle record (HCR 2) was recorded.

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

It provides information concerning the extent of surface reconstruction as a consequence of the various reduction steps. Moreover, TPR results are quite sensitive to the method of preparation and storage of the catalysts before use.

3. Results

The results for TPR of oxidized unsupported sample 4Co-1Cr are given in Fig. 1. This shows that the hydrogen consumption for HCR 1 is four times higher than the hydrogen consumption for HCR 2. The two HCR differ only quantitatively. In HCR 1, the hydrogen consumption begins at temperatures higher than 300°C and reaches its maximum at 400°C; in HCR 2, a significant maximum is recorded at 280°C in addition to the 400°C maximum which is still present but to a lower extent.

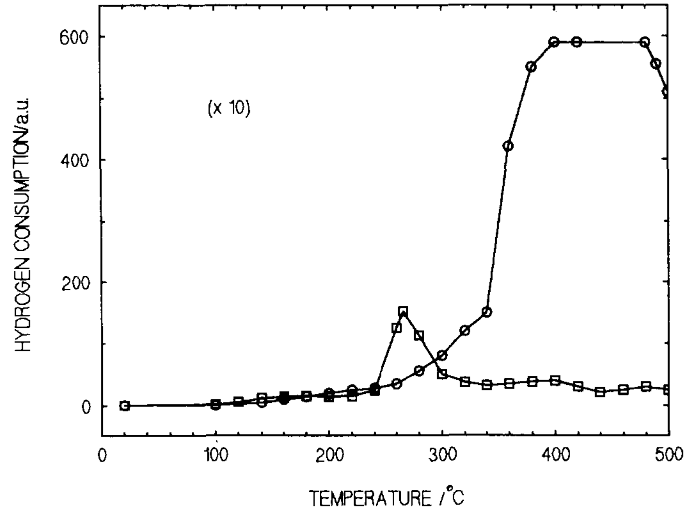

Fig. 1. The heating cycle records HCR 1 (○) and HCR 2 (□) for the unsupported catalyst.

Figs. 2 and 3 show the TPR results for catalysts C_1 and C_3 supported on γ-alumina. As one can see from these figures, the different preparation procedures result in differences in the hydrogen consumption which is twice higher for the sample C_3 in HCR 1.

For HCR 1 both samples exhibit a peak above 400°C and a shoulder at 380°C. HCR 2 shows only the peak at approximately 400°C, but to a lower extent. Of the samples supported on alumosilica, only sample C_4 exhibits a significant consumption of

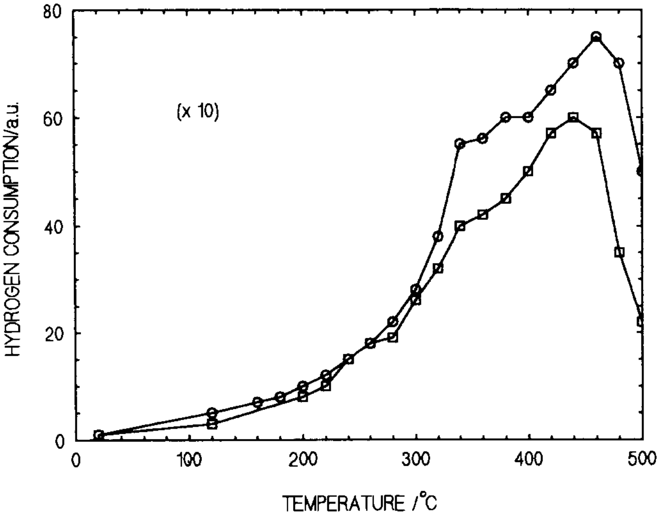

Fig. 2. HCR 1 (○) and HCR 2 (□) for sample C_1.

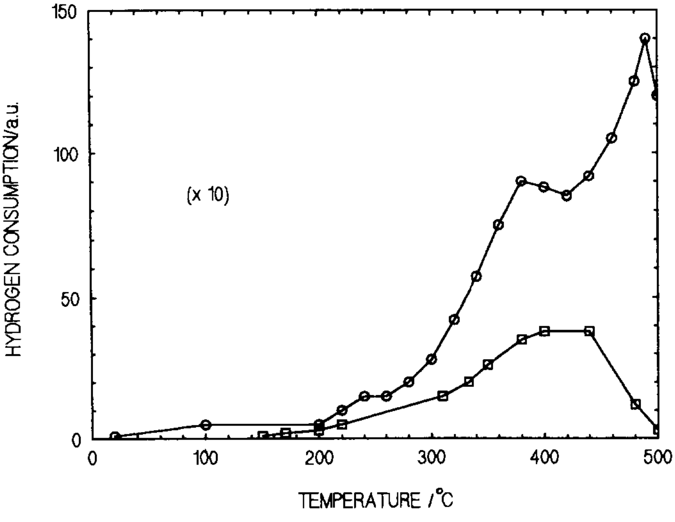

Fig. 3. HCR 1 (○) and HCR 2 (□) for sample C_3.

hydrogen (Fig. 4). HCR 1 exhibits a maximum at 480°C. HCR 2 does not show any hydrogen consumption.

Although not shown qualitatively, the TPD curves for the samples C_1, C_3 and C_4 are similar. The thermodesorption begins at 250°C and follows a continuous curve to 500°C. The TPD curve for sample C_3 is given in Fig. 5.

