

## COMPARATIVE STUDY OF THE REDUCTION KINETICS OF MAGNETITES AND DERIVED AMMONIA SYNTHESIS CATALYSTS

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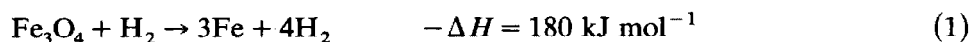
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### ABSTRACT

A study of the reduction behaviour of both natural and synthetic magnetite, as ammonia synthesis catalyst precursors, as well as of the synthesized catalysts, was performed by differential thermal analysis and thermogravimetric analysis in hydrogen under nonisothermal conditions. The presence of promoters in the synthesized catalysts caused shifting of the temperatures of the beginning and end of the reduction toward higher values relative to those of the starting magnetites. The close values of the activation energy of the reduction ( $E$ ) indicated the existence of the same mechanism of reduction of the catalysts and the precursors. Wüstite was not detected by the applied Mössbauer spectroscopic measurements.

### INTRODUCTION

The reduction of magnetite is an important step in the formation of the active form of ammonia synthesis catalysts; it takes place according to the following overall stoichiometric equation



From the standpoint of mechanism, this is a complex reaction which occurs as a summation of processes comprising the diffusion of gaseous reactants and products, diffusion through the solid phase, adsorption and desorption, as well as the chemical reaction itself. It is accepted that the

mechanism of magnetite reduction by hydrogen follows the zonal model, according to which the reduction progresses from the surface inwards to the grain centre [1–3]. In the initial stage (induction period) a thin layer of the oxide FeO (wüstite) is formed on the surface, and through this layer  $\text{Fe}^{2+}$  ions and electrons migrate towards the FeO/ $\text{Fe}_3\text{O}_4$  interface and reduce  $\text{Fe}^{3+}$  ions, forming new FeO molecules. In this way the reduction advances both by enlarging the FeO lattice inside the  $\text{Fe}_3\text{O}_4$  on one side, and extending the reaction of the FeO/gaseous phase on the other, i.e. by shifting the FeO/ $\text{Fe}_3\text{O}_4$  interface towards the interior of the grain.

It was found that the reduction of magnetite proceeds autocatalytically after the induction period [2]. On the kinetic curves a change in the reaction rate was observed under some experimental conditions, and was ascribed to the following two-step reduction:



Although wüstite is thermodynamically unstable below  $570^\circ\text{C}$ , where it decomposes to magnetite ( $\text{Fe}_3\text{O}_4$ ) and elemental iron (Fe), it has been reported that the wüstite phase can be detected below the temperature of its thermodynamic stability [4–7].

The presence of catalysis promoters which are irreducible oxides may affect the course of magnetite reduction, either by changing the electronegative shielding of the iron atoms or by “screening” the iron oxides from hydrogen.

In the present work differential thermal analysis (DTA), thermogravimetry (TG) under nonisothermal conditions and Mössbauer spectroscopy were used in order to perform a comparative study of the reduction behaviour in hydrogen of natural and synthetic magnetites and of the catalysts obtained by crystallization of magnetite melt to which promoters had been added.

## EXPERIMENTAL

### *Sample preparation*

As the basis for the synthesis of catalysts, natural magnetite from Majdanpek Mine (sample 1) and magnetite obtained by precipitating iron(III) hydroxide and reducing it by heating with glucose at  $600^\circ\text{C}$  in an inert nitrogen atmosphere (sample 2) were selected. The catalysts were synthesized in the oxide form by melting mixtures containing fixed proportions of magnetite, an oxide of Al, Ca, Mg or Si, and  $\text{K}_2\text{CO}_3$  in an electrical resistance furnace at  $1600^\circ\text{C}$ , and subsequent crystallization of the melt by fast cooling. Sample 3 was synthesized from natural magnetite, and sample 4 from magnetite obtained by precipitation. A more detailed description of

the procedure for the synthesis of magnetite and catalysts is given elsewhere [8]. For comparative studies a sample of commercial catalyst of a similar composition (sample 5) was used.

### *Sample characterization*

The characterization of magnetite and catalyst comprised both chemical and phase analysis.

The total iron content, the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio in magnetite and synthesized catalysts as well as the promoter contents in catalysts are listed in Table 1.

In the course of catalyst synthesis by melting, the magnetite base was oxidized to some extent, so that the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio in the catalysts was decreased relative to that of the starting magnetite.

The phase composition and the structure of magnetites and catalysts were investigated by X-ray diffraction and Mössbauer spectroscopy. The X-ray analysis was performed on a diffractometer with Cu  $K\alpha$  radiation at 45 kV and 25 mA, using a graphite monochromator. Mössbauer spectroscopy of samples was carried out at room temperature on a spectrometer with constant velocity operation and a  $^{57}\text{Co}$   $\gamma$  radiation source. Calibration of the scanning speed was performed by means of quadrupole splitting of an  $\alpha$ -Fe polycrystalline sample.

