STUDIES ON THE REDUCTION OF IRON OXIDE WITH HYDROGEN

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Abstract—Kinetic studies have been carried out on the hydrogen reduction of pure α-Fe_2O_3 doped with foreign metal oxides employing a sensitive micro-gravimetric technique. The results show that the reduction of pure Fe_2O_3 proceeds by a consecutive two-step mechanism via Fe_3O_4, the overall rate being controlled by the topochemical reduction of Fe_3O_4 while that of doped oxides and hematite ore takes place by a different mechanism involving the mixed ferrite formed. In addition, the reduction of pure Fe_2O_3 is catalysed by metal additives in the presence of water vapour. This enhancement in reduction rate is attributed to a "hydrogen spill-over" effect.

INTRODUCTION

The increasing industrial interest in the direct reduction of hematite ores with gaseous reductants containing hydrogen stems from several technical advantages that this method offers over the conventional blast furnace process.

Interest in establishing optimal conditions for the direct reduction reactors has stimulated fundamental studies on the kinetics of iron oxides and ores, which are complicated by the complex heterogeneous nature of the reduction process which comprises several simultaneous reactions. In fact, in the reduction of hematite itself different intermediate oxides have been identified. From a detailed study of the reaction diagram for the reduction of iron oxide by hydrogen, Heizmann and coworkers [1–6] have deduced that the process can be described by three possible mechanisms involving, respectively, a chain of single reactions, a combination of single and double reactions, or a triple reaction. Because of the simultaneous occurrence of several elementary and multiple reactions, studies with pure iron oxide as well as with Fe_2O_3 samples to which small quantities of various other oxides have been added, can be expected to provide useful information on the mechanistic aspects of the direct reduction process. Previous studies by Turkdogan and Vinters [7], Engell and Kohl [8] and Tittle [9] have shown that the reduction rate of α-Fe_2O_3 is generally retarded in the presence of foreign metal oxides.

Another interesting aspect of metal oxide reduction, in general, relates to the role of the so-called hydrogen spill-over (HSO) mechanism. Following the interesting discovery by Khoobiar [10] and Benson et al. [11] that tungstic oxide is reduced by hydrogen to blue H_xWO_3 even at room temperature in the presence of platinum and water vapour, several investigators have reported the catalytic effect of noble metal additives on the reduction of other metal oxides such as V_2O_5 [12], MnO_2 [13], NiO [14, 15], Fe_2O_3, Fe_3O_4 [16], FeO [17], MoO_3 [18], Co_3O_4 [19], UO [19] and CuO [20]. In all these cases, the presence of water vapour is necessary for the catalytic effect of metal additives to be manifested.

These effects have been attributed to the marked activity of the added foreign metal for the dissociative chemisorption of hydrogen and to the activated surface migration or "spill-over" of the chemisorbed hydrogen atoms onto the oxide surface in the presence of water vapour. The role of hydrogen spill-over in topochemical catalytic reactions has been reviewed by Bond and Sermon [21], Il'chenko [22] and Sastri [23]. While there are many instances of foreign metal additives (notably Pt and Pd) acting as HSO catalysts, examples of self-catalysis by the metal oxide to be reduced are relatively few. Autocatalytic HSO effects in such systems are difficult to identify unequivocally and, further, they do not lend themselves readily to systematic investigation. The present paper sets forth the results of a systematic kinetic study of the reduction of pure iron oxide, iron oxide doped with other metal oxides, as well as of natural hematitite with hydrogen. Inter alia, the study furnishes evidence of the role of HSO in the reduction kinetics.

EXPERIMENTAL

Materials

Pure α-Fe_2O_3 was prepared by heating pure ferric nitrate at 475°C to constant weight (8 h). Chemical and X-ray analyses confirmed its purity and phase identity as α-Fe_2O_3. The doped samples were prepared by mixing Fe_2O_3 with weighed amounts of Li_2O, MgO, CaO, Al_2O_3, In_2O_3 and TiO_2 (0.5–5% w/w) and heating the mixture at 850°C for 8 h. The hematite ore sample used in the present study (obtained from Goa, India) had the composition: Fe_2O_3 87.7%; moisture 5.3%; insolubles 3.9% and R_2O_3 (Al_2O_3, TiO_2, etc.) 3.3%.

Pure dry hydrogen was obtained directly from an Elhygen electrolytic hydrogen generator (Milton Roy Co., Petersburg, Florida, U.S.A.) provided with a Pd–Ag alloy diffuser tube cathode.

