

REACTIVITY WITH HYDROGEN OF PURE IRON OXIDE AND OF IRON OXIDES DOPED WITH OXIDES OF Mn, Co, Ni AND Cu

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Using dynamic TG in H₂, X-ray powder diffraction and Mössbauer Spectroscopy the reactivities for hydrogen reduction of Fe₂O₃ prepared at different temperatures, Fe₂O₃ doped with oxides of Mn, Co, Ni and Cu prepared at 300°C from nitrate precursors and intermediate spinels derived from above samples during reduction have been explored. The reactivity is higher for finely divided Fe₂O₃ prepared at 250°C. The reduction is retarded by Mn, marginally affected by Co and accelerated by Ni and Cu, especially at higher (5 at.%) dopant concentration. These reactivities confirmed also by isothermal experiments, are ascribed to the nature of disorder in the metastable intermediate spinels and to hydrogen 'spill over' effects.

The reactivities of several solids are known to be influenced by their history of preparation, defect state, particle sizes and by the presence of solutes or impurities in small quantities [1]. The reduction of iron oxides by CO and H₂ particularly in the high temperature range have been extensively investigated [2-5]. Hot stage microscopic experiments [3] have shown that cracks arise during the reduction of hematite to magnetite. The reason for this may be the dependence of the morphology on temperature, and the transformation stresses during the reduction of hematite. Geiger and Wagner [6] infer from conductivity studies that in pure and doped hematite, the reactivity is influenced by oxygen vacancies below 850° and by electron defects above 850°.

A review of reduction of iron oxides by H₂ and O is given by Prasad and Sant [7]. The influence of preparation history of Fe₂O₃ on its reactivity for hydrogen reduction was studied by Shimokawabe *et. al.*, [8]. The oxides prepared at lower temperature had higher reactivity. They have attributed

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the accelerating affect of the dopants Al^{3+} , Mg^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Li^+ to the formation of solid solution or of ferrites. The effect of origin and physico-chemical properties and ionizing radiation on the kinetics of reduction of mixed $\text{NiO-Fe}_2\text{O}_3$ oxides by hydrogen is given by Pospisil and Topinka [9, 10].

A survey of the literature indicates that the kinetics of reduction of iron oxides are affected by the methods of preparation and presence of dopants. However, in the lower temperature range the mechanism of the reduction process and the quantitative effects of dopants on the reaction rates is not clear. Therefore a detailed study of the low temperature reduction by hydrogen of pure iron oxide and iron oxides with dopants such as oxides of Mn, Co, Ni and Cu was undertaken. It is also of interest to explore the possibilities of enhancing the reaction rates so as to carry them out at relatively low temperatures.

Experimental

The pure iron oxide, $\alpha\text{-Fe}_2\text{O}_3$ was prepared at 250° , 300° and 400° by thermal decomposition of ferric nitrate in air for four hours. $\alpha\text{-Fe}_2\text{O}_3$ doped with 1 at% of Mn, Co, Ni and Cu and also 5 at% of Ni and Cu were prepared by thermal decomposition of mixture of corresponding nitrates in the desired ratio at 300° for four hours. A preliminary study on the decomposition of various nitrates used for preparation of the above oxides was conducted in order to establish the above preparation conditions of the oxides [11].

X-ray powder diffraction studies were carried out on a Philipps Diffractometer using $\text{Co-K}\alpha$ radiation ($\lambda = 1.79021 \text{ \AA}$). A scanning rate of 2 deg/min was used. Mössbauer studies were carried out in the constant acceleration mode using a ^{57}Co source in rhodium matrix and the details of the instrument used are given elsewhere [12]. The isomer shifts are given with respect to metallic iron. The experimental data was computer fitted on DEC 1090 system using a versatile computer program "MOSFIT". The details of the thermobalance and the experimental setaup used for reduction studies are given in our earlier work [12-14].

Dynamic thermogravimetry (TG) in hydrogen of $\alpha\text{-Fe}_2\text{O}_3$ samples prepared at different temperatures and of iron oxides doped with oxides of Mn, Co, Ni and Cu prepared at 300° was carried out with a heating rate of 2 deg/min and a flow rate of 2.7 l/h. In each reduction stage the initial temperature T_i was determined by measuring the onset temperature of

weight decrease and the final temperature T_f by measuring the temperature when there is no further weight decrease. The accuracy of T_i and T_f is $\pm 2^\circ$.

Isothermal studies were also carried out. The experimental setup is similar to that used in our earlier studies [12, 13].

