

A STUDY OF THE PREPARATION OF SOLID SOLUTIONS IN THE SYSTEM $\alpha\text{-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$

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ABSTRACT

In order to elucidate the formation of precipitated iron catalysts for ammonia synthesis, the formation of solid solutions between $\alpha\text{-Fe}_2\text{O}_3$ and Al_2O_3 was studied in the temperature range 500–950°C. The Al_2O_3 content in the solid solutions was found to be below 15 mole%. At temperatures of 800–950°C, solid solutions are formed at an appropriate rate. Specimens with relatively large specific surface areas are obtained at 800°C.

INTRODUCTION

The $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ system has been the subject of a series of studies [1–11]. The close ionic radii of Fe^{3+} (0.67 Å) and Al^{3+} (0.57 Å) favour the formation of solid solutions between their oxides. However, the results of the different authors on the concentration limits of solubility are very contradictory [4–10]. Rubinshtein et al. [6] and Muan [9] established a solid solution with an Al_2O_3 content of up to 10 mole%. Passarini [4] and David [5] found the amount of Al_2O_3 to reach 25 mole%, whereas Butenko et al. [8] reported a solid solution even at 28 mole%. In a study of the same system obtained by oxidation of alumo-magnetite, Michell and Pouillard [10] established a wider range of solubility.

These contradictions and the interest in the formation and phase composition of precipitated and partly sintered catalysts for ammonia synthesis were the reasons for carrying out a more detailed investigation on the system.

EXPERIMENTAL

Various samples of oxides and their mixtures were prepared by thermal decomposition of coprecipitated and separately obtained iron and aluminium hydroxides. Appropriate amounts of the corresponding nitrates were used as initial compounds. Coprecipitation was carried out with a solution of NH_4OH (12.5%) at 20°C and pH 9. Specimens containing different amounts of Al_2O_3 were heated at 500, 600, 800 and 950°C for 4 h. The phases and

TABLE 1

Sample composition

Sample no.	Al ₂ O ₃ (mole%)	Fe ₂ O ₃ (mole%)
1	100	0
2	0	100
3	1.0	99.0
4	2.9	97.1
5	4.8	95.2
6	9.2	90.8
7	13.2	86.8
8	16.8	83.2
9	33.6	66.4

their lattice parameters were determined with a DRON-1 X-ray diffractometer, while the processes taking place during the calcination were registered by the DTA of samples dried at 80°C. The DTA and TG studies were performed at 20–1300°C with a heating rate of 6°C min⁻¹. The Mössbauer spectra of samples containing different amounts of Al₂O₃ and pure α-Fe₂O₃ and heated at 800°C were obtained. The specific surface areas were measured by a modified BET method [17], whereas the BET method using low-temperature krypton adsorption was applied to surface areas smaller than 2 m² g⁻¹. The composition of the samples is given in Table 1.

RESULTS AND DISCUSSION

Figure 1 shows the TG and DTA curves of ferric hydroxide, aluminium hydroxide and their coprecipitated mixtures. Figure 1 (1) illustrates an endothermal effect of dehydration at 180°C and an exothermal effect at 400°C, which is attributed to the transition from amorphous to crystalline ferric oxide. In accordance with previous studies, Fig. 1 (2) shows endothermal effects corresponding to step-wise dehydration. This is confirmed by the weight loss established during the TG analysis. The first endothermal effect, at 210°C, corresponds, according to ref. 12, to partial dehydration.



The second endothermal effect, at 300°C, is due to further dehydration with the formation of boehmite.



The third endothermal effect, at 450°C, is produced by the complete removal of the hydrate water followed by the formation of amorphous oxide. After that, there is a wide temperature range within which the amorphous substance crystallizes in the form of γ-Al₂O₃. The exothermal effect at 1200°C corresponds to the transition of γ-Al₂O₃ into α-Al₂O₃.