Kinetic measurement

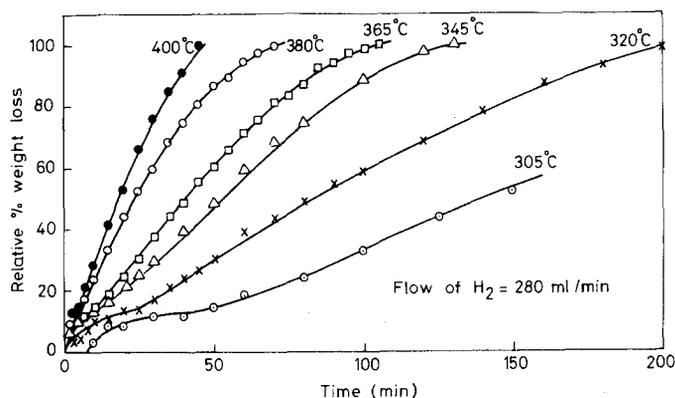The reduction kinetics of the samples (ca 200 mg)

Fig. 1. Plot of percentage weight loss as a function of time for the reduction of pure α-Fe_2O_3 by hydrogen at various temperatures.

were studied gravimetrically using a quartz spring balance with a sensitivity of 2 mg mm^{-1}. The samples were heated in flowing nitrogen until the desired temperature constancy was attained, after which the gas flow was switched over to hydrogen at the desired rate, and the weight change was followed as a function of time.

X-Ray diffraction studies

X-Ray diffraction studies of the unreduced, partially reduced and fully reduced samples were recorded with a Philips X-ray diffractometer at a scan rate of 1° (2θ) per minute using Co-K$_\alpha$ radiation with an iron filter.

RESULTS AND DISCUSSION

### Reduction of pure α-Fe_2O_3

As the rate of reduction was independent of the hydrogen flow rate at 280 ml min^{-1}, the degree of reduction was measured as relative weight loss per cent vs time at various temperatures in the range 300–500°C. The results are shown in Fig. 1. In each of the rate curves obtained at temperatures below 400°C and at hydrogen flow rates < 280 ml min^{-1}, there is break at a relative weight loss of about 11% (which corresponds to the quantitative conversion of Fe_2O_3 to Fe_3O_4). Similar breaks in the rate curves have been observed by

Table 1. X-Ray diffraction data for partially reduced ferric oxide samples

Fe_2O_3*		Fe_3O_4†		Fe‡		Fe_2O_3 reduced to <11%		Fe_2O_3 reduced to >11%		Fe_2O_3–Li_2O reduced to >11%	
d (nm)	I/I_o	d (nm)	I/I_o	d (nm)	I/I_o	d (nm)	I/I_o	d (nm)	I/I_o	d (nm)	I/I_o
		0.297	70			0.297	21	0.297	15		
0.269	100					0.265	33			0.269	19
0.251	50	0.253	100			0.253	100	0.253	100	0.253	100
0.220	30	0.210	69			0.220	10				
				0.2025	100	0.210	21	0.210	24	0.210	28
								0.2025	33	0.2025	60
0.184	40	0.171	60			0.184	10				
0.169	60	0.162	85			0.171	7				
0.159	16					0.169	15				
0.149	35	0.149	85			0.162	22	0.162	18	0.162	30
0.145	32					0.149	43	0.149	24	0.159	25
0.131	20	0.133	20			0.145	1			0.149	48
		0.128	30							0.145	11
0.116	10	0.126	10					0.128	7		
0.114	12	0.121	20	0.117	30			0.117	14	0.128	18
		0.112	30	0.0906	12					0.117	45
0.105	18									0.112	8
										0.105	21

Powder diffraction file publication, Joint Committee on Powder Diffraction Standards, Pennsylvania, 19103, U.S.A. File No. (*) 13.0534, (†) 19.0629, (‡) 6.096.

Colombo et al. [24] as well as by Gazzarini and Lanzavecchia [25]. When plotted as a function of the degree of reduction, the rate reaches a maximum at 11% reduction and then falls to a steady value for the rest of the reduction.