Results

The pure and doped oxide samples prepared from decomposition of corresponding nitrates were first characterised by X-ray powder diffraction technique. The X-ray diffractograms given in Fig. 1 a, b indicate that pure oxides prepared at higher temperatures (400°), give sharp diffraction peaks, characteristic of crystalline α - Fe_2O_3 , whereas the peaks were broad for samples prepared at lower temperatures.

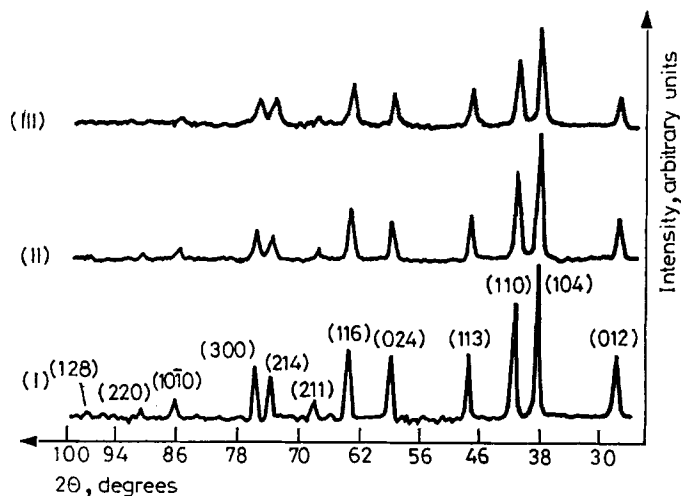


Fig. 1a X-ray diffractograms of pure α - Fe_2O_3 samples prepared at different temperatures by thermal decomposition of nitrates in air (i) 400°C (ii) 300°C and (iii) 250°C

The iron oxides doped with oxides of Mn, Co, Ni and Cu also showed similar X-ray diffractograms to that of pure α - Fe_2O_3 . The broadening of the diffraction peaks were used to calculate the apparent average crystallite size using the Scherrer formula [15]. For the purpose of these calculations, it is assumed that the broadening is only due to the variation in crystallite size although additional contribution to line broadening is possible. The lattice parameters were calculated using the Nelson-Riley function. The variation

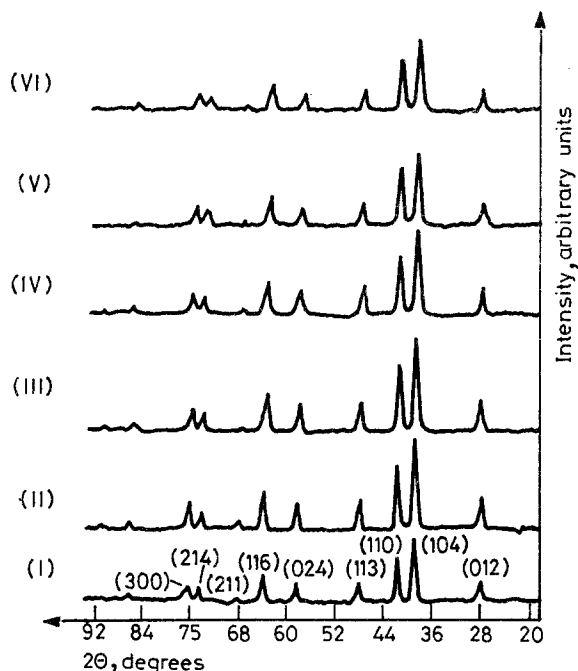


Fig. 1b X-ray diffractograms of doped α - Fe_2O_3 samples with oxides of Mn, Co, Ni and Cu prepared at 300°C by thermal decomposition of corresponding nitrates in air
(i) 1 at% Mn (ii) 1 at% Co (iii) 1 at% Ni (iv) 1 at% Cu (v) 5 at% Cu (vi) 5 at% Ni

of the lattice parameters, volume of the unit cell and crystallite size with preparation temperature of the sample and also with different dopants are given in Table 1. The lattice parameters in case of iron oxides containing 5 at% dopants do not vary very much when compared to 1 at% implying that all the solute atoms may not have gone into solid solution and some amount of it remains as a second phase which is undetected in the x-ray diffraction pattern.

The samples prepared were then ground lightly in an agate mortar and pestle and sieved through 325 mesh. The range of average particle size using an optical microscope was found to be between 3 to 13 microns. The samples were found from scanning electron microscopy to be of irregular shape.

