Journal of Thermal Analysis, Vol. 6 (1974) 183–192

THERMOGRAVIMETRIC STUDY OF MAGNETITE REDUCTION AT LOW TEMPERATURE

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(Received August 18, 1972; in revised form December 12, 1972)

Results on hydrogen reduction of pure magnetite to iron at low temperature are reported as part of research on ammonia synthesis catalyst. Experimental work was carried out by thermogravimetry and by electron microscopy.

The reduction has a typical S-shaped kinetic curve, with a poorly reproducible induction period. The slope of the reduction curve at 50% conversion ($k_{0.5}$) was found to depend on sample mass (2–50 mg), particle size, temperature (220–280°C) and presence of moisture in the hydrogen ($p_{H_2O} = 1.2$ mm).

The results suggest both interparticle and intraparticle (through iron ash) diffusion to be slow. Morphological examinations of the sample at various reduction degrees support this interpretation.

The reduction of transition metal oxides by hydrogen to give the corresponding metals is a process of great industrial interest, as it is widely used both in the preparation of metallic catalysts and in metallurgical processes.

A great number of papers have been published about this subject and an excellent comprehensive treatise recently appeared [1]. In latter years highly sensitive balances have been increasingly used to study the kinetics of oxide reduction [2]. The availability of highly sensitive gravimetric techniques has allowed the use of very small samples and work with strictly controlled temperature and gaseous phase composition.

In the present paper we report some results on the low-temperature reduction of pure magnetite to iron as part of research on ammonia synthesis catalyst. The work has been carried out with highly sensitive thermogravimetry combined with electron microscopy. Results on the reduction of alumina-containing magnetite will be reported later.

Experimental

Preparation of magnetite

Pure magnetite was prepared by precipitation with ammonia under nitrogen from a boiling solution of pure grade ferric and ferrous chlorides (molar ratio 2 : 1). The precipitate was washed, by magnetic decantation, with oxygen-free water until the disappearance of chlorides, then with ethanol and eventually with acetone. Afterwards, it was heated at 450° in pure argon for 5 hours, then at 1000° for 8 hours in contact with a flowing gas phase of composition 5% CO and 95% CO_2 [3], and finally quickly quenched. A powder X-ray diffraction pattern showed the presence of stoichiometric magnetite.

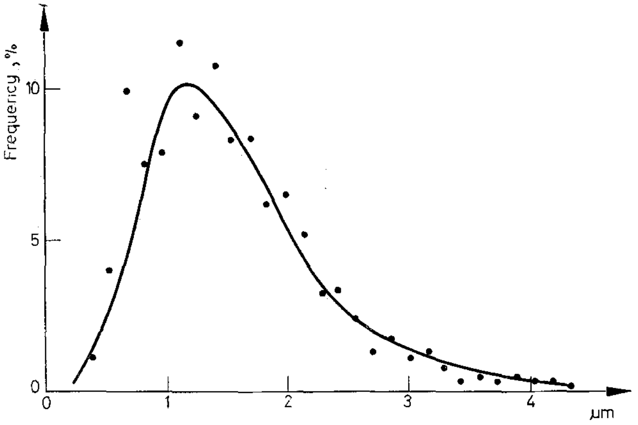


Fig. 1. Grain size distribution, calculated on 2000 particles

The grain size distribution of the sample is reported in Fig. 1. The metal impurities in the magnetite were within 100 ppm (mainly Mn).

Thermogravimetric apparatus

A Cahn RG electrobalance was used, equipped with an antiinductive furnace and a temperature programmer. The thermocouple was placed just below the sample-containing platinum flat pan, suspended from the balance by a tungsten wire. A pressure lower than $5 \cdot 10^{-5}$ torr was obtained near the sample, by means of two oil diffusion pumps followed by liquid nitrogen traps. The gas inlet system consists of fine regulation valves connected with precision flowmeters; it allows a high constancy of the gas flow rate.

Procedure

Kinetic runs were carried out under strictly isothermal conditions (±0.2°). Sample amounts were in the range 2–50 mg. The electrobalance signal was recorded continuously. The sensitivity was 10 μg/chart division in the runs with sample weight higher than 10 mg, and 1 μg/chart division in the runs with sample weight lower than 10 mg.

