

TEMPERATURE PROGRAMMED REDUCTION STUDY OF ALUMINA SUPPORTED Fe³⁺ CATALYSTS

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The influence of the calcination temperature and Fe³⁺ content on the solubility of iron(III) in the alumina lattice has been investigated, using temperature programmed reduction (T.P.R.). It was found that the main quantity of Fe³⁺ species is dissolved in the region 200–320 °C. The solubility of the Fe³⁺ was almost constant in the range of 320–665 °C. This is found to be the case irrespective of the Fe³⁺ content at 665 °C. The surface Fe³⁺ species generally differs from the bulk α -Fe₂O₃.

Было исследовано влияние температуры обжига и содержания Fe³⁺ на растворимость железа(III) в решетке окиси алюминия с помощью температурно-программированного восстановления. Было найдено, что в большинстве частицы Fe³⁺ разбавлены в области 200–320 °C. Растворимость Fe³⁺ держалась почти постоянной в интервале температур 320–665 °C. Оказалось, что при 665 °C это не зависит от содержания Fe³⁺. Поверхностные частицы Fe³⁺ обычно отличаются от блочных α -Fe₂O₃.

INTRODUCTION

The ever increasing interest for hydrocondensation of CO, NO reduction and catalytic synthesis of low molecular weight olefins from CO + H₂ on alumina supported Fe³⁺ catalysts [1, 3] requires a reexamination [4] of the structure and texture of these catalysts in relation with their preparation conditions. A complete characterization demands the joint use of various physicochemical techniques. The following important points must be confronted: How much of Fe³⁺ is diluted into the carrier lattice at a given calcination temperature? What kind of Fe³⁺ species is formed on the carrier? What is the Fe³⁺ coordination symmetry at various calcination temperatures and iron(III) contents? Finally, what are the texture modifications of the carrier caused by the iron(III) species? To answer the above questions, we have started the examination of the title system, using a variety of techniques

including temperature programmed reduction, x-ray powder analysis, diffuse reflectance spectroscopy, differential scanning calorimetry and gas-solid chromatography.

In this preliminary communication, we report only the temperature programmed reduction results, which help refine the first of the above mentioned points. A full treatment of our results, as regards the characterization of the above system, will be presented in the near future.

EXPERIMENTAL

Two series of specimens, both denoted by Fe-X-Y-Z, were prepared by the well known dry impregnation of alumina (B. D. H. Broockman II) with Fe(NO₃)₃ x 9H₂O (Merck p.a.) aqueous solutions. In the above formula X denotes the composition as mmol Fe³⁺ per g of alumina, Y the calcination temperature in °C and Z the duration of the calcination in h. The first series contains the samples Fe-X-665-12 (X:0.172, 0.245, 0.388, 0.615 and 0.974); the second one comprises the samples Fe-0.974-Y-12 (Y:200, 320, 420, 500, 600 and 665).

The set-up used and the procedure followed to obtain the T. P. R. curves were similar to those reported elsewhere (5).

RESULTS AND DISCUSSION

Figures 1 and 2 illustrate the T. P. R. curves of the Fe-0.974-Y-12 and Fe-X-665-12 specimens, respectively. The T. P. R. curve of the Fe(NO₃)₃ x 9H₂O calcined at 665 °C for 12 h is also depicted in Fig. 2 (a-Fe₂O₃).

Since the T. P. R. experiments with the support used showed that it was not reducible under our experimental conditions, the peaks appearing in the T. P. R. spectra reflect reducible Fe species.

The most interesting result emerging from an inspection of Fig. 1 is the dramatic loss of reducible Fe³⁺ species brought about by the increase of calcination temperature from 200 to 320 °C. This demonstrates that the main quantity of Fe³⁺ species is diluted into alumina in the temperature region of 200-320 °C. Additional increase of the calcination temperature from 320 to 665 °C causes no visible changes in the amount of diluted Fe³⁺. Moreover, the T. P. R. curves shown in Fig. 2 demonstrate that the quantity of Fe³⁺ diluted into the bulk of the carrier at the maximum calcination temperature, is independent of the Fe³⁺ content. Further, it must be noted that the increase of the calcination temperature and iron(III) content provokes slight modifications of the surface Fe³⁺ species inferred from the

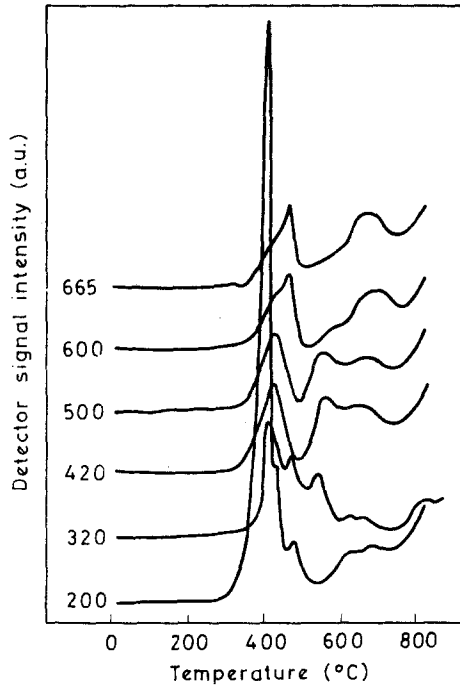


Fig. 1. T. P. R. spectra of the Fe-0.974-Y-12 specimens. The values of Y are indicated. The curves are spaced upwards for clarity

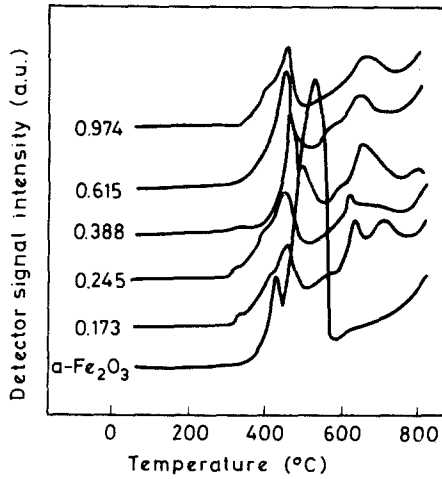


Fig. 2. T. P. R. spectra of the Fe-X-665-12 samples. X values are indicated. The curves are spaced along the coordinate axis for clarity

minor changes observed in the T. P. R. spectra. Finally, a comparison of the T. P. R. curves with that obtained for $\alpha\text{-Fe}_2\text{O}_3$ (produced by the thermal dissociation of $\text{Fe}(\text{NO}_3)_3 \times 9\text{H}_2\text{O}$), suggests that the Fe^{3+} surface species are generally quite different as compared with bulk $\alpha\text{-Fe}_2\text{O}_3$

REFERENCES

1. N. Nahon, V. Perrichon, P. Turlier, P. Bussi re: *React. Kinet. Catal. Lett.*, *11*, 281 (1979).
2. K. Tanabe, H. Ikeda, T. Iizuka, H. Hattori: *React. Kinet. Catal. Lett.*, *11*, 149 (1979).
3. D. Commereuc, Y. Chauvin, F. Hugues, J. M. Basset, D. Olivier: *J. C. S., Chem. Commun.*, *4*, 154 (1980).
4. G. T. Pott, McNicol: *J. C. S. Faraday I*, *68*, 121 (1972).
5. A. Lycourghiotis, C. Defoss , F. Delannay, J. Lemaitre, B. Delmon: *J. C. S. Faraday I*, *76*, 1677 (1980).