Representative Mössbauer spectra of the pure oxides and doped iron oxides are given in Figs 2a, b and the Mössbauer parameters, the isomer shift (I. S.), quadrupole splitting (Q. S.), full width at half maximum (FWHM) and the internal field (H_{int}) are given in Table 2. The Mössbauer

Table 1 Results of powder X-ray diffraction of pure and doped iron oxides

Samples	Lattice parameters, Å		Volume of unit cell Å ³	Average crystallite size, Å
	<i>a</i>	<i>c</i>		
	± 0.002			± 20
I. α -Fe ₂ O ₃ prepared at different temperatures				
Preparation temperature, °C				
400	4.996	14.06	910.86	243
300	5.004	14.002	910.91	185
250	5.042	13.723	911.83	152
II. Doped α -Fe ₂ O ₃ samples prepared at 300°C				
Dopants				
1 at% Mn	5.037	13.720	904.38	172
1 at% Co	5.040	13.745	907.11	193
1 at% Ni	5.000	13.780	908.03	202
1 at% Cu	5.016	13.915	909.60	168
5 at% Ni	5.036	13.779	907.90	146
5 at% Cu	5.041	13.767	908.92	137

spectra of the pure oxides prepared at lower temperatures (250 and 300°) and iron oxides doped with transition metals are indicative of a six line spectrum characteristic of α -Fe₂O₃ [2] and a very small broad peak which is more pronounced in some of the doped samples (e. g. in 1 at% Mn and 5 at% Ni). The α -Fe₂O₃ has the crystal structure of α -Al₂O₃ with a close packed oxygen lattice and Fe³⁺ cations in octahedral sites. The spectrum of the iron oxide prepared at higher temperature (400°) shows only the sextet.

Dynamic TG curves for the reduction in hydrogen of pure oxides and iron oxides doped with oxides of Mn, Co, Ni or Cu are given in Fig 3. The dynamic TG experiments indicate that both the pure oxides and doped iron oxides show three stages except α -Fe₂O₃ prepared at 250° which shows four stages. The first two stages of dynamic TG in case of the Fe₂O₃ sample prepared at 250° and the first stage of the other samples is due to loss of water. Thus all the samples have a small amount of water associated with them, which could be ascribed to chemisorbed water on the surface or surface hydroxide. The additional water in the sample prepared at 250° could be more loosely bound water which is either physically adsorbed or capillary condensed. It is also possible that it is the water associated with small

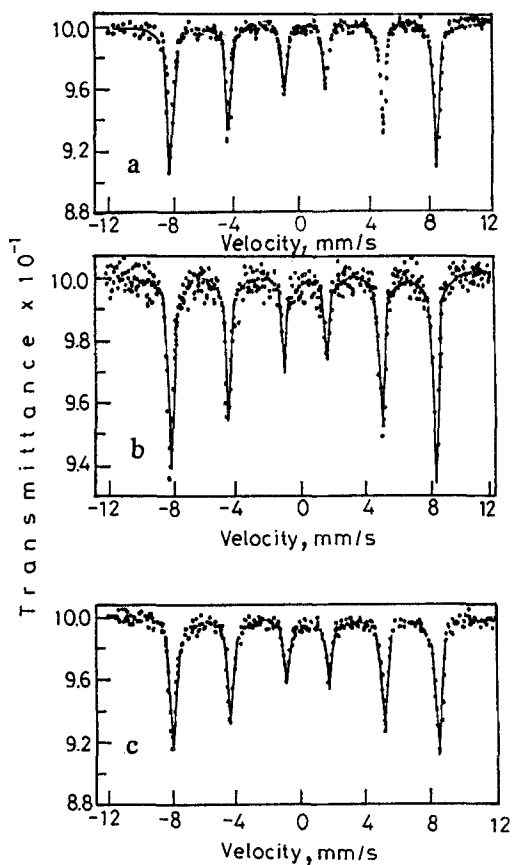


Fig. 2a Room temperature Mössbauer spectra of pure α - Fe_2O_3 samples prepared at different temperatures (a) 400°C (b) 300°C (c) 250°C

amount of ferrihydrite suggested to be present by both X-ray diffractograms as well as the Mössbauer spectra of these samples.

The last two stages of the reaction involving mainly the reduction of the pure or doped Fe_2O_3 samples by hydrogen are of particular interest. In the first reduction stage magnetite or spinel solid solutions are formed and in the second reduction stage these are reduced mainly to the metallic state.