After evacuation at room temperature at $5 \cdot 10^{-5}$ torr, the sample was quickly heated to reaction temperature, and then the hydrogen flow was started. At atmospheric pressure a stationary flow condition was reached after nearly three minutes, during which weight recording was not possible. As a slight dependence of the reaction rate on the hydrogen flow rate was detected, the latter was kept constant at 12 Nl/h in all the runs. Hydrogen was carefully purified ($H_2O < 5$ ppm; $O_2 < 2$ ppm) by means of Deoxo units and liquid nitrogen traps.

In the runs performed in presence of water (0.15% vol.) the hydrogen was passed through an ice saturator kept at −15° by means of an ultracryostat.

Electron microscopy examinations

Examinations were made by transmission electron microscopy, both directly and on replicas. The replication method has been described elsewhere [4]. In direct examinations, a few micrograms of sample was put on a grid coated with a thin film of SiO, and then reduced with hydrogen. The reduction was carried out after having introduced the sample-holding grid in a suitable teflon holder. Replica examinations were carried out both on unreduced powder and on samples partially reduced with the same procedure used for the kinetic runs. In the latter case the reduction in the TG apparatus was stopped at the required conversion degree, and then the sample was treated with 0.01N HCl (only iron dissolves) and replicated. It was ascertained that such a treatment does not change the morphological aspect of the magnetite.

The average size counting was carried out on replicas. About 2000 particles were measured for each sample by means of a TG 3 Zeiss counter.

Results

Thermogravimetry

While the hydrogen flow rate (in the range 5−20 Nl/h) was found to have practically no influence on the reduction kinetics, the sample mass proved to be an important parameter. In Fig. 2 the reduction rate, taken as the slope of the reduc-

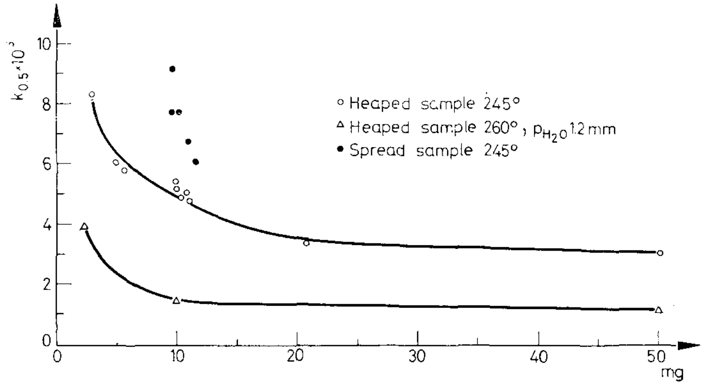


Fig. 2. Dependence of $k_{0.5}$ on sample mass and on sample disposition on the pan

tion curve at 50% conversion ($k_{0.5}$), is plotted versus the sample mass. As may be seen, the reduction rate decreases with the increase of the sample mass, finally reaching a constant value. The reduction rate also depends on the manner of loading the sample on the pan: the reduction process was slower but more reproducible when magnetite powder was heaped than when it was spread (full points in Fig. 2). For this reason the subsequent runs were carried out with heaped samples only. In the presence of water the same behaviour occurs. Moreover, water strongly decreases the reduction rate.