By the X-ray analysis of magnetites and of the magnetite phase, a small amount of the wüstite phase was detected in the precipitated magnetite (sample 2). Mössbauer spectroscopy of magnetite samples confirmed the regularity of the crystal lattice in both samples. Analysis of the phase composition of the catalysts showed that the basic phases are magnetite and haematite ( $\alpha$ - $\text{Fe}_2\text{O}_3$ ), the latter being formed by oxidation in the course of melting. According to the results of Mössbauer spectroscopy the magnetic structure is disturbed by the presence of promoter cations which have replaced iron cations in the magnetite lattice in the course of melting. A more complete definition of the phase composition and the structure of magnetites and catalysts was described elsewhere [8].

TABLE 1

Chemical composition of magnetites and catalysts (wt.%)

Sample	$\text{Fe}_{\text{tot}}$	$\text{Fe}^{2+}/\text{Fe}^{3+}$	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	CaO	MgO	$\text{K}_2\text{O}$
1	69.12	0.63	2.00	1.50	0.32	0.29	—
2	73.58	0.56	—	—	—	—	—
3	60.20	0.38	1.18	4.98	1.32	1.60	2.90
4	63.72	0.37	1.38	3.90	1.18	1.80	2.73
5	67.00	0.70	0.55	3.30	3.00	0.67	0.65

## Reduction

The reduction process was monitored by differential thermal and thermogravimetric analysis in a flowing atmosphere of nitrogen purified by passing it over palladium catalyst to remove oxygen and through columns of calcium chloride and 4A molecular sieve for drying. The experiments were performed on a Linseis L 81/22 apparatus, in the temperature range from ambient to the end of reduction (600–700 °C), at a standard heating rate of 10 ° min<sup>-1</sup> and a hydrogen flow of 10 l h<sup>-1</sup>, using Al<sub>2</sub>O<sub>3</sub> as reference.

The determination of kinetic parameters of the reduction, i.e. the activation energy ( $E$ ) and the reaction order ( $n$ ), was performed by treating the nonisothermal thermogravimetric curves according to the method given by Coats and Redfern [9].

Changes in the phase composition of samples in particular reduction steps under conditions of the thermal analysis were analyzed by Mössbauer spectroscopy. The reduction of samples was interrupted when, according to the TG curve, a definite degree of reduction had been attained, by switching off the heating of the sample furnace and replacing hydrogen by nitrogen.

## RESULTS AND DISCUSSION

The results of the thermal analysis in hydrogen of natural magnetite, the synthesized catalyst and the commercial catalyst (samples 1, 3 and 5, respectively) are shown in Fig. 1. The results obtained for the synthetic magnetite and the derived catalyst are given in Fig. 2 (samples 2 and 4, respectively).

On the DTA curves of all the investigated samples (Figs. 1 and 2) a wide asymmetric endothermic peak corresponding to the reduction of Fe<sub>3</sub>O<sub>4</sub> was detected, while on the TG curves different changes in the slope were observed; both findings indicate the complexity of the magnetite reduction process.

The temperatures of the beginning ( $T_i$ ) and the end ( $T_e$ ) of the reduction according to the DT and TG curves, total mass losses ( $-\Delta g$ ) according to the TG curves and the expected mass losses calculated on the basis of the chemical analysis are listed in Table 2.

The temperatures of the beginning and end of the reduction of synthesized catalysts were very close in value one to another, but shifted towards higher temperatures with respect to those of magnetite precursors, as a result of the effects of the promoters. The investigated commercial catalyst sample exhibited somewhat different behavior: the reduction ended at lower temperature than in the case of synthesized samples, and on the TG curve (Fig. 1) a stepwise mechanism of the reduction process was more pronounced. This may be attributed to the existing differences in promoter contents and