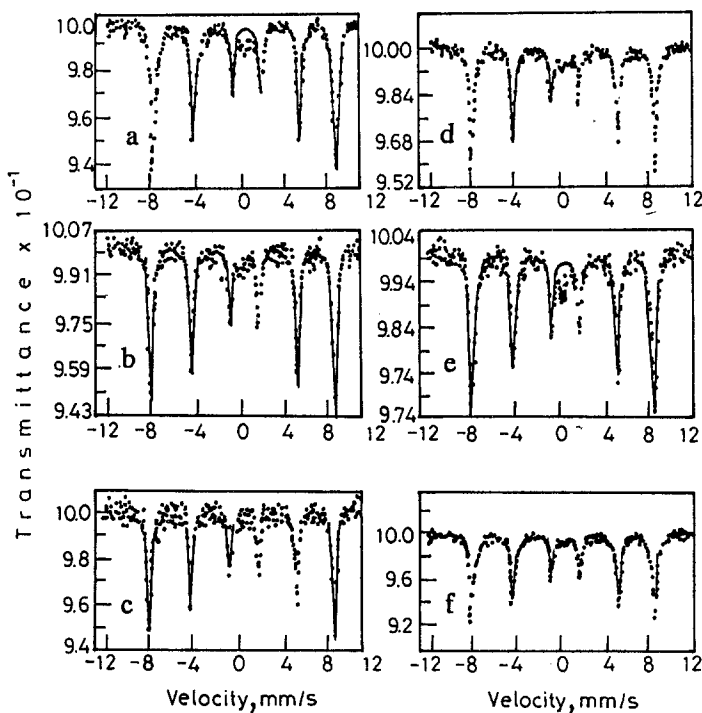


Fig. 2b Room temperature Mössbauer spectra of doped α - Fe_2O_3 samples with oxides of Mn, Co, Ni and Cu prepared at 300°C (a) 1 at% Mn (b) 1 at% Co (c) 1 at% Ni (d) 1 at% Cu (e) 5 at% Ni (f) 5 at% Cu

Discussions

Pure oxides

The broad X-ray lines of iron oxides could be due to variation of crystallite size or disorder. The sample prepared at higher temperature (400°) show only the hyperfine Mössbauer spectrum. The small broad peak at the centre in the samples prepared at 200° and 300° could be attributed to the presence of ferrihydrite or superparamagnetic ultra fine α - Fe_2O_3 . It is also seen that the sextet is less broad in the samples prepared at higher temperatures indicating greater structural regularity.

The results of dynamic TG are given in Tables 3 and 4. The hydrogen reduction of Fe_2O_3 at low temperatures is a two step process after the initial evolution of water below 150° . The two steps involved are:

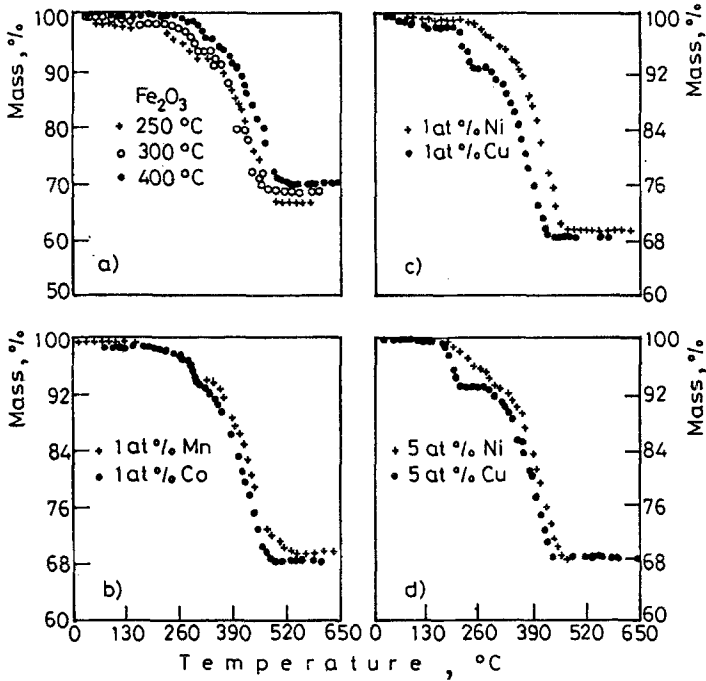
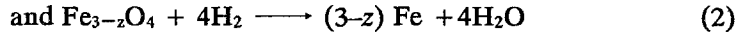
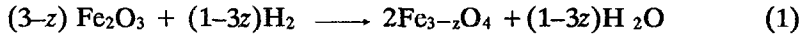


Fig. 3 Dynamic TG in hydrogen of pure and doped Fe_2O_3 samples. Heating rate: 2 deg/min and flow rate: 2.7 l h^{-1} (a) Fe_2O_3 samples prepared at different temperatures (b), (c), and (d) Doped Fe_2O_3 samples prepared at 300°C

Under dynamic TG conditions at 2 deg/min heating rate two well separated reduction reaction stages are found and it is desirable to determine whether these correspond to the above reactions or not. Also the T_i values for the first stage of reduction in dynamic TG vary with the initial preparation temperature of $\alpha\text{-Fe}_2\text{O}_3$. Higher the preparation temperature, higher is the T_i value indicating that oxides prepared at lower temperatures are more reactive. The lower initial reduction temperatures, T_i of both the stages of reduction in the Fe_2O_3 samples prepared at lower temperatures indicates that the reactivities of these samples are higher and can be related to finer crystallite sizes, higher surface areas and porosities and to greater disorder. Although the surface areas and porosities have not been measured in the present work, it is well known that during decomposition reactions the

surface areas and porosities are higher if the decomposition is conducted at lower temperatures. The activation energies for the reduction of $\text{Fe}_{3-z}\text{O}_4$ derived from Fe_2O_3 precursor prepared at 250° is also lower than that for the sample prepared at higher temperatures and this continues throughout the reduction process as has been found from the isothermal studies [16].