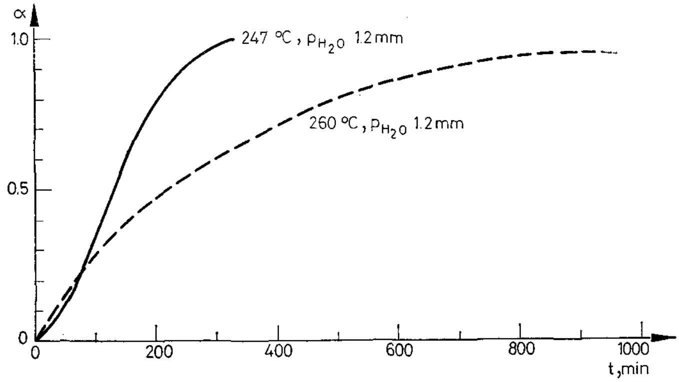


Fig. 3. Typical reduction kinetics

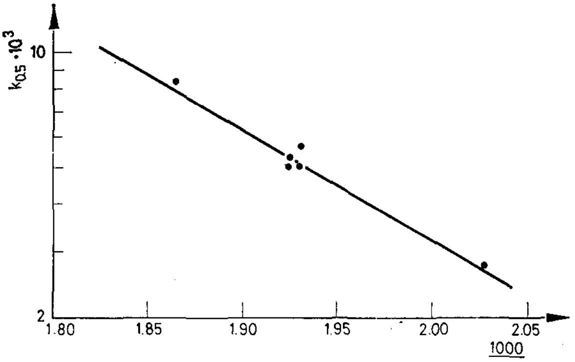


Fig. 4. Arrhenius plot for reduction of pure magnetite

Two typical isothermal curves are reported in Fig. 3. Their shapes are different according to whether or not there is water in the inlet hydrogen. It must be stressed that the initial part of the curve, including the induction period, is poorly reproducible, and that its shape seems to be strongly influenced by the pretreatment of the sample. However, it seems that in presence of water the induction period tends to disappear (that is, reduction starts with the highest rate).

The apparent activation energy, calculated from the Arrhenius plot reported in Fig. 4, is 14.5 Kcal/mole.

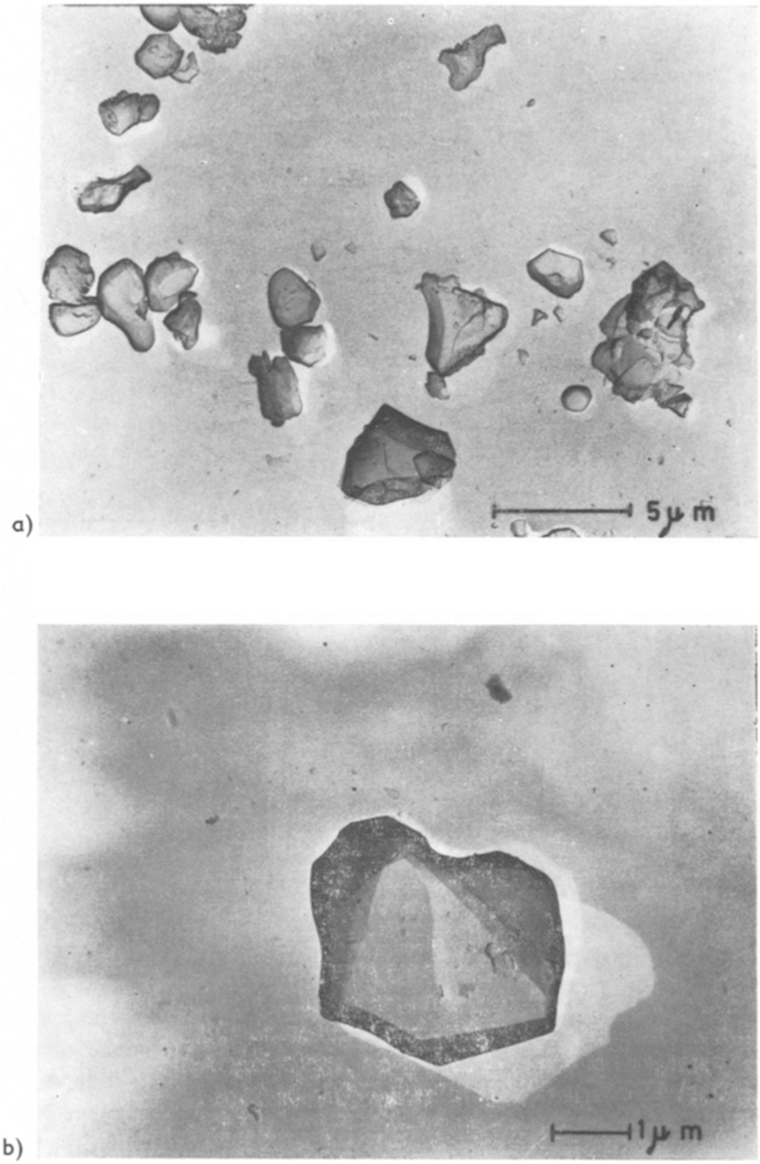


Fig. 5. Carbon platinum replica of unreduced magnetite; a) typical morphological aspect of the powder; b) large and well-grown particle