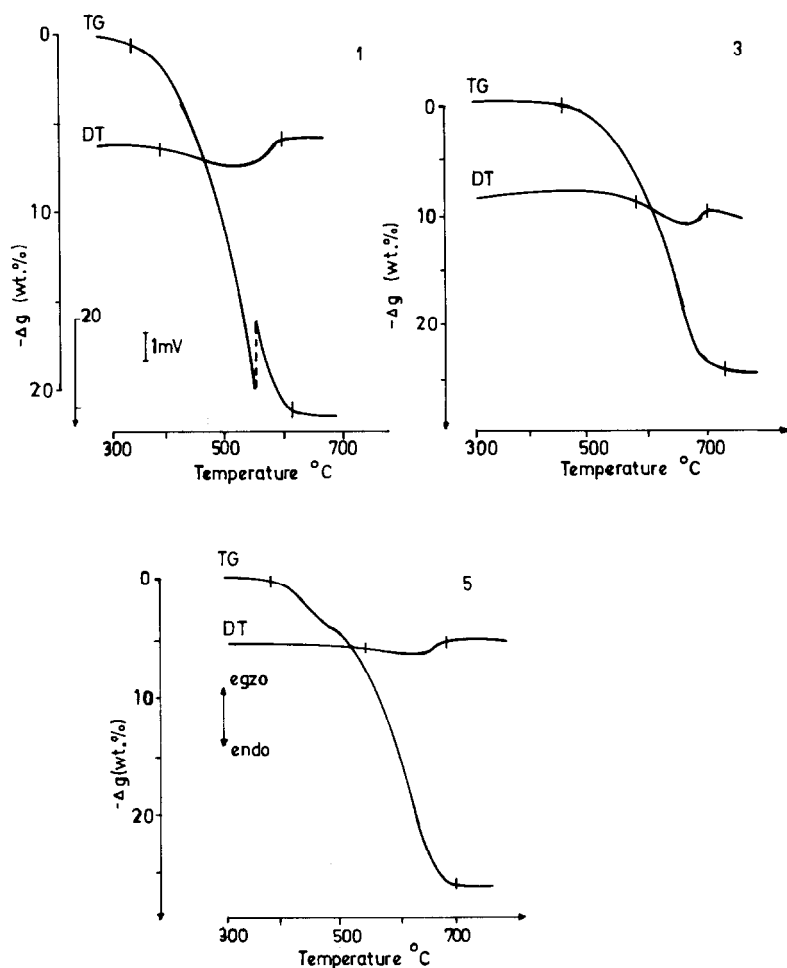


Fig. 1. DTA and TG curves for natural magnetite (1), synthesized catalyst (3) and commercial catalyst (5).

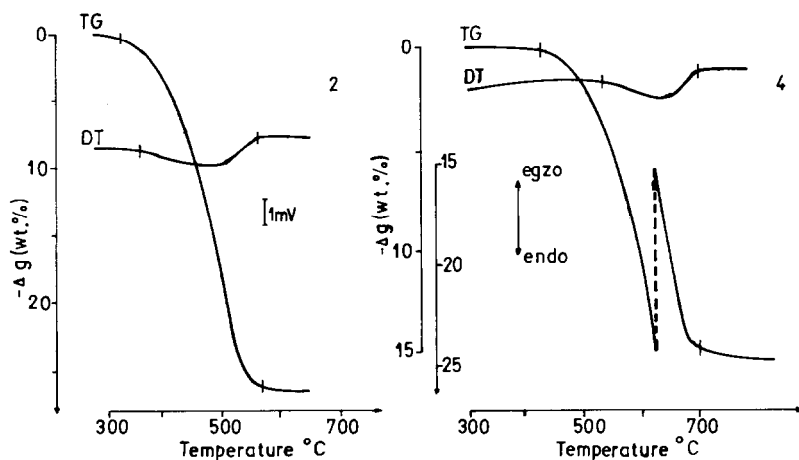


Fig. 2. DTA and TG curves of synthetic magnetite (2) and the derived catalyst (4).

TABLE 2

Results of the thermal analysis of magnetites and catalysts

Sample	DTA		TG		- $\Delta g$ (wt.%)	
	$T_i$ ( $^{\circ}\text{C}$ )	$T_e$ ( $^{\circ}\text{C}$ )	$T_i$ ( $^{\circ}\text{C}$ )	$T_e$ ( $^{\circ}\text{C}$ )	Recorded	Calculated
1	396	600	344	617	25.6	26.5
2	355	562	527	570	26.6	27.6
3	580	700	458	718	24.3	24.3
4	540	700	430	700	24.4	24.6
5	550	680	390	700	26.2	25.4

in the preparation conditions between the synthesized and the commercial catalysts, which resulted in different promoter distribution in the bulk catalyst grains.

The total mass losses due to the reduction are consistent with those calculated on the basis of chemical analysis data, indicating that the reduction of magnetite was complete.

In order to check the stepwise mechanism of the reduction process carried out under conditions of thermal analysis, partly reduced catalyst samples were investigated using Mössbauer spectroscopy.

The reduction was interrupted at temperatures at which the appearance of bivalent iron oxide might be expected. Since the reported temperature (lower than  $570^{\circ}\text{C}$ ) varied over a wide range, from  $500^{\circ}\text{C}$  [6] to  $245^{\circ}\text{C}$  [10], the choice of the temperature of interruption of heating was made on the basis of weight losses on the TG curves corresponding to a 20% degree of reduction for the particular sample. This is a somewhat lower degree than the calculated value of 25% for the total reduction of  $\text{Fe}_3\text{O}_4$  to  $\text{FeO}$ , if considered as a distinct step of the process. In some catalyst samples the reduction was interrupted when a 70% degree of reduction was obtained, which took place at temperatures higher than  $570^{\circ}\text{C}$ .