Table 2 Mössbauer parameters of pure and doped Fe_2O_3

Sample**	I.S.* mm/sec ± 0.047	Q.S. mm/sec ± 0.047	FWHM mm/sec ± 0.047	H_{int} , KG ± 3
I. Pure Fe_2O_3 prepared at different temperatures				
Preparation temperature, $^\circ\text{C}$				
400	0.38	0.202	0.344	516
300	0.376	0.186	0.363	514
250	0.382	0.199	0.419	513
II. Doped Fe_2O_3 prepared at 300°C				
Dopants				
1 at% Mn	0.434	0.2	0.512	510
1 at% Co	0.379	0.201	0.367	512
1 at% Ni	0.376	0.201	0.367	514
1 at% Cu	0.376	0.197	0.368	514
5 at% Ni	0.415	0.173	0.504	509
5 at% Cu	0.384	0.186	0.482	508

* With respect to metallic iron.

** All the samples were prepared by thermal decomposition of the nitrates in air for four hours.

In order to elucidate the reactions taking place in the two stages of dynamic TG, we have assumed that the first reduction stage between $220\text{--}330^\circ$ in the dynamic TG of pure oxides leads to the formation of non-stoichiometric magnetite $\text{Fe}_{3-z}\text{O}_4$ (reaction 1) [17] and these samples get further reduced to the metallic state (reaction 2) in the last stage of dynamic TG. The percent weight losses for these two stages in the dynamic TG are given in Table 4. The apparent value of z for nonstoichiometry is obtained by considering the mass differences between the calculated values for the formation of stoichiometric magnetite Fe_3O_4 from Fe_2O_3 and its reduction to metallic state and the experimental values. This apparent value of z may not represent the correct value of nonstoichiometry due to the possibility of small amounts of unreduced starting sample present in the short interval of

the horizontal portion of the dynamic TG or of further reduction of active areas of spinel to metallic state. More reliable values can be obtained from Mössbauer measurements [17]. The value of z in $\text{Fe}_{3-z}\text{O}_4$ varies depending on the preparation temperature of pure $\alpha\text{-Fe}_2\text{O}_3$. This apparent value of z was used to calculate the percent weight loss for reaction 2. The discrepancies in the percent weight loss for the formation of metallic state from $\text{Fe}_{3-z}\text{O}_4$ between the calculated and experimental values implies that some amount of metallic Fe has formed in the first reduction stage of dynamic TG.

Table 3 Results of dynamic TG in hydrogen atmosphere of $\alpha\text{-Fe}_2\text{O}_3$ prepared at different temperatures and doped $\alpha\text{-Fe}_2\text{O}_3$ prepared at 300°C

Hydrogen flow rate: 2.7 l/h, Heating rate: 2 deg/min					
Samples	First reduction Reaction		Second reduction Reaction 2		
	T_i^*	T_f	T_i	T_f	
	°C		°C		
I. Pure $\alpha\text{-Fe}_2\text{O}_3$ prepared at different temperatures					
Preparation temperature, °C					
250	223	307	329		500
300	229	300	329		500
400	239	330	339		517
II. Doped $\alpha\text{-Fe}_2\text{O}_3$ prepared at 300°C					
Dopants					
1 at% Mn	222	300	329		538
1 at% Co	205	310	321		490
1 at% Ni	210	306	314		474
1 at% Cu	181	240	275		441
5 at% Ni	186	251	261		459
5 at% Cu	161	217	268		450

* $\pm 2^\circ\text{C}$

Doped oxides

All samples of doped $\alpha\text{-Fe}_2\text{O}_3$ prepared at 300° had broad X-ray lines indicating both small crystallite size and considerable disorder depending on the nature and amount of the dopant present.