Electron microscopy

The unreduced sample, whose grain size distribution is shown in Fig. 1, consists of large well-grown particles with smooth facets, on which it is possible to find very small particles deposited during dispersion, and of small particles of irregular shape (Fig. 5). A partially reduced sample is shown in Fig. 6. The reduced phase (iron) can be seen on the edges of the particles as dendritic microcrystals. The replicas of some particles of a sample at a 65% degree of reduction treated with diluted HCl, are shown in Fig. 7. Many large particles not yet attacked by hydrogen are still present, together with partially reduced ones. Other particles appear heavily reacted and crumbled. Two typical partially reduced particles are shown in Fig. 7b.

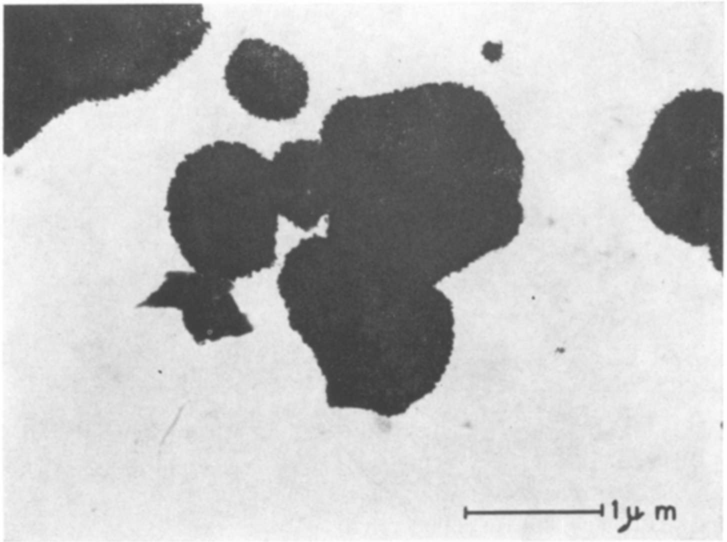
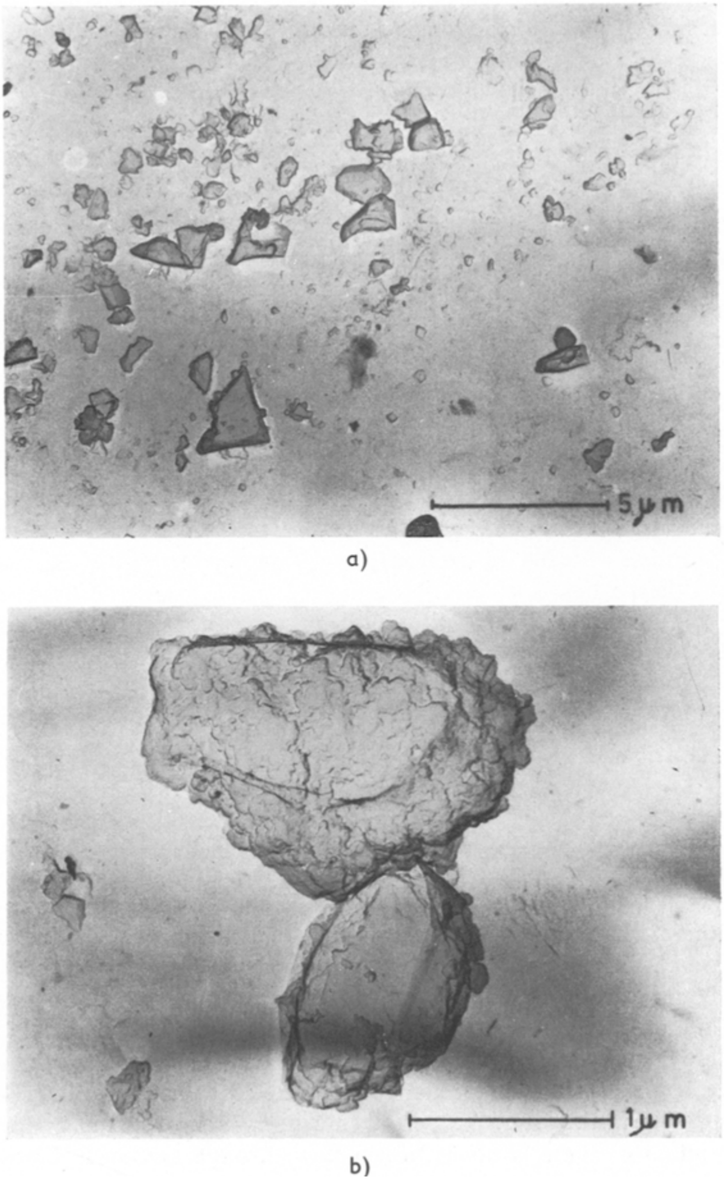


