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Structural Study of the Al_2O_3-Promoted Ammonia Synthesis Catalyst

II. Reduced State

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The validity of a structural model previously proposed by Hosemann, Preisinger, and Vogel, *Ber. Bunsenges. Phys. Chem.* **70**, 796 (1966) for the ammonia synthesis catalyst (α-Fe promoted with alumina) has been investigated by X-ray diffraction, Mössbauer spectroscopy and DTA. X-Ray diffraction data confirm the presence of paracrystallinity in the catalyst promoted with alumina; however, the Hosemann model ($FeAl_2O_4$ groups statistically dispersed in the lattice of α-Fe) is not in accordance with our Mössbauer spectroscopy results, which can be better accounted for by a model consisting in $FeAl_2O_4$ clusters occluded inside the α-Fe crystallites. The DTA data show that the α–γ transition of the Fe structure plays an important role in the segregation of the oxide clusters.

INTRODUCTION

Herbstein and Smuts (*1*) found the presence of lattice disorder in some commercial iron-based catalysts for ammonia synthesis and for the Fischer–Tropsch process, but its nature was not clarified. By means of a study of the broadening of X-ray diffraction peaks, Hosemann, Preisinger and Vogel (*2*) showed that in the case of catalysts singly promoted with Al_2O_3, the lattice disorder is due to paracrystalline distortions probably caused by the presence of $FeAl_2O_4$ groups inside the bcc structure of α-Fe.

The possibility of insertion of $FeAl_2O_4$ groups inside the lattice of α-Fe was explained by Hosemann, Preisinger, and Vogel on the basis of the compatibility between the steric encumbrance of $nAlO_2^-$ groups and of $3n$ Fe atoms and on the basis of the similarity of the distance between two oxygen atoms tetrahedrally bonded to one aluminum atom, with respect to the distance Fe–Fe in α-Fe along the [100] crystallographic direction. We found it of interest to perform a deeper experimental analysis of the model proposed by Hosemann, Preisinger, and Vogel (*2*). This model substantially differs from the previously accepted structural model (*2*, *3*), in which all the alumina is considered to be epitactically fixed at the surface of the iron particles as a consequence of the analogy existing between the lattices involved. On the other hand, using only the X-ray data obtained by Hosemann, Preisinger, and Vogel, it is not possible to establish for a certainty if $FeAl_2O_4$ groups are statistically dispersed inside the lattice of α-iron or if they form "clusters." In this paper we report on a study of the structural properties of the Al_2O_3-singly-promoted catalyst using three different techniques, viz., X-ray diffraction, Mössbauer spectroscopy and differential thermal analysis (DTA). The samples used were previously studied in the oxidized state as reported in the preceding paper (*4*).

EXPERIMENTAL TECHNIQUES

The samples were prepared by reduction of Al-substituted magnetites containing 2% Al in cationic per cent. The method of preparation of the unreduced samples is reported in the previous paper (*4*). The reduction of the Al-substituted magnetites was performed in a hydrogen atmosphere at 500°C for 20 hr. At the end of the reduction process the samples were passivated at room temperature with nitrogen containing 0.1–0.2% of oxygen. The diffraction spectra for the study of lattice disorder were taken under vacuum with a double Guinier–Jagodzinsky AEG Camera, provided with a Johannson monochromator, using Mo$K\alpha_1$ radiation. Kodirex single emulsion films were employed.

The camera orientations with respect to the primary beam were 0 and −45°. In this way it was possible to obtain all the peaks up to (620) ($s = 2.2\,\text{Å}^{-1}$), the profiles of which were traced by means of a Joyce–Loebl III CS microdensitometer.

The instrumental broadening was measured using a sample of pure Merck iron powder. To correct the experimental integral breadths for the instrumental broadening, we used the Cauchy square function: $(1 + Ks^2)^{-2}$, where K is a constant and s is the reciprocal space variable, as reported in the previous paper (*4*). Following Hosemann, Preisinger and Vogel (*2*), the corrected integral breadths, β, were plotted versus s^2, in order to detect the paracrystalline distortions of the iron lattice of the catalyst.

The Mössbauer spectra of the Al_2O_3-promoted catalyst, and for comparison that of a pure α-iron powder, were obtained at room temperature using a constant-velocity automatic Elron Electronic Industries spectrometer.[1] Velocity scans were calibrated by means of the quadrupole splitting of a polycrystalline sample of α-Fe_2O_3.