A survey of the phase diagrams available in literature indicate that the solid solubility of Mn oxide in Fe_2O_3 is considerable whereas oxides of Co,

Table 4 Analysis of weight losses in different stages of thermogravimetric studies in hydrogen

Samples	First reduction reaction % wt loss ± 0.05		Apparent value of <i>z</i> ± 0.01	Second reduction reaction % wt loss ± 0.05	
	Expt.	Cal.*		Expt.	Cal.**
I. α -Fe ₂ O ₃ prepared at different temperatures					
250°C	4.83	3.340	0.06	26.60	26.5
300°C	5.17	3.340	0.08	25.60	26.21
400°C	4.1	3.340	0.03	26.07	27.86
II. Doped Fe ₂ O ₃ with dopants as					
1 at% Mn	3.84	3.340	0.02	24.92	27.25
1 at% Co	5.87	3.338	0.11	25.38	25.69
1 at% Ni	3.86	3.338	0.02	26.20	27.20
1 at% Cu	5.66	3.337	0.10	24.26	25.85
5 at% Ni	6.58	3.240	0.14	23.91	25.11
5 at% Cu	5.87	3.234	0.11	24.15	25.68

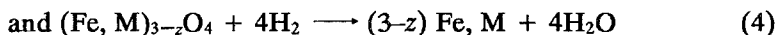
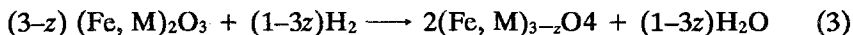
* The percent weight loss calculated assumes the formation of stoichiometric magnetite Fe₂O₃ or mixed spinel (Fe,M)₃O₄.

** This percent weight loss calculation assumes the initial composition of the sample to be Fe_{3-*z*}O₄ or (Fe,M)_{3-*z*}O₄ with the *z* value reported in column 4.

Ni or Cu have little or negligible solid solubility in Fe₂O₃. But in the lattice of Fe₃O₄ these oxides have considerable solid solubility. One can therefore assume that Mn oxide forms equilibrium solid solution with α -Fe₂O₃ and also with magnetite derived from it by partial reduction. In case of Fe₂O₃ doped with 1 at% Co, Ni or Cu, during the thermal decomposition of the respective nitrates metastable solid solutions are formed as inferred from the altered lattice parameters as well as changes in the Mössbauer parameters as compared to the pure sample prepared at same temperature (300°) (Table 2).

The Mössbauer spectra of doped iron oxides are similar to that of the pure oxide. The variation in the FWHM is due to the distribution of internal fields. In the oxide containing 1 at% Mn, the Mössbauer parameters vary, suggesting interaction between Mn and Fe in the oxide. In case of iron oxide containing other dopants, at 1 at% level, the variation in these parameters is less. However, for samples containing higher concentration (5 at% Ni or Cu) the Mössbauer parameters vary significantly indicating appreciable interaction between the dopant cations and those of iron.

The hydrogen reduction of doped (Fe, M)₂O₃ samples at low temperatures is a two step process after the initial evolution of water. The two steps involved are:



The first reduction reaction (Eq. 3) leads to the formation of spinel solid solutions which are non-stoichiometric (Table 4). The calculated percent weight loss in column 3 of Table 4 for the first stage of the reduction is based on the assumption that the doped ferric oxide forms a stoichiometric spinel (Fe, M)₃O₄. The apparent value of *z*, calculated in a similar manner as in the case of pure oxides, varies depending on the nature of the dopant. The second reduction reaction which occurs in the last stage of dynamic TG of these samples is due to further reduction of the metastable spinel solid solutions (Fe, M)_{3-z}O₄ to metallic state, except in the system containing Mn where Mn is in a partially reduced state (lower oxide of Mn). The discrepancies in the percent weight loss for the formation of metallic state between the calculated (which are in each case higher) and experimental values implies that some amount of metallic M or Fe-M alloy has formed in the first reduction stage of dynamic TG. This implies that less of the mixed spinel is available for reduction in the last stage of dynamic TG.

If the first reduction stage of the dynamic TG of pure and doped Fe₂O₃ samples prepared by thermal decomposition of corresponding nitrates at 300° are considered, it is seen that in all the doped samples the reduction reaction starts at a lower temperature than the pure oxide. While doped samples with 1 at% Mn, Co, Ni or Cu affect the reactivities slightly, the samples with 5 at% Ni or Cu have significantly higher reactivities for hydrogen reduction. The sample with 5 at% Cu is most reactive, the reduction reaction proceeding nearly 70–80° below that of the pure oxide.

Similar but more marked effects are found in the second reduction reaction (in the final stage of dynamic TG). Here the reacting samples are the metastable non-stoichiometric spinel solid solutions containing probably small amounts of metallic species formed in the surface layers which are easily accessible to the reducing gas.