The Mössbauer spectra of samples 3 and 5 reduced to degrees of 20% and 100% are shown in Fig. 3.

The Mössbauer spectra of sample 4 reduced to degrees of 20%, 70% and 100% are given in Fig. 4. In samples reduced to a degree of 20%, wüstite was not detected by Mössbauer spectroscopy, but solely iron and magnetite phases. The results indicated that, under the reduction conditions applied, the removal of a certain amount of oxygen ions from the magnetite lattice led to the destruction of the spinel and the diminution of  $\text{Fe}^{3+}$  concentration without formation of a stable wüstite phase. Nor were there visible the small amounts of wüstite detected by X-ray diffraction in unreduced samples 2 and 5. In any case, the change in the activation energy at that point of the TG curve suggests the existence of new active centers besides the  $\text{Fe}^{3+}$  ions taking part in the further step of the reduction process. In samples

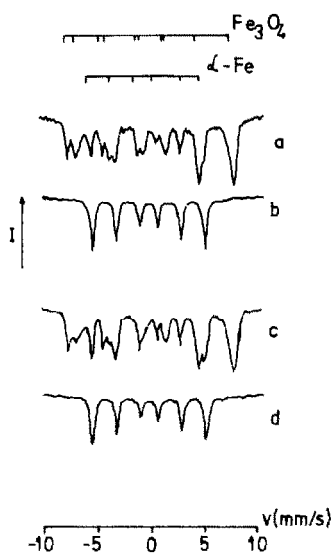


Fig. 3. Mössbauer spectra of samples 2 and 5: a and c, reduced by 20%; b and d, reduced by 100%.

reduced to higher degrees (70% and 100%), only the iron phase was identified; the latter exhibited an inner magnetic field ( $H_i$ ) of 330 kOe, which is very close to the value reported in ref. 11 for pure iron ( $H = 330$  kOe at  $27^\circ\text{C}$ ).

The absence of iron oxide phases at a degree of reduction of 70% may be due to a degree of sample reduction actually higher than that at which the process was interrupted, caused by some additional reduction of iron oxide

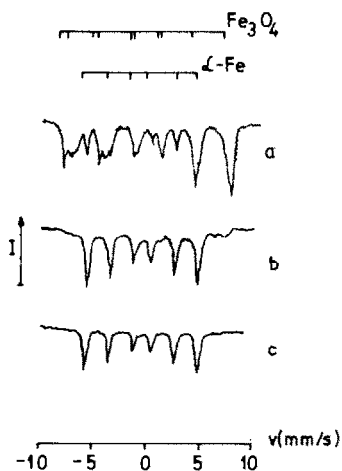


Fig. 4. Mössbauer spectra of sample 4 reduced by: a, 20%; b, 70%; c, 100%.

TABLE 3

Activation energy of reduction

Sample	Temperature range (°)	E (kJ mol <sup>-1</sup> )
1	390–580	86.0
2	370–540	87.7
3	490–700	85.8
4	490–700	85.8
5	450–650	46.5

which may take place until hydrogen is completely substituted for the inert gas in the measuring tube during cooling from the higher temperatures.

The calculated activation energies of the reduction of magnetites and derived catalysts are listed in Table 3. The temperature intervals for which the activation energies were calculated correspond to a range of reduction degree changes from 5–90%.

The activation energies for the investigated magnetic samples and derived catalyst samples are close one to another. A lower activation energy for the commercial catalyst sample (sample 5) relative to the activation energies for synthesized catalysts may be explained by a lower total content of promoters. The reported values for the activation energy of catalyst reduction are different. Thus, values of 60 kJ mol<sup>-1</sup> [12] and 75–79 kJ mol<sup>-1</sup> [13] have been reported, whereas in ref. 14 the values of 113 kJ mol<sup>-1</sup> and 146 kJ mol<sup>-1</sup> were obtained from the temperature dependence of the time required to attain a definite degree of reduction.

Simultaneous determination of the reaction order was achieved by a suitable choice of the exponent in the equations given by Coats and Redfern. The regression degree ( $R$ ) as a measure of the deviation of points from a straight line is closest to 1 (for all samples  $R > 0.996$ ) provided that the reaction order  $n = 1$ , which is in agreement with some of the reported data [13] obtained by other methods for the reduction of magnetite catalysts.

## CONCLUSION

The reduction process of catalysts containing, besides magnetite, reducible oxides of silicon, aluminium, calcium and magnesium is more difficult in the sense that the reduction is shifted towards higher temperatures relative to those of the starting magnetites. Close values for the activation energy and the reaction order of the reduction obtained for the initial magnetites and synthesized catalysts point to the reduction mechanism probably being the same in both cases. The presence of wüstite as a separate phase accumulated during the reduction of catalysts was not detected.



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