In the reduction of Fe_2O_3 with hydrogen below 570°C, the first step of the process, namely Fe_2O_3 to Fe_3O_4, is exothermic and the reduction to metal is endothermic [26]. Employing the technique of DTA, Keely [27], Viswanath et al. [28] and Ford and Walker [29] have obtained evidence for the stepwise reduction of Fe_2O_3. Further proof for this is provided by Viswanath et al. [30] employing X-ray diffractometry (Table 1), Mössbauer spectroscopy and photomicrography to identify the phases formed at the various stages of reduction. At any stage of reduction, only two phases co-exist, either Fe_2O_3 and Fe_3O_4 or Fe_3O_4 and Fe. Accordingly, the consecutive steps for the reduction of pure Fe_2O_3 as proposed by Russian [31] and Japanese [32] workers are

$$3\,FeO_3 + H_2 \xrightarrow{k_1} 2\,Fe_3O_4 + H_2O$$

$$Fe_3O_4 + 4\,H_2 \xrightarrow{k_2} 3\,Fe + 4\,H_2O$$
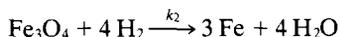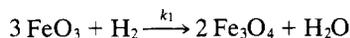
with $k_1 \gg k_2$.

In order to determine whether it is the topochemical process or any of the mass transport steps that prevails as the overall rate-determing step of ferric oxide reduction, the kinetic data have been fitted into various equations applicable to gas–solid reactions [33]. It has been found that the reduction is governed by the topochemical reaction at the interface as the experimental data yield linear plots when plotted as $1 - (1 - x')^{1/3}$ vs time where x' is the fraction reduced corrected to the fraction reduced with respect to magnetite formed. These conclusions are in agreement with one of the theoretical models proposed by Bessieres et al. [34].

Effect of other oxides on the kinetics of oxide reduction

Turkdogan and Vinters [7] have studied the effect of doping with CaO on the reduction of iron oxide and reported that the hematite phase is present until 90% reduction is completed. They have attributed this to the
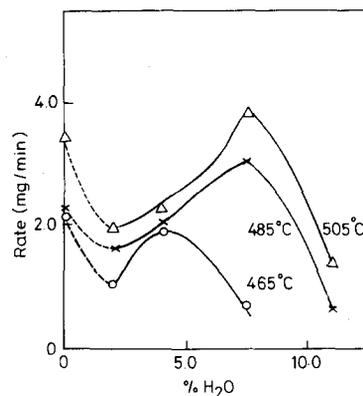

Fig. 2. Variation of rate of reduction of pure α-Fe_2O_3 by hydrogen as a function of water vapour content in the feed.

blocking of interconnecting pores in the hematite by the calcium ferrite formed. From similar studies on mixed oxides, Engell and Kohl [8] have concluded that the oxide with higher enthalpy of formation gets reduced first and as the reduction proceeds the less noble metal (i.e. the one with the lower enthalpy of formation) diffuses with the formation of the metal phase inside the oxide. Further studies on iron ores and solid solutions have led them [35] to conclude that the separation of oxygen and iron involves a diffusion process in the solid phase. A similar conclusion has been arrived at by Tittle [9] for the reduction of iron oxide present in granular calcined bauxite by hydrogen. According to him, the reduction occurs in two steps as follows:

$$Fe_2O_3 + 2\,Al_2O_3 \xrightarrow{H_2} 2\,FeAl_2O_4 \qquad \text{(fast)}$$

$$FeAl_2O_4 \xrightarrow{H_2} Fe + Al_2O_3 + H_2O \quad \text{(slow)}$$

We have also studied the effect of added metal oxides like Li_2O, MgO, CaO, Al_2O_3, In_2O_3 and TiO_2 on ferric oxide reduction [36] and the results obtained are summarised below.

(1) The addition of small amounts of foreign metal oxides retards the overall reduction rate, *irrespective*

Table 2. Activation energy values for the reduction of Fe_2O_3 with different oxides in the range 460–500°C

No.	Sample	Energy of activation (kJ mol^{-1})
1	Pure Fe_2O_3 (without heat treatment)	57.1
2	Fe_2O_3 heated to 850°C	72.7
3	Fe_2O_3 mixed with MgO	110.5
4	Fe_2O_3 mixed with Al_2O_3 Fe_2O_3 mixed with In_2O_3 Fe_2O_3 mixed Li_2O	108.4
5	Fe_2O_3 mixed with TiO_2	130.0
6	Hematite ore	89.9

of the nature of the oxide, indicating thereby that the structural factor plays an important role in the reduction kinetics of iron oxide. This is clear from the values of activation energy for reduction of various iron oxide samples given in Table 2. The rate is independent of the concentration of the added oxide which again shows that electronic factors are not relevant in the reduction process. It is possible that Fe^{3+} ions in Fe_3O_4 (an inverse spinel) occupy both tetrahedral and octahedral holes, while all the Fe^{2+} ions are in octahedral geometry. Because of the similarity of the co-ordinate geometry, the Fe^{3+} ions can easily undergo reduction to the Fe^{2+} state, which undergoes, in turn, further reduction after a critical concentration of Fe^{2+} ions is reached. In the case of the doped ferric oxide samples, the spinel phase formed (normal and inverse) and its accumulation at the surface could be controlling factors so that the crystal field around Fe^{3+} ions does not permit an easy reduction step. Such structural factors may be controlling the rate of reduction of the natural ores as well as samples doped with foreign oxides.

