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TPR data regarding the effect of sulfur on the reducibility of α-Fe_2O_3

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Abstract

The temperature programmed reduction (TPR) method has been used to study the effect of residual sulfur on the reducibility of α-Fe_2O_3 prepared both using iron(II) and iron(III) sulfate. The values of the kinetic parameters characteristic of the reduction of the hematite to magnetite, of the magnetite to metallic iron, as well as of the processes involved in the elimination of the sulfate anions, were evaluated by simulation of the TPR curves. The effect on the reducibility of α-Fe_2O_3 is reflected in the values of the kinetic parameters when the sulfur is dispersed into the sample's bulk. If the sulfur exists only on the surface, its influence on the reducibility of the sample is mainly due to the fact that the reduction of the hematite starts only after the elimination of the sulfate anions begins. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: *α-Fe_2O_3; Temperature programmed reduction; Kinetic parameters*

1. Introduction

The water–gas shift (WGS) reaction over iron-containing catalysts is one of the oldest catalytic processes in the chemical industry. Nevertheless, the search for novel catalysts and methods of preparation are questions of present interest. A principal way of selecting highly active and economically beneficial catalysts is to prepare precursors with optimum structure and properties [1].

Normally the starting material for preparing such catalysts is iron(II) or iron(III) sulfate and the problems of sulfur removal during the initial period of the catalyst's reduction are important particularly from the economical point of view. However, reference data on the effect of sulfur and sulfur bonding strength in the crystal lattice on iron oxide reducibility are missing.

The aim of the present study is to clarify, by means of temperature programmed reduction (TPR), the effect of residual sulfur on the reducibility of iron oxide WGS catalysts prepared from various raw materials. In a first approximation, the decrease of the reducibility of α-Fe_2O_3, due to the presence of sulfur, is proved by the increase of the temperature at which the peak typical of the reduction of hematite to magnetite is located in the TPR curve (Fig. 1). What we want to evidence is, however, the influence of the sulfur on both reduction processes:

$$\text{hematite} \xrightarrow{H_2} \text{magnetite} \xrightarrow{H_2} \text{metallic iron}$$

as this fact is reflected in the values of the kinetic parameters typical to both processes. We will estimate therefore the values of the corresponding kinetic parameters and we will compare these values with

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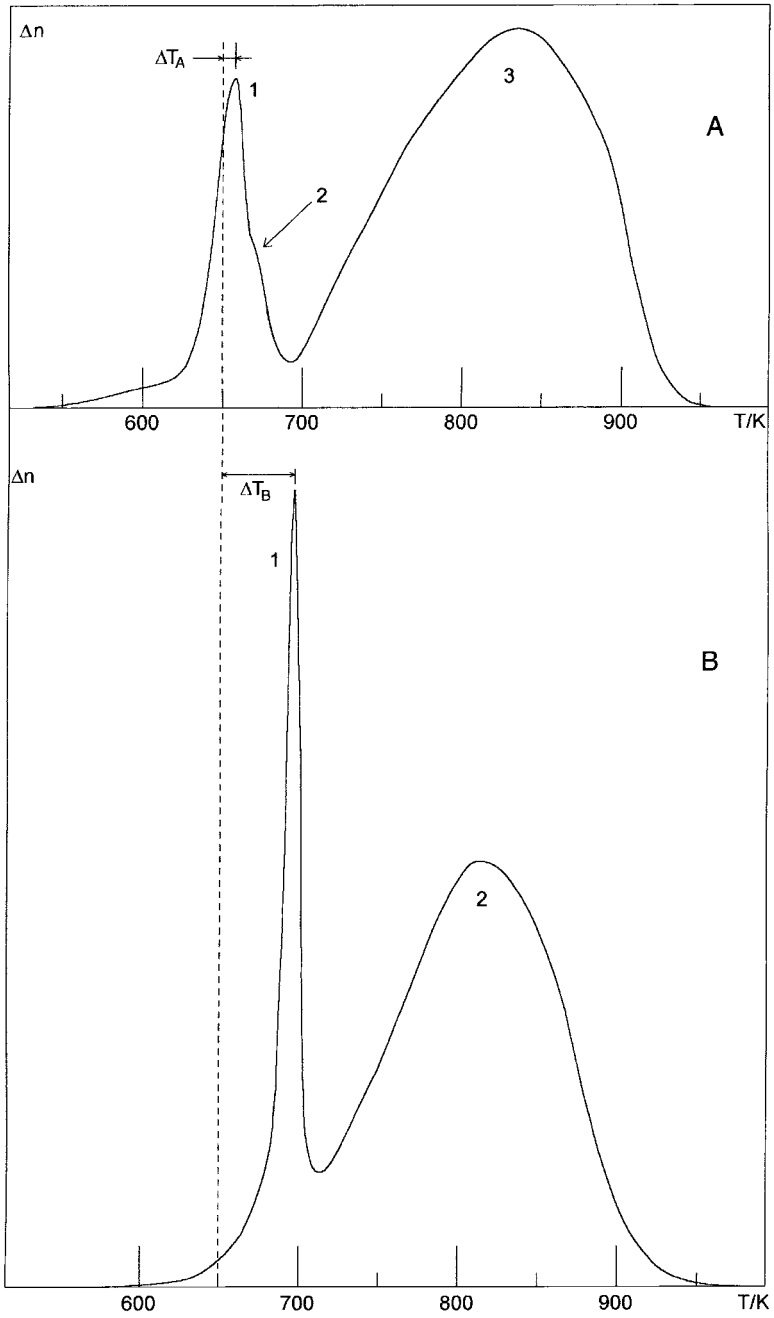