Fig. 6. Partially reduced magnetite. Small dendritic iron crystals are visible on the surface of the particles.

Discussion

I) The reaction rate at 50% conversion

The dependence of the reaction rate on both the sample mass and the manner of loading, as reported in Fig. 2, strongly suggests the presence of important interparticle diffusion phenomena. It should be stressed that, under our experimental conditions, there is no hydrogen flow through the oxide heaps, so that a concentration gradient may easily arise between sample and hydrogen stream. In other words, the magnetite heaps should tend to react as a whole grain, from the outer layer towards the interior, as long as interparticle diffusion is rate-determining. The presence of many unreacted particles in samples reduced up to 65% (Fig. 7) should be regarded as a further indication of such behaviour. The poisoning effect of water can be fitted into this picture. Indeed, in the runs with moist



a)

b)

Fig. 7. Carbon platinum replica of a 65% reduced magnetite, after iron ash dissolution (see text): a) unreduced particles, together with heavily reacted ones, are still present in the sample; b) examples of partially reacted particles

hydrogen the same behaviour of $k_{0.5}$ with the sample mass has been observed, although less pronounced, so that the decrease of the reaction rate due to water could be simply related to the smaller concentration gradient between sample and hydrogen stream. The decrease of $k_{0.5}$ with the sample mass has already been found for other gas-solid reactions, such as nickel oxide reduction [2] and dihydrate nickel oxalate dehydration [5]. In these reactions water was ascertained to have an inhibitory effect, as in our case; however, in nickel oxide reduction the situation seems more complex, though interparticle diffusion has been implicitly suggested [6] to be present in this case too. However, it is not possible to explain the relatively high value of the activation energy and the small rate dependence on the flow rate on the grounds of interparticle diffusion alone. Indeed, runs carried out with a natural magnetite (containing about 0.25% SiO_2, 0.20% MgO and 0.24% Al_2O_3), ground to about 0.4 mm and to $1-5$ μm, showed the $k_{0.5}$ of the latter sample to be four times higher than the $k_{0.5}$ of the former. Further, while in the $1-5$ μm sample the dependence of $k_{0.5}$ on the sample mass was comparable with that reported in Fig. 2, in the 0.4 mm sample this dependence was practically absent.

As a possible explanation, both interparticle and intraparticle ash diffusion of water could be determining under our experimental conditions. The very high reactivity of finely powdered iron (Fig. 6) towards oxygenated compounds, and the relatively high value of the activation energy, suggest that intraparticle ash diffusion consists of water adsorption-desorption steps from the oxide-iron interface up to the particle surface. Furthermore, as the magnetite heaps react as a whole grain, in our case interparticle diffusion would consist of water adsorption - desorption steps taking place at the outer iron surface of the grains inside the heap, until the hydrogen stream is reached.