If one considers the reduction temperatures for the final reduction stage in the dynamic TG by hydrogen, it is seen from Table 3 that at the level of 1 at% dopants, Mn retards the reduction reaction of the spinel, Co is marginally hastening the reaction and Ni and Cu are considerably accelerating

Table 5 Comparison of reactivities of spinel solid solutions prepared at 300°C

Parameters	Solutes						
	Mn 1 at%	Co 1 at%	Pure Fe _{3-z} O ₄	Ni 1 at%	Cu 1 at%	Ni 5 at%	Cu 5 at%
Initial reduction temperature from dynamic TG							
<i>T_i</i> , °C	329	321	329	314	275	261	268
Time in mins for percent reacted α from isothermal TG at 340°C							
$t\alpha = 0.5$	200	215	170	168	142	134	130
$t\alpha = 0.75$	316	324	252	244	210	188	180
Percent Fe formed isothermally by H ₂ reduction in 1hr							
by XRD							
at 300°C	0	6.3	6.0	8.5	17	11	24
at 350°C	14	32	31	50	70	46	67
by Mössbauer							
300°C	0	3.7	4.5	7	12.5	8	28.7

the reduction reactions. At 5 at% dopant levels, both Ni and Cu are even more reactive. Under optimal conditions it is possible to conduct the reduction reaction at about 70° below that of pure magnetite.

The small grain sizes and the very fine crystallite sizes of the spinels formed at relatively lower temperatures in the present work would lead to the expectation that the reduction process of these spinels could proceed more easily. However, this effect would not vary very much with samples containing different dopants. It is therefore of interest to seek the reasons for the higher reactivities of the spinel solid solutions involving Co and particularly those containing Ni and Cu and for lower reactivity of that containing Mn. This is attempted in Table 5 in which the results of separate isothermal experiments conducted by the present authors [16] are also included. The Table 5 also gives, as a measure of reactivities of metastable spinel solid solutions, the time (in minutes) required for 50% ($t\alpha=0.5$) and 75% ($t\alpha=0.75$) of the reduction reaction by H₂ to be completed in isothermal TG at 340°.

Another measure of the reactivities is obtained in experiments conducted in a reaction tube isothermally at 300° and 350° for 1 hour in H₂ and the reduced samples examined by powder X-ray diffractometry and by Mössbauer spectroscopy. The percent Fe in metallic state in these measurements are estimated. Some differences between X-ray diffraction and

Mössbauer results are obtained. These are to be expected since x-ray gives a phase analysis while Mössbauer is sensitive only to iron. The trends in both sets of measurements are quite clear in reflecting the reactivities of these samples for reduction by hydrogen. They both indicate that relative to pure non-stoichiometric magnetite, at 1 at% level of dopants, Mn in the spinel retards the reduction, Co affects only marginally, Ni accelerates the reduction process and Cu accelerates it the most. At higher concentration of dopants (5 at%) both Ni and Cu are even more effective in accelerating the reduction to metallic state.

It is clear from the above facts that the influence of the solute atoms on the reactivities for H₂ reduction of the corresponding spinel solid solutions formed during the reduction of doped iron oxides is in the order:



at the same level of solute concentration (a at%).

In order to understand how these dopants/solutes influence the reactivities for hydrogen reduction, it is necessary to consider the defect structures of these spinels. The order of reactivities has no correlation with the apparent z values (corresponding to the cation vacancies) obtained for the spinels either from dynamic TG in the present work (Tabla 4) or the z values obtained from Mössbauer measurements [17]. Mn as well as Co can exist in both di- and tri-valent states, whereas Ni is divalent and Cu which is divalent can also exist in the monovalent state. Mn is not reduced to the metallic state in the temperature range studied but only to a lower oxide. To better understand the role of those dopants, it is necessary to study in detail the kinetics of reduction and to characterize the disorder in the intermediate spinel solid solutions formed. These are metastable spinel solid solutions with appreciable defect concentration due to their low temperature of formation. They could also have in them, for the same reason, site disorder for the cations which under some conditions could result in changes in the oxygen sub-lattice and/or electrical properties of the metastable spinels.

An additional possibility is the initial formation of metallic Ni or Cu in the corresponding systems, particularly in the surface layers. Metallic Ni or Cu can contribute substantially to the enhanced reactivities by a hydrogen 'spill over' process providing large concentrations of atomic hydrogen at sites extending to large areas of the sample [18]. These possibilities are considered separately in papers to follow.

Conclusions

1. Using dynamic TG in H₂, X-ray powder diffractometry and Mössbauer spectroscopy the reactivities for hydrogen reduction has been studied for, (a) Fe₂O₃ prepared at different temperatures by thermal decomposition of the nitrates in air,

(b) Fe₂O₃ doped with oxides of Mn, Co, Ni and Cu prepared similarly from corresponding nitrates at 300°,

(c) non-stoichiometric magnetite and spinel solid solution intermediates formed during the reduction of pure and doped iron oxides.