Fig. 1. The experimental TPR profiles for the two samples, A and B. Δn – hydrogen consumption in relative units. The vertical broken line marks the position of the peak corresponding to the reduction of pure hematite to magnetite. (A) The peaks denoted by 1 and 3 correspond to the hydrogen consumption due to the reduction of hematite to magnetite and to the reduction of magnetite to metallic iron, respectively. The shoulder denoted by 2 corresponds to the hydrogen consumption due to the elimination of sulfate anions. (B) The peak denoted by 1 corresponds to the hydrogen consumption due to the elimination of sulfate anions+the reduction of hematite to magnetite. The peak denoted by 2 corresponds to the reduction of magnetite to metallic iron. ΔT_A and ΔT_B mark, for the two samples A and B, the shifts of the peak attributed to the reduction of hematite to magnetite, compared to the same peak for pure iron oxide.

those of the kinetic parameters which characterize the reduction of pure iron oxide.

2. Experimental

Two samples were prepared by oxidative hydrolysis of iron(II) or hydrolysis of iron(III) sulfate following the procedure described in [1,2]. These samples are denoted as samples A and B, respectively. X-ray diffraction and TEM data have shown that, after calcination, the samples contained spherical α-Fe_2O_3 crystallites, but the initial precursors (dried samples) were very different. The precursors were α-FeOOH for sample A and ferrihydrite for sample B [1].

All the TPR measurements were carried out by means of a versatile apparatus as described in [3]. Its scheme is shown in Fig. 2. There were used the following conditions: hydrogen–argon mixture (10% H_2) at a flow rate of 24 ml min^{-1}, temperature rise at a rate of 15 K min^{-1}, sample mass 0.01 g [2]. The BET areas of samples A and B were 74 and 108 $m^2\,g^{-1}$, respectively. The sulfur content of the samples was 0.40 and 1.72 mass % for sample A and sample B. The TPR curves of these two samples are shown in Fig. 1.

3. Assignment of the TPR peaks

The peaks denoted by 1 and 3 in the TPR curve of sample A (see Fig. 1(A)) have been assigned to hydrogen consumption owing to the reduction of the hematite to metallic iron according to the following reaction scheme:

$$3Fe_2O_3 \xrightarrow{+H_2} 2Fe_3O_4 + H_2O \xrightarrow{+8H_2} 6Fe + 8H_2O \tag{1}$$

The above assignment is supported by the fact that the hydrogen consumption in the two processes, as well as the areas of the peaks 1 and 3, have the ratio 1:8.