DTA tests were performed with a Stone Model 12 B apparatus at a heating rate of 7.5°C/min. The reference material was Al_2O_3. The samples were previously treated with hydrogen at 400°C for 4 hr to eliminate the passivating oxide layer on the surface of the catalyst, and then sealed under vacuum in quartz ampoules. Each sample was repeatedly run to detect changes in peak area and shape. The last run was preceded by 5 to 6 hr annealing at 950°C to remove disorder. An iron sample prepared by reducing a pure magnetite was examined for comparison with the Al_2O_3-promoted catalyst.

RESULTS AND DISCUSSION

In accordance with the results reported by Hosemann, Preisinger, and Vogel (*2*) and by Nielsen (*5*), the catalyst samples were found to show no deviation from the bcc lattice edge value of pure α-iron, within less than 0.02%. In Fig. 1 we report the plots of integral breadths β as a function of s^2 for the X-ray diffraction peaks of the Al_2O_3-promoted catalyst. One of these samples, (a), comes directly from the reduction process made at 500°C for 20 hr. By annealing portions of this sample in an inert

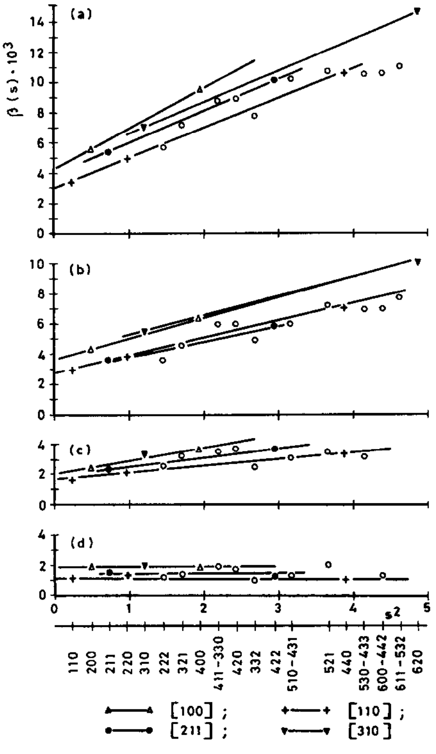

FIG. 1. Integral breadths as functions of the square reciprocal space variable for various crystallographic directions: (a) sample treated at 500°C for 20 hr; (b) sample treated at 800°C for 20 hr; (c) sample treated at 900°C for 20 hr; (d) sample treated at 950°C for 20 hr. Open circles refer to other crystallographic directions.

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[1] Measurements taken at Weizmann Institute, Rehovot, Israel.

atmosphere at 800, 900, and 950°C for 20 hr, we obtained the samples (b)–(d), respectively.

In Table 1 we report, for the crystallographic directions [*h*00] and [*hh*0], the average dimensions of the α-Fe crystallites and the slope *Z* of the plots, both calculated from Fig. 1. The trend of the integral breadths as a function of s^2 for the sample (a) is very similar to that obtained by Hosemann, Preisinger and Vogel (*2*). According to Hosemann's theory, the linearity of the increase of the breadths of the three (*hh*0) reflections is strictly dependent on the presence of paracrystalline distortions. This is supported by the fact that on annealing at 800 and at 900°C, the X-ray peaks are still broadened (Fig. 1), while, if disorder of the first kind were present, the thermal treatment should have caused it to disappear. On the other hand, by means of Mössbauer spectroscopy, no differences were detected between the diagram of the Al_2O_3-promoted catalyst sample and that of a pure iron sample with regard to the position of the six lines of the Zeeman spectrum. This fact does not appear to support a statistical dispersion of $FeAl_2O_4$ groups inside the α-iron structure. In the previous paper we reported the fact that in the unreduced catalyst (2% Al-substituted magnetite), a statistical distribution of nonparamagnetic ions, such as aluminum, inside the spinel structure of magnetite lowers the values of the hyperfine internal magnetic fields. Such an effect could be expected also for the reduced catalyst. The fact that the internal magnetic field inside the iron structure does not decrease with the presence of alumina could be explained in two different ways:

TABLE 1

Average Crystallite Dimensions $\bar{L}$ and Slope *Z* for Al_2O_3-Promoted α-Iron Samples as a Function of the Annealing Conditions

Sample	Crystallographic direction	$\bar{L}$ (Å)	*Z*
(a) (500°C–20 hr)	[*h*00]	230 ± 40	2.7
	[*hh*0]	330 ± 40	2.0
(b) (800°C–20 hr)	[*h*00]	270 ± 40	1.4
	[*hh*0]	360 ± 50	1.1
(c) (900°C–20 hr)	[*h*00]	490 ± 70	0.9
	[*hh*0]	590 ± 70	0.4
(d) (950°C–20 hr)	[*h*00]	540 ± 70	—
	[*hh*0]	830 ± 100	—

(1) alumina or iron aluminate is at the surface of iron crystallites, according to the classical model (*3*);

(2) iron aluminate groups form "clusters" inside the structure of α-iron.