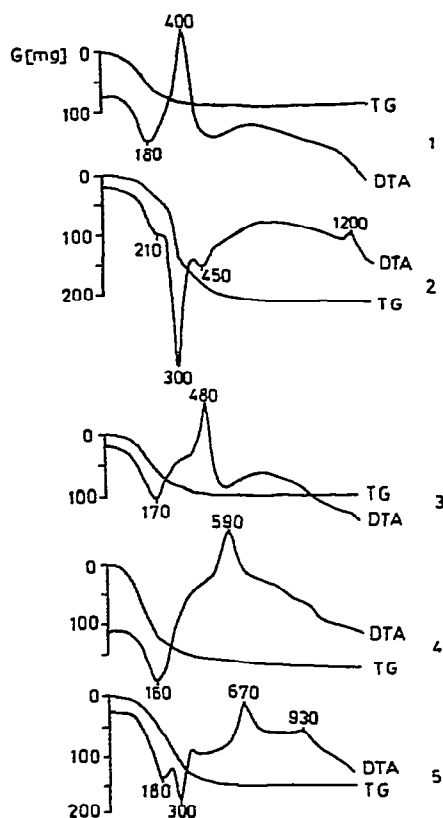


Fig. 1. DTA and TG curves of (1) $\text{Fe}(\text{OH})_3$ *; (2) $\text{Al}(\text{OH})_3$ *; (3) $\text{Fe}(\text{OH})_3 + \text{Al}(\text{OH})_3$ ($\text{Al}_2\text{O}_3 = 4.8$ mole%); (4) $\text{Fe}(\text{OH})_3 + \text{Al}(\text{OH})_3$ ($\text{Al}_2\text{O}_3 = 13.2$ mole%); (5) $\text{Fe}(\text{OH})_3 + \text{Al}(\text{OH})_3$ ($\text{Al}_2\text{O}_3 = 33.6$ mole%).

The DTA curves of some coprecipitated mixtures of ferric hydroxide and aluminium hydroxide [Fig. 1(3–5)] are very similar and are reminiscent of those of the individual hydroxides, with a certain shift of the thermal effects. Obviously, there is an endothermic effect of dehydration at 160–180°C and an exothermic effect of crystallization of Fe_2O_3 at temperatures of 480°C for coprecipitated Fe and Al hydroxides with 4.8 mole% Al_2O_3 , 590°C for 13.2 mole% Al_2O_3 , and 670°C for 33.6 mole% Al_2O_3 . Similar temperature effects for amorphous Fe_2O_3 and $\text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ mixtures were reported in ref. 7. Figure 1 (5) shows a weak exothermic effect at 930°C, which is probably due to the transformation of $\gamma\text{-Al}_2\text{O}_3$ into $\alpha\text{-Al}_2\text{O}_3$. The temperature of transformation is lower than in the case of pure Al_2O_3 (1200°C). This decrease in the presence of $\alpha\text{-Fe}_2\text{O}_3$ was reported previously [6]. No thermal effects indicating solid phase reaction between the two oxides can be seen in the DTA curves.

The values of the specific surface areas are given in Table 2. It is evident that the specific surface area decreases with increasing temperature due to recrystallization and sintering processes and significantly increases with increasing Al_2O_3 concentration.

The X-ray study showed a change in lattice parameters of the samples

* The conventional formulae are given here.

TABLE 2

Specific surface area of samples at different temperatures

Al ₂ O ₃ content (mole%)	Surface area (m ² g ⁻¹) at			
	500°C	600°C	800°C	950°C
0	34.2	4.9	0.29	0.22
1.0	38.7	10.8	0.60	0.30
2.9	42.3	14.4	1.94	0.26
4.8	47.0	19.3	2.18	0.27
9.2	60.5	28.8	4.5	0.26
16.8	84.0	45.7	9.6	1.70
33.6	129.0	81.5	16.2	3.2

compared with those of pure α -Fe₂O₃ ($D_{3d}^6 = R3C$; $a = 5.4224 \text{ \AA}$, $\alpha = 55^\circ 17'$). The extent of this change is different with samples heated at 500, 600 and 800°C. No such difference in the change of the lattice parameter was observed with samples heated at 950°C. The change in lattice parameter with increasing Al₂O₃ concentration and after calcination at different temperatures is given in Fig. 2. It is obvious that in the case of samples heated at 800°C the increase in concentration of Al₂O₃ is associated with a decreasing change of the lattice parameter, which reaches an almost constant value at 13–16.8 mole % Al₂O₃. At 600°C this effect is less pronounced whereas at 500°C a similar tendency is observed. For all samples heated at 500, 600, 800 and 950°C, it can be assumed, on the basis of the change in the lattice parameter, that solid solutions have been formed [13]. The lack of such changes after a given Al₂O₃ concentration indicates a concentration limit of the solubility of Al₂O₃ in α -Fe₂O₃.