2. The reactivities of α -Fe₂O₃ prepared by thermal decomposition of ferric nitrate varies with the preparation temperature and is highest when prepared at lower temperature (250°) when it has a smaller crystallite size and greater extent of disorder.

3. The T_i values for the reduction of doped Fe₂O₃ samples to spinel solid solutions (non-stoichiometric), are decreasing in the order:



4. At the same level of solute concentration (1 at%) in the intermediate spinel solid solutions formed, the reactivities for their reduction follows the order:



with Mn retarding the reaction, Co slightly affecting the reaction, and Ni and Cu accelerating the reaction.

5. Fe₂O₃ doped with 1 at% Cu, 5 at% Cu or 5 at% Ni show higher reactivity. The intermediate spinels containing 5 at% Ni or Cu enable them to be reduced at about 70° lower temperature than the pure oxide.

6. The higher reactivities of Ni and Cu containing spinel solid solutions could be ascribed to the nature of the disorder in the spinels formed as metastable intermediates and possibly to hydrogen 'spill over' effects.

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References

- 1 V. V. Boldyrev, M. Bulens and B. Delmon, *The Control of the Reactivity of Solids (Studies in Surface Science and Catalysis, Vol. 2)*, Elsevier, Amsterdam 1979.
- 2 U. Colombo, F. Gazzarrini and G. Lanzavecchia, *Mat. Sci. Eng.*, 2 (1967) 125.
- 3 L. V. Bogdandy and H. J. Engell, *The Reduction of Iron Ores*, 1971.
- 4 J. O. Edstrom, *J. Iron Steel Inst.*, (1953) 289.
- 5 N. A. Warner, *Trans. Met. Soc. AIME*, 230 (1964) 163.
- 6 H. Geiger and J. B. Wagner Jr., *Trans. Met. Soc. AIME*, 233 (1965) 2092.
- 7 T. P. Prasad and B. R. Sant, *J. Scient. Ind. Res.*, 30 (1971) 538.
- 8 M. Shimokawabe, R. Furuichi and T. Ishii, *Thermochim. Acta*, 28 (1979) 287.
- 9 M. Pospisil and J. Topinka, *Collection Czechoslovak Chem. Commun.*, 51 (1986) 2098.
- 10 M. Pospisil and J. Topinka, *Collection Czechoslovak Chem. Commun.*, 51 (1986) 1561.
- 11 D. N. Drakshayani and R. M. Mallya, in preparation.
- 12 D. N. Drakshayani, Ch. Sankar and R. M. Mallya, *Thermochim. Acta*, 144 (1989) 313.
- 13 R. M. P. Sathyavathiamma, N. G. Puttaswamy and R. M. Mallya, *Mat. Chem. Phys.*, 9 (1983) 539.
- 14 D. N. Drakshayani, *Reactivity of Solids: Reduction of Some Transition Metal Oxides and of Marine Manganese nodules by Hydrogen*. M. Sc. (Eng.) Thesis, 1987.
- 15 D. Cullity, *Elements of X-ray Diffraction (second ed.)*, Addison Wesley Publishing Company, Inc. 1978.
- 16 D. N. Drakshayani and R. M. Mallya, in preparation.
- 17 D. N. Drakshayani, Ch. Sankar and R. M. Mallya, in preparation.
- 18 H. Charcosset and B. Delmon, *Ind. Chim. Belg.*, 38 (1973) 481.

Zusammenfassung – Mittels Debye-Scherrer-Aufnahmen, Mössbauer-Spektroskopie und DTG in Wasserstoffatmosphäre wurde die Reaktivität bezüglich der Reduktion mit Wasserstoff von Fe_2O_3 , versetztem Fe_2O_3 und von intermediären Spinellen aus der Reduktion obiger Proben untersucht. Die reinen Fe_2O_3 -Proben wurden bei verschiedenen Temperaturen hergestellt. Mit Oxiden von Mn, Co, Ni und Cu versetzte Fe_2O_3 -Proben wurden bei 300°C aus Nitrat-Vorläufern hergestellt. Eine höhere Aktivität besteht für fein zerkleinertes, bei 250°C hergestelltes Fe_2O_3 . Die Reduktion wird durch Mn verzögert, durch Co unwesentlich beeinflusst und durch Ni und Cu beschleunigt, besonders bei höheren Konzentrationen (5 mol%). Diese Reaktivitäten, die auch durch isotherme Experimente bestätigt werden konnten, wurden der Ungeordnetheit in den metastabilen intermediären Spinellen sowie Wasserstoff-"Überschuß"-Effekten zugeschrieben.