However, only the second case is in agreement with both the X-ray data of Hosemann, Preisinger, and Vogel, and of ourselves, showing paracrystallinity. In this case, as the average number of iron atoms which are neighbours to aluminum atoms strongly decrease with the increasing of cluster size, at a certain value of this size the Mössbauer spectrum should be no more influenced by the presence of alumina in the α-iron lattice, in accordance with our results.

From our X-ray measurements the average size found for iron crystallites is about 250 Å. If we assume, as an extreme hypothesis, that only one iron aluminate cluster is present for each iron crystallite, it is possible to calculate for it an average size of 25 Å. As a matter of fact, the presence of smaller clusters inside each iron crystallite appears to be the most probable average situation. Obviously, on the basis of statistical considerations and taking into account the smallness of the particles, this conclusion does not exclude that a small amount of alumina or $FeAl_2O_4$ is present at the surface of iron crystallites.

The model of an α-iron lattice including iron aluminate clusters has been indirectly confirmed by DTA. It may be seen in Fig. 2 that the α–γ transition of the iron structure (endothermic peak at about 970°C) is greatly influenced by the degree of order of the starting material. In the case of a pure iron sample obtained by reducing pure magnetite, it is possible to obtain a well defined endothermic peak at 970°C for the α–γ transition. In the case of the Al_2O_3-promoted catalyst, on the other hand, the first run reveals only a very small flat peak

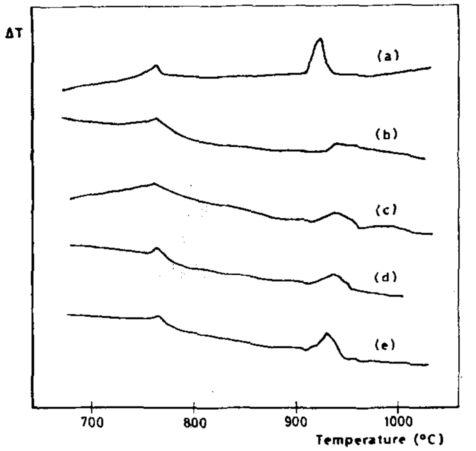

FIG. 2. DTA curves of pure and Al_2O_3-promoted α-Fe. (a) pure iron; (b) Al_2O_3-promoted sample, first run; (c) second run; (d) third run; (e) run performed after prolonged heating at 950°C.

which, during the subsequent cycles of cooling and heating, becomes increasingly sharp. As a possible interpretation of this fact we suppose that the presence of aluminate clusters endotactically occluded in the α lattice gives rise to a slight stabilization of this lattice with respect to the γ-lattice, in various amounts for different iron crystallites. This fact hinders the α–γ structural transformation: actually the transition is diffuse and the corresponding temperature is higher than that of pure iron α–γ transition. At temperatures equal to or higher than the transition temperature, a gradual segregation of iron aluminate crystals occurs; accordingly, by increasing the heating time, the transition peak becomes sharper and the transition temperature falls. From an X-ray analysis of the product at the end of the thermal cycles, iron aluminate diffraction lines were detected, confirming that segregation and recrystallization had occurred.

While the samples annealed at 800 and 900°C have maintained a small amount of lattice disorder, the sample treated for the same time at 950°C was perfectly free of paracrystalline distortions. This confirms that the α–γ transition is the most important cause responsible for the disappearance of disorder, due to segregation of $FeAl_2O_4$ clusters, as suggested by DTA results.

It is worth noticing that from a rough crystallographic analysis it was possible to conclude that the conditions of compatibility for the occlusion of iron aluminate groups in the bcc α lattice of iron (see Introduction) cannot be valid for the fcc γ lattice of iron.

CONCLUSIONS

On the basis of our experimental results, obtained with various techniques, the classical structural model of the Al_2O_3-promoted catalyst is not confirmed, as already shown by Hosemann, Preisinger and Vogel (*2*) from X-ray diffraction data alone. On the other hand, the model proposed by these authors, in which statistically dispersed $FeAl_2O_4$ groups are considered embedded in the lattice of α-iron is not in accordance with our Mössbauer spectroscopy results. It seems more probable that iron aluminate forms clusters (<25 Å, on the average) inside each α-iron crystallite. These clusters are not sufficient, however, to give detectable X-ray diffraction patterns. The DTA data are also in agreement with this picture.

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