The method of preparation of sample A, by oxidative hydrolysis of iron(II) sulfate, suggests incorporation of the larger part of the sulfate anions into the bulk of the iron oxide [4,5]. Consequently the shoulder denoted by 3 (Fig. 1(A)) has been assigned to the hydrogen consumption due to the hydrogenation of sulfate anions existing in the bulk of sample A. We considered that these sulfate anions are hydrogenated according to the following reaction scheme:

$$SO_4 \xrightarrow{+H_2} SO_3 + H_2O \xrightarrow{+3H_2} S + 3H_2O \xrightarrow{+H_2} H_2S \tag{2}$$

In the case of Fe(III) hydrolysis of $Fe_2(SO_4)_3$ solution (sample B), the SO_4^{2-} ion occupies the first ligand sphere of Fe^{3+} in the early stage of preparation [6]. Therefore, the sulfate anions lie, in case of this sample, mainly on the surface. The presence of a larger part of tightly bonded sulfate ions on the surface probably

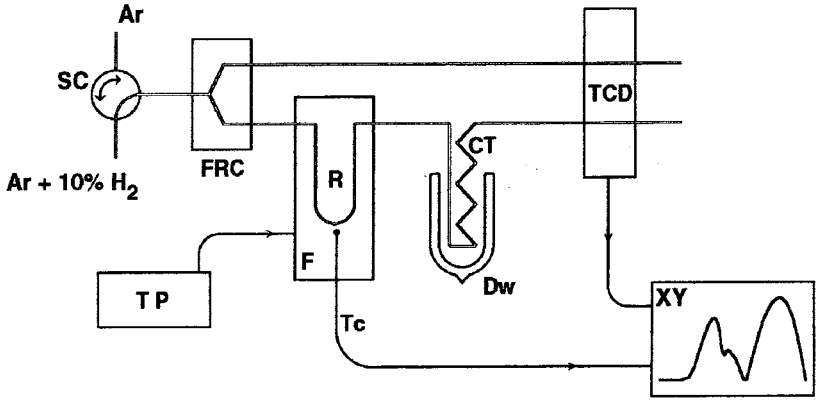
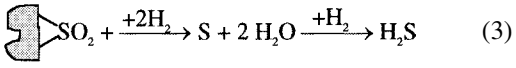


Fig. 2. Diagram of the chromatographic apparatus used for TPR measurements. SC – gas sample inlet stop-cock; FRC – flow rate controller; R – reactor; F – furnace; CT – cold trap (−40°C); Dw – Dewar flask; TCD – thermal conductivity detector; Tc – thermocouple; TP – temperature programmer; XY – XY recorder.

leads further to the blockage of the hematite reduction to magnetite.

In the TPR curve of sample B there are only two peaks, their areas having the ratio 1.6:8. This fact means that the first peak, denoted by 1 in Fig. 1(B), is not due only to the reduction of hematite to magnetite. It hides an additional process that is probably due, in our opinion, to the hydrogenation of sulfate anions on the surface of sample B.

The hydrogen consumption originating in the reduction of hematite to magnetite is regarded as an internal standard. The ratio of hydrogen consumption assigned to the elimination of sulfate anions from the two (A and B) samples was determined as 1:2.4. Taking into account this finding, as well as that the sulfur contents in the two samples are in the ratio 1:4.3, we have concluded that in sample B the surface "sulfate anions" have a structure close to SO_2. Consequently, to eliminate the bonded SO_2 in sample B, we have considered the following two processes:



(3)

The second peak from the TPR curve of sample B, denoted by 2 in Fig. 1(B), has been assigned to the reduction of magnetite to metallic iron.

4. Simulation of the TPR curves

The hydrogen consumption due the elimination of the OH groups from the surface was neglected, although both the samples had not been dehydrogenated before performing the TPR measurements.

The two reduction processes, described by Eq. (1), as well as those specific to the elimination of sulfate anions, described by Eqs. (2) and (3), were approximated by second-order reactions. We adopted this procedure because the elimination of any oxygen atom, whether it belongs to an iron oxide or to a sulfate anion, may be regarded as reaction of the type:

$$H_2 + \{O\}_S \rightarrow \{\square\} + H_2O \tag{4}$$

where $\{O\}_S$ denote a surface oxygen atom and $\{\square\}$ the oxygen vacancy on the surface.