(2) The mechanism of the reduction of pure iron oxide and that of iron oxide mixed with other oxides follow fundamentally different paths. In the first case, the reduction proceeds by a two-step consecutive process, while in the latter case it follows a concurrent mechanism which is confirmed by the simultaneous presence of all three phases at any instant of reduction by X-ray diffraction (Table 1) and Mössbauer spectroscopy. In this case, as in the case of ores, the reduction kinetics can be described by the reaction triangle model proposed by Bessieres *et al.* [34].

(3) In either case (pure and doped), the reduction kinetics are controlled by the topochemical reaction of Fe^{3+} in the spinel matrix.

(4) The reduction kinetics of naturally occurring ores are similar to the concurrent mechanism followed by the doped iron oxide.

Effect of products on the rate of reduction

It has been shown that water vapour generally retards the reduction. Its effect is more pronounced on the reduction step of Fe_3O_4 to Fe than on that of Fe_2O_3 to Fe_3O_4 [37]. Similarly, studies on the effect of added metallic iron have given some interesting results. Pakhvisnev and Abdelrassul [38] found that metallic iron powder has a catalytic effect on the reduction of iron oxide. Korneeva and Vorontsov [39] found that platinized platinum has a similar effect in the reduction of Fe_2O_3. The ease of oxide–reduction in the presence of the noble metals has been attributed to the ability of the latter to chemisorb hydrogen dissociatively as atoms, and of these reactive species to migrate to the oxide surface with the assistance of water vapour as a "transporting agent". Il'chenko [22] has, however, drawn attention to the limited understanding of the mechanisms of such reactions and has emphasized the need for detailed experimental studies covering a number of oxides. We have also studied the effect of the presence

of free metal and water vapour on the kinetics of iron oxide reduction [40, 41]. The main features of the results obtained are:

(1) The rate of reduction of Fe_2O_3 is increased by the addition of fresh metal powders while the addition of aged electrolytic iron powders does not have any effect.

(2) With pure Fe_2O_3, the rate of reduction at first decreases with increase of water vapour content up to 2.5%, but increases with a further increase in water vapour content up to 7.5%, beyond which the rate decreases again (Fig. 2). On the other hand, in all other cases (doped Fe_2O_3 or ores) the rate decreases continuously with increase in water vapour content.

(3) The reduction of pure Fe_2O_3 with or without the addition of freshly reduced iron at 255°C does not proceed beyond the stage of Fe_3O_4 formation, in pure *dry* hydrogen atmosphere (achieved by inclusion of a "cold finger" in the reactor), whereas without the removal of water vapour the reduction goes through to completion.

The anomalous increase in the rate of reduction of pure Fe_2O_3 with increase in water vapour content in the range 2.5–7.5% (shown in Fig. 2) can be rationalized on the basis of hydrogen spill-over from the metal surface onto the reducible oxide surface through the medium of water vapour, which functions presumably as an interface or adlineation layer between the metal surface and the reducible oxide particles. The spill-over effect would also account for the observed substantial lowering of the reduction temperature in the combined presence of metal and water vapour. As the adsorptive capacity and adsorption energies of hydrogen will vary for different metal additives, the rate of HSO-dependent metal-catalysed reduction of iron oxide also varies for different metal additions. Thus, freshly reduced iron and nickel are active in this respect while aged iron powder has no effect.

CONCLUSIONS

The main conclusions of the present study are:

(1) The reduction of pure Fe_2O_3 proceeds by a consecutive two-step mechanism via Fe_3O_4 with the overall rate controlled by the topochemical reduction of Fe_3O_4 to Fe, namely by the formation and nucleation of metallic iron rather than by any of the mass transport steps. On the other hand, the reduction of doped oxides and of the hematite ore proceeds by a different mechanism involving the mixed oxides (ferrites) formed at the surface of Fe_2O_3.

(2) The change in reduction kinetics from pure Fe_2O_3 to doped Fe_2O_3 is not due to electronic factors but due to structural factors.

(3) The kinetics of reduction of pure Fe_2O_3 are catalysed by the presence of metal additives and are dependent on the partial pressure of the water vapour added. The increased rate of reduction in the pres-

ence of water vapour (2.5–7.5 volume per cent) has been attributed to a hydrogen spill-over effect which provides the necessary active hydrogen at the reduction centres.

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