

Note

Effect of activated sorption processes on the results of thermoprogrammed reduction investigations on Fe-Al₂O₃ catalysts

T. PARYJCZAK*, P. ZIELIŃSKI and M. J. FARBOTKO

Institute of General Chemistry, Technical University of Łódź, ul. Zwirki 36, 90-924 Łódź (Poland)

(Received May 22nd, 1984)

Gas chromatography involving thermoprogrammed reduction of catalysts is becoming more popular^{1,2}. This technique is very useful, as it provides information on the course of reduction, its extent, the amount of oxide phases, etc., and for multi-metallic catalysts it allows conclusions to be drawn concerning alloying of the components and their mutual effect on reduction. It is generally assumed that it requires the species to be present in a reducible form².

The investigations presented here for an Fe-Al₂O₃ catalyst show that, in addition to typical reduction processes, temperature-activated hydrogen adsorption can also be observed. Such a phenomenon may complicate the shape of the spectra and lead to incorrect interpretations of the results obtained, so before thermoprogrammed reduction investigations its occurrence or otherwise should be confirmed.

EXPERIMENTAL

Catalysts

Iron catalysts (3%, w/w) were prepared by impregnation³ using as the support 40-60 mesh alumina (Carlo Erba) (BET surface area, 246 m²/g). They were pre-reduced in a stream of electrolytic hydrogen, the temperature being increased gradually from 300 to 870°K.

Methods

The apparatus used for thermoprogrammed reduction measurements, the method of obtaining oxygen and hydrogen and purification of the gases were described previously^{4,5}. The flow-rate of the gas [argon or hydrogen-argon (10:90, v/v)] was 30 cm³/min (STP).

The temperature was increased linearly from 300 to 870°K at the rate of 15°K/min. After heating, the catalysts were stored at the maximum temperature (870°K) for about 30 min. Before thermoprogrammed reduction measurements the catalysts were oxidized at a temperature (T_0) of 300 or 870°K in a stream of electrolytic oxygen for 30 min.

RESULTS AND DISCUSSION

Fig. 1 shows the spectra of 3% Fe-Al₂O₃ obtained after thermoprogrammed reduction of the catalyst sample in Ar-H₂ at 870°K, followed by the treatments indicated for each curve in the legend.

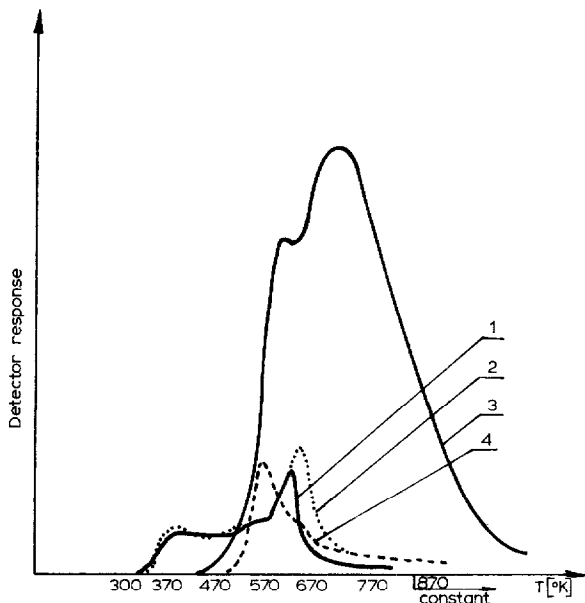


Fig. 1. Spectra for 3% Fe-Al₂O₃ obtained after thermoprogrammed reduction of the catalyst sample in a mixture of 10 vol.-% H₂ in Ar at 870°K, followed by (curve 1) cooling in Ar-H₂ to 300°K, rinsing with argon (30 min) and oxidation (30 min), (curve 2) rinsing with argon (30 min) at 870°K, cooling to 300°K and oxidation (30 min), (curve 3) rinsing with argon (30 min) at 870°K, oxidation at 870°K (30 min) and cooling to 300°K, or (curve 4) rinsing with argon (30 min) at 870°K and cooling to 300°K.

On curve 4, which is a kind of "baseline" of the thermoprogrammed reduction process, one sharp maximum is observed at about 570°K. The procedure used to obtain this curve (contact with oxygen impossible) suggests that the hydrogen sorption observed during temperature increase cannot be due to reduction of earlier oxidized species. Based on previous investigations³ of thermoprogrammed desorption of hydrogen on 3% Fe-Al₂O₃, which showed high hydrogen sorption above 473°K, the maximum observed on curve 4 can be ascribed to temperature-activated sorption. Comparison of this peak with the shapes and sizes of the high-temperature peaks (curves 1 and 2) suggests that they are not due to reduction of the iron oxide phase, but to temperature-activated hydrogen sorption. A shift in the high-temperature maxima (curves 1 and 2) towards higher temperatures may be due first to reduction of oxidized surface layers of iron and only then to temperature-activated hydrogen sorption. In the high-temperature range a difference in courses of curves 1 and 2 is observed, which suggests that oxidation for 30 min at about 300°K does not remove part of the hydrogen sorbed as a result of hydrogen temperature activation, which is removable by rinsing with argon at 870°K (curve 2). The fact that this part of the

hydrogen cannot be removed by means of multi-layer oxidation at room temperature⁶ may indicate that it is not connected with surface layers of metal. This may be one more prerequisite for our earlier considerations concerning the nature of the sorption³.

Quantitative determination of the degree of oxidation of iron catalyst for $T_0 \approx 300^\circ\text{K}$ based on the spectra in Fig. 1 may result in as high as a 2–3-fold error. This is due to the effect of the high percentage (about 70%) of activated hydrogen sorption in the total amount of hydrogen sorbed in the thermoprogrammed reduction process. The percentage error decreases with increasing T_0 (curve 3) because of the considerable increase in total amount of hydrogen sorbed.

It can be concluded that activated hydrogen sorption may have a substantial qualitative and quantitative effect on the course of the thermoprogrammed reduction process, and simple analyses of the spectra ascribing individual peaks to various oxide phases may lead to false interpretations.

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