For the reaction rate we have used the relationship [7,8]:

$$v = -\frac{dn_{ox}}{dt} = \frac{2n_0D_0}{V_r(T_0/T)(p/p_0) + (2D_0/n_{ox}k_0)\exp(E/RT)} \tag{5}$$

where n_{ox} stands for the concentration of the oxidic form, n_0 is the hydrogen concentration at the entrance of the reactor, D_0 is the flow rate in normal conditions of pressure and temperature, V_r is the volume of the reaction space, p and T are the pressure and temperature in the reaction space, respectively, p_0 and T_0 are the values of the same parameters in normal conditions, k_0 is the pre-exponential factor, E is the activation energy, R is the gas constant.

The concentrations of the oxidic species, of sulfate anions as well as of sulfur atoms, as functions of temperature, were determined by numerical integration of the reaction rate equation, Eq. (5), using the fourth-order Runge–Kutta method [9]. The total hydrogen consumption has been calculated by means of the continuity equation:

$$\Delta n = V_r \sum v_i/D \tag{6}$$

where v_i stands for the reaction rate of species i from the surface and D for the flow rate.

5. Results and discussion

The values of the kinetic parameters characteristic of the above mentioned processes were evaluated by fitting the computed TPR spectra to the experimental ones. In such a procedure one has always to take into account the physical significance of the results obtained. It is possible to obtain a good fit using for the kinetic parameters values without any physical significance. For example, if one assumes that the first peak from curve B (Fig. 1(B)) is due to only one hydrogen consuming process (neglecting the above conclusion that this peak is due to at least two different processes) we obtain a value for the activation energy of 774±0.4 kJ mol^{-1}. This value is, of course, abnormally high, suggesting again that this peak is due to the superposition of, at least, two hydrogen consuming processes.

Taking into account this fact and the conclusions mentioned in Section 3, one has considered that the two peaks from the curve B (see Fig. 1(B)) are due to the hydrogen consumption that appears in the processes described by Eqs. (3) and (1). The first peak is due, of course, to the overlap of the elimination of sulfur impurities and reduction of hematite to magnetite. These processes are consecutive, the reduction of hematite starting after the elimination of sulfate anions has begun.

In the case of sample A (see Fig. 1(A)) the processes described by Eqs. (1) and (2) are considered to be parallel.

For estimating the kinetic parameters we have also taken into account some additional observations. Thus, we note that, although sulfur is present in the two samples in different forms, the two mechanisms for its elimination are also different (see Eqs. (2) and (3)) but have as final step a unique reaction:

$$S + H_2 \rightarrow H_2S$$

Since the hydrogen consumption due to this reaction was recorded, for both samples, in the same temperature range, the values of the kinetic parameters characteristic of this process must have similar values for these two samples.

These two samples must also have similar values for the kinetic parameters which characterize the reduction of magnetite to metallic iron. The processes proceed, for the two samples, in the same temperature range, and at the temperature at which the reduction of magnetite begins, the sulfur impurities are mostly eliminated from both samples.

The values of the kinetic parameters characteristic of the hydrogen consuming processes which take place during the reduction of the two samples are given in Tables 1 and 2.

A comparison of the kinetic parameters mentioned above with those evaluated for the reduction of pure iron oxide [10] shows the following: at 500 K, a temperature at which pure hematite begins to reduce, the rate constants characteristic of hematite reduction to magnetite lie in the ratio $k_{1A}:k_{1B}:k_{1P}=0.03:0.49:1.00$. Note that the presence of sulfur is reflected in the value of the rate constant in the case of sample A only. For this sample, the reduction rate of hematite is about 33 times lower than that of pure hematite, whereas in the case of sample B the reduction rate is about half of the value for pure hematite.