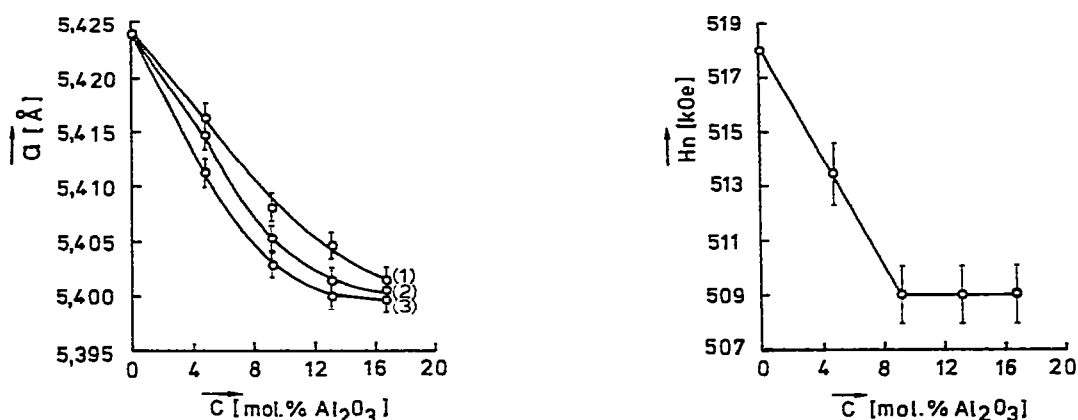


Fig. 2. Change of the lattice parameter with Al₂O₃ content at heating temperatures of (1) 500°C; (2) 600°C; (3) 800°C.

Fig. 3. Internal magnetic field of a α -Fe₂O₃ — Al₂O₃ solid solution vs. Al₂O₃ concentration.

As is known [14], in cases of limited solubility in the homogeneity range, the physico-chemical properties change, normally depending on the composition, according to regularities which are valid for complete solubility. The lattice parameter changes in a similar way, i.e. Vegard's law can be applied to the case under consideration. When Vegard's law is applied to samples with 4.8 mole% Al_2O_3 heated at 800°C , it is established that, at this temperature, almost the whole amount of Al_2O_3 participates in the formation of a solid solution. At 600°C , 3.3 mole % Al_2O_3 is involved in the formation of a solid solution, whereas at 500°C , the participating amount is 2.8 mole%. It should be noted that here Vegard's law is used as a first approximation. There are magnetic interactions in the system and probably it would not be possible to find the concentration dependence of the lattice parameters on the basis of geometric considerations alone. Under our experimental conditions, the concentration of Al_2O_3 in the solid solution changes with the heating temperature. A temperature of 800°C seems to be the most appropriate low temperature for the formation of a solid solution of Al_2O_3 in $\alpha\text{-Fe}_2\text{O}_3$, the whole amount of Al_2O_3 being dissolved. On the other hand, when the Al_2O_3 content is above the limit of solubility, it should act as an independent second phase. X-Ray analysis confirmed the existence of a second phase, $\gamma\text{-Al}_2\text{O}_3$, in a sample containing 33.6 mole % Al_2O_3 heated at 800°C , whereas with a sample containing 16.8 and 33.6 mole% Al_2O_3 heated at 950°C , the second phase is $\alpha\text{-Al}_2\text{O}_3$. Therefore, the X-ray study also confirms the transition of $\gamma\text{-Al}_2\text{O}_3$ to $\alpha\text{-Al}_2\text{O}_3$ in the presence of $\alpha\text{-Fe}_2\text{O}_3$ at temperatures considerably lower than those of the same transition in pure Al_2O_3 . The lattice parameter of $\alpha\text{-Al}_2\text{O}_3$ formed as a second phase differs by 0.44% from that of pure $\alpha\text{-Al}_2\text{O}_3$ obtained by the thermal decomposition of $\text{Al}(\text{OH})_3$ (1200°C , 5 h). Therefore, the second phase of $\alpha\text{-Al}_2\text{O}_3$ for a sample containing 33.6 mole% Al_2O_3 and heated at 950°C is also a solid solution of Fe_2O_3 in $\alpha\text{-Al}_2\text{O}_3$ (according to Vegard's law there must be 7 mole % Fe_2O_3 in $\alpha\text{-Al}_2\text{O}_3$).