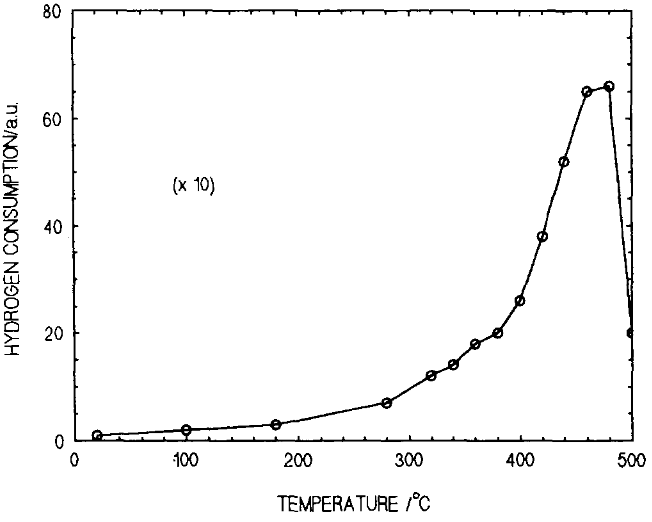

Fig. 4. HCR 1 for sample C_4.

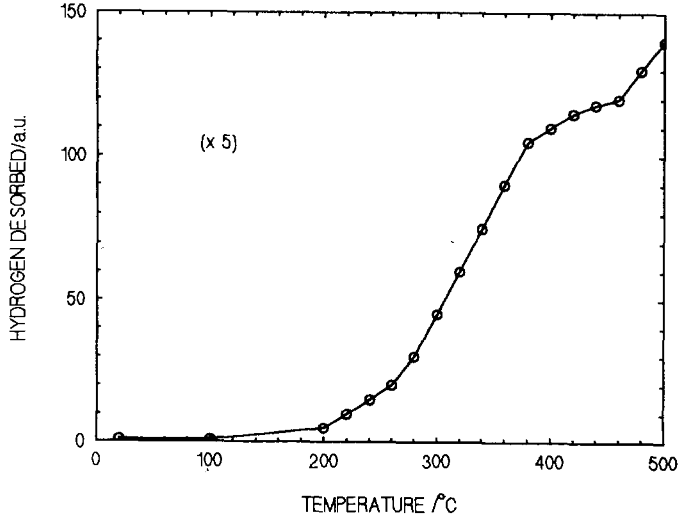

Fig. 5. TPD curve for sample C_3.

The X-ray diffraction data of the unsupported catalyst showed the existence of a solid solution of Co_3O_4 and $CoCr_2O_4$.

In the samples supported on γ-alumina and alumosilica, only the crystalline forms of the supports were identified.

The TPR of Co_3O_4 with hydrogen showed two peaks [4–6] located at 320 and 390°C assigned to the transformation

$$Co_3O_4 \rightarrow CoO$$

$$CoO \rightarrow Co$$

The presence of the support as well as the introduction of Cr^{3+} ion in the spinel structure of Co_3O_4 decreases its reducibility [6].

Depending on the experimental conditions, as well as on the investigated temperature range, as many as four TPR peaks located between 400 and 800°C have been found for Co_3O_4 [9]. Total reduction to metallic cobalt may occur after keeping the sample for a long time at 500°C.

The results obtained using the TPR method confirm those obtained by X-ray diffraction, as well as the results of other authors [4–10]. The existence of HCR 1 and HCR 2 show that the first heating cycle of the sample with hydrogen does not determine the total reduction. The reduction is activated and it occurs in a certain time. Moreover, the sharp peak from HCR 2 at 280°C may be interpreted as oxidic phases which lead to a surface reconstuction. As expected, the supported samples give wide peaks due to the higher surface non-uniformity.

The existence of HCR 2 is probably due to the adsorption of hydrogen on the metallic clusters that appeared during reduction to cobalt as well as to reduction of the oxide traces.

The results obtained by TPD measurements show that hydrogen is strongly bound to the surface and can be desorbed only at temperatures higher than 300°C. No weakly bound hydrogen was detected by the applied methods.

The catalysts supported on alumina exhibited a higher degree of reducibility than those supported on alumosilica, as shown by the higher hydrogen consumption at the reduction.

The existence of strongly adsorbed hydrogen which can be desorbed at high temperatures was confirmed by our TPD experiments.

4. Conclusions

The presence of the support lowers the reducibility of the sample, thus indicating a strong interaction with oxides.

Below 500°C, the reducible forms are Co_3O_4 and CoO. At high temperatures the desorption occurs of hydrogen adsorbed on the metallic forms which appeared on the surface due to the reduction.

Our data concerning catalytic behaviour during the total oxidation of benzene are in preparation for publication.

Acknowledgements

The authors are indebted to G. Dobrescu and V. Chihaia for information processing.

References

[1] X. Xiaoding, E. Doesburg and J. Scholten, Catal. Today, 2 (1987) 125.
[2] M. Blanchard, M. Derule and P. Canesson, Catal. Lett., 2 (1989) 319.
[3] M. Teodorescu, I. Sitaru, A. Banciu and E. Segal, Thermochim. Acta, 233 (1994) 317.
[4] R. Brown, M. Cooper and D.A. Whan, Appl. Catal., 3 (1982) 177.
[5] A Lycourghiotis, C. Defosse, F. Delanney, J. Lemaitre and B. Delmon, J. Chem. Soc. Faraday Trans. 1, 76 (1980) 1677.
[6] T. Paryjczak, J. Rynkowski and I. Karski, J. Chrom., 188 (1980) 254.
[7] Z.T. Fattakova, A. Ukharskii, P. Shiryaev and A.D. Berman, Kinet. Katal., 27 (1986) 884.
[8] G. Busca, F. Trifiro and A. Vaccari, Langmuir, 6 (1990) 1440.
[9] P. Arnoldy and J.A. Moulijn, J. Catal., 93 (1985) 38.
[10] N.W. Hurst, S.J. Gentry, A. Jones and B.D. McNicol, Catal. Rev. Sci. Eng., 24 (1982).