II) The induction period

The interpretation of the initial part of the reduction kinetics, including the induction period, is difficult, because it depends strongly on random variables introduced during sample pretreatment [7], thus indicating the presence of complex phenomena [8]. Metal nucleation on the oxide surface has been shown to be the initial rate-determining step for iron [9, 10] and nickel oxide reduction. In the case of nickel, nucleation should also depend on the presence of gaseous hydrocarbons coming from diffusion pump oil cracking during vacuum pretreatment [2, 7]. The autocatalytic effect due to the presence of the first metallic germs is ascribed either to hydrogen "spill-over" phenomena [11] or to growth and spreading of the germs [9]. In runs carried out on mixed magnetite-Pt black (10%) samples no changes in the induction period (nor in $k_{0.5}$, as was expected) were found with respect to pure magnetite [12]. In contrast, small amounts of water modify the initial part of the reduction curve (Fig. 3), shortening and often suppressing the induction period. These data, together with the results of Boudart [11] on hydrogen addition to WO_3, suggest that under our experimental conditions, the initial slow step could be the hydroxylation of the oxide surface. The autocatalytic effect could be due to the easier surface migration, by means of hydroxyls on the surface, of the hydrogen activated [11] by iron germs formed during sample pretreatment; their presence could explain both the absence of the accelerating effect of platinum black and the low reproducibility of the initial part of the reduction kinetics.

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RÉSUMÉ — On communique les résultats obtenus en réduisant par l'hydrogène à basse température la magnétite pure en fer, travail faisant partie de recherches sur les catalyseurs pour la synthèse de l'ammoniac. Les expériences ont été effectuées par thermogravimétrie et par microscopie électronique.

La courbe cinétique de la réduction présente la forme en S type, avec une période d'induction peu reproductible. Il est apparu que la pente de la courbe de réduction, pour un taux de conversion de 50% ($k_{0.5}$) dépendait de la prise d'essai (2–50 mg), de la dimension des particules, de la température (220 à 280°) et de la présence d'humidité dans l'hydrogène ($p_{H_2O} = 1.2$ mm).

Ces résultats permettent de conclure que les processus de diffusion sont lents, qu'ils soient de type interparticule ou intraparticule. L'examen morphologique des échantillons pour divers degrés de réduction a confirmé cette interprétation.

ZUSAMMENFASSUNG — Die Ergebnisse der Reduktion von reinem Magnetit zu Eisen durch Wasserstoff bei niedrigen Temperaturen werden als Teil einer Forschungsarbeit über Katalysatoren zur Ammoniak-Synthese mitgeteilt. Die Versuche wurden mittels Thermogravimetrie und Elektronenmikroskopie durchgeführt.

Die Reduktion verläuft nach einer typisch S-förmigen kinetischen Kurve, mit einer schlecht reproduzierbaren Induktionsperiode. Es wurde festgestellt, daß die Steile der Kurve bei 50% Konversion ($k_{0.5}$) von der Probenmenge (2–50 mg), der Teilchengröße, der Temperatur (220 bis 280°) und der Feuchtigkeit des Wasserstoffes ($p_{H_2O} = 1.2$ mm) abhängt.

Diese Ergebnisse lassen darauf schliessen, daß sowohl die interpartikuläre als auch die intrapartikuläre Diffusion (durch die Eisen-Asche) langsam ist. Diese Deutung wird durch morphologische Prüfung des Musters bei verschiedenen Reduktionsstufen unterstützt.

Резюме — Описаны результаты, полученные при восстановлении водородом чистого магнетита в железо, что является частью исследований в области катализаторов синтеза аммиака. Экспериментальная работа проведена термогравиметрическим методом и на электронном микроскопе.

Восстановление характеризуется S-образной кинетической кривой, первая часть которой плохо воспроизводится. Установлено, что ход кривой восстановления при превращении 50% ($\kappa_{0\cdot5}$) зависит от массы образца (2—50 мг), размера зерна, температуры (220°—280°) и от присутствии влаги в водороде (pH_2O) = 1,2 мм).

''Эти результаты говорят о том, что диффузия, как между зернами, так и внутри зерен, происходит медленно. Такая интерпретация подтверждается морфологическими исследованиями образца различной степени восстановления.