Table 1
The values of the kinetic parameters characteristic of the reduction of sample A

Process	k_0 ($m^3\ mol^{-1}\ s^{-1}$)	E ($kJ\ mol^{-1}$)
$3Fe_2O_3+H_2 \rightarrow 2Fe_3O_4+H_2O$	1.2×10^{18}	246±0.4
$2Fe_3O_4+8H_2 \rightarrow 6Fe+8H_2O$	1.8×10^{3}	93.2±0.4
$SO_4+H_2 \rightarrow SO_3+H_2O$	2.4×10^{15}	223.5±0.4
$SO_3+3H_2 \rightarrow S+3H_2O$	1.2×10^{17}	236.1±0.4
$S+H_2 \rightarrow H_2S$	4.8×10^{14}	188.0±0.4

k_0 is the pre-exponential factor and E is the activation energy.

Denoting the shifts of the two peaks, corresponding to the reduction of hematite to magnetite for the two samples, compared to the position of the same peak for pure hematite, as ΔT_A and ΔT_B, one sees that $\Delta T_A<\Delta T_B$. Taking account of this fact, the result mentioned above, i.e. $k_{1A}<k_{1B}<k_{1P}$, is surprising. One should have expected that $k_{1A}>k_{1B}$. However, this result is explicable and the contradiction is only apparent. In the case of sample A almost all of the sulfur is dispersed in the volume of sample and its elimination occurs after the reduction of hematite. The reduction of hematite from this sample occurs in the presence of sulfur which brings about the decrease of rate constant. In the case of sample B most of the sulfur lies at the surface and reduction of hematite begins only after its elimination. Once most of the sulfur has been eliminated, reduction of hematite occurs with a rate close to that of pure hematite. The sulfur traces existing in the volume of the sample cause the reduction of hematite sample B to occur at a rate lower than pure hematite.

Consequently the relation $k_{1A}<k_{1B}<k_{1P}$ existing between rate constants is explainable. The relationship which exists between the shifts of the two peaks (see

Table 2
The values of the kinetic parameters characteristic of the reduction of sample B

Process	k_0 ($m^3\ mol^{-1}\ s^{-1}$)	E ($kJ\ mol^{-1}$)
$>SO_2+2H_2 \rightarrow S+2H_2O$	3.5×10^{19}	254.3±0.4
$S+H_2 \rightarrow H_2S$	9.0×10^{13}	175.5±0.4
$3Fe_2O_3+H_2 \rightarrow 2Fe_3O_4+H_2O$	2.9×10^{10}	162.1±0.4
$2Fe_3O_4+8H_2 \rightarrow 6Fe+8H_2O$	1.2×10^{4}	103.6±0.4

k_0 is the pre-exponential factor and E is the activation energy.

Fig. 1), $\Delta T_B > \Delta T_A$, occurs not because $k_{1A} > k_{1B}$, but because, in the case of sample B, the reduction of hematite, as mentioned above, is a process consecutive to the hydrogenation of sulfur, elimination of sulfur being, in other words, the rate limiting step. In the case of sample A, hydrogenation of sulfur and reduction of hematite are parallel processes, reduction of hematite being influenced by the presence of sulfur in the direction of decreasing the rate constant.

In connection with the reduction of magnetite at 700 K, a temperature which triggers the reduction of pure magnetite, the rate constants correspond to a ratio $k_{2A}:k_{2B}:k_{2P}=0.19:0.22:1.00$. Note that in the case of magnetite reduction to metallic iron the effect of sulfur is sensed directly in the values of the rate constants, sulfur acting directly upon the reduction reaction. This finding is consistent because the reduction of magnetite is influenced by sulfur traces which have penetrated deeply into the structure of the iron oxide.

To fit the TPR profiles without employing unusually high values of the kinetic parameters one has to take into account supplementary first-order processes, for both samples A and B, that precede the reduction of hematite and the hydrogenation of sulfate anions, respectively. These first-order processes probably hide reactions which have not explicitly been taken into account. We mention that preliminary tests have shown that similar fits could be obtained considering the adsorption/desorption processes as well. The values of the kinetic parameters characteristic of these first-order processes are: $k_A=2.0\times10^{16}\ s^{-1}$, $E_A=217.3\pm0.4$ kJ mol^{-1}, $k_B=2.5\times10^{18}\ s^{-1}$, $E_B=220.5\pm0.4$ kJ mol^{-1}.

We shall report more details in a following paper dedicated to the role of the adsorption/desorption processes in the reduction reactions.

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