The limited solubility of Al_2O_3 in $\alpha\text{-Fe}_2\text{O}_3$ is also confirmed by the measurements of the internal magnetic field by Mössbauer spectroscopy [15]. Data concerning samples with up to 16.8 mole % Al_2O_3 and heated at 800°C are given in Fig. 3. With increasing Al_2O_3 concentration, the internal magnetic field (H_n kOe) decreases from 518 ± 1.4 kOe for $\alpha\text{-Fe}_2\text{O}_3$ to 509 ± 1.4 kOe for a sample containing 9.2 mole % Al_2O_3 , after which the value remains constant.

The addition of Al_2O_3 to $\alpha\text{-Fe}_2\text{O}_3$ and the formation of a solid solution affects the internal magnetic field in two ways. On the one hand, the electron density increases with changing unit cell volume, which results in an increase of the internal magnetic field. On the other hand, with changing surroundings of the Fe^{3+} ion, the internal magnetic field decreases due to "magnetic dilution" of the system. The resulting effect is, in this case, a decrease in the internal magnetic field. This is in agreement with the data of other authors [16]. As is evident from Fig. 3, the decrease in internal magnetic field of the solid solution compared with that of $\alpha\text{-Fe}_2\text{O}_3$ is relatively small. Due to this, the sensitivity of the Mössbauer spectroscopy is inappropriate for the case under consideration.

The X-ray data and the data from the Mössbauer study are in good agree-

ment. They show a limited solubility of Al_2O_3 in $\alpha\text{-Fe}_2\text{O}_3$ which does not exceed 15 mole%. At 800°C and above, solid solutions are formed at an appropriate rate. At the same time, specimens with large specific surface areas can be obtained.

REFERENCES

- 1 R. Brill, *Z. Elektrochem.*, 38 (1932) 669.
- 2 A. Mittach and E. Keuneke, *Z. Elektrochem.*, 38 (1932) 666.
- 3 G.F. Hutig, T. Meyer and H. Kittel, *Z. Anorg. Allg. Chem.*, 224 (1935) 225.
- 4 L. Passarini, *Gazz. Chim. Ital.*, 60 (1930) 544; 62 (1932) 85.
- 5 J. David and A. Welch, *Trans. Faraday Soc.*, 52 (1956) 1642.
- 6 A.M. Rubinshtein, V.M. Akimov and A.A. Slinkin, *Izv. Akad. Nauk SSSR*, 2 (1960) 162.
- 7 M. Dimitrov and R. Banov, *Khim. Ind. (Sofia)*, 1 (1967) 17.
- 8 A.N. Butenko, N.F. Kleshchev and V.I. Atroshchenko, *Katal. Katal.*, 14 (1978) 53.
- 9 A. Muan and C.L. Gee, *J. Am. Ceram. Soc.*, 39 (1957) 207.
- 10 A. Michell and E. Pouillard, *Compt. Rend.*, 228 (1949) 680.
- 11 S.S. Lachinov, A.M. Rubinshtein and V.M. Akimov, *Kinet. Katal.*, 5 (1964) 478.
- 12 A.M. Kalinina, *Zh. Neorg. Khim.*, 4 (1959) 1260.
- 13 E. Kren, B. Molnar and E. Svab, *Solid State Commun.*, 15 (1974) 1707.
- 14 Ya.M. Ugai, *Vvedenie v Khimiyu Poluprovodnikov*, Ed. Visshaya Shkola, Moscow, 1965, p. 308.
- 15 T. Ruskov, *Efekt na Mössbauer*, Nauka i Izkustvo, Sofia, 1975, p. 200.
- 16 D.E. Cox, G. Shirane and S.L. Ruby, *Phys. Rev.*, 125 (1962) 1163.
- 17 G. Bliznakov, I. Bakardjiev and E. Gocheva, *Commun. Bulg. Acad. Sci.*, 4 (1971) 11.