JOURNAL OF MATERIALS SCIENCE 31 (1996) 1101–1105

Formation of highly active iron oxide catalysts

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The role of the preparation method on the physicochemical properties of iron oxide catalyst precursors has been investigated. The influence of some specific properties of the iron oxide percursors on the catalytic activity in the water–gas shift reaction has been explained on the basis of the concept of an associative mechanism.

1. Introduction

The water–gas shift reaction (WGSR) over iron-containing catalysts is one of the oldest catalytic processes in modern chemical industry. In spite of this, its importance has not decreased and the improvement of iron catalysts for WGSR is still a current task. The basic direction for the improvement of this catalyst is the formation of ferric oxide precursors possessing certain features, that should ensure the optimal qualities of the operating form of the catalyst (magnetite spinel).

Our previous studies [1–3], devoted to one of the most promising methods for the preparation of α-Fe_2O_3, i.e. the oxidative hydrolysis of iron (II), enabled us to reveal some essential features of the mechanism of the goethite phase formation. This phase is the precursor for obtaining α-Fe_2O_3, which is a well-crystallized phase of regular and compact hexagonal crystals. The hydrolysis of iron (III), in the absence of iron (II), leads to the formation of the amorphous ferrihydrite phase [3–7]. The α-Fe_2O_3, obtained from this precursor, has a large number of crystal defects, which determines the specific features favourable, to a great extent, to the preparation of the operating form of the catalyst, highly active with respect to WGSR.

The relationship between the preparation method and the physico-chemical properties of the iron oxide precursors of the catalysts for WGSR has been investigated in the present work by means of an appropriate set of physical and chemical methods. The role of some specific properties of the precursor for the preparation of a highly active catalyst has been explained on the basis of the concept of an associative mechanism by which WGSR proceeds.

2. Experimental procedure

Two samples were synthesized in the following ways.

Sample 1 was obtained by the hydrolysis of iron (III) sulphate with ammonia at pH $= 4.5$ at 60 °C. The air-dried (AD) sample is denoted by Fe(III) AD, the calcined (C) one by Fe(III) C.

Sample 2 was obtained by oxidative hydrolysis of iron (II) sulphate with ammonia at pH $= 4.5$ at 60 °C (the notation is analogous; Fe(II) AD and Fe(II) C.)

The two samples were prepared in the automated laboratory reactor "Contalab" (Contraves, Switzerland) under complete control of all parameters. The chemicals used were $FeSO_4 \cdot 5H_2O$, $Fe_2(SO_4)_3 \cdot 9H_2O$ and NH_4OH grade "p.a.". The suspension was filtered and the samples were washed carefully with distilled water until all SO_4^{2-} was eliminated, followed by drying at 100–110 °C and calcination for 2 h at 400 °C.

The specific surface area of the samples was determined by the BET method, using a "Flow Sorb II-2300" device.

The samples for X-ray diffraction were prepared with Synocryl 9122X in a diluted toluene solution and X-rayed in a Guinier-de Wolff-Nonius camera Mark IV, using FeK_α radiation and an exposure time of 20 h. Some of the samples, whose patterns show very weak and broad reflections, were examined in the form of a densitometer trace (Kipp and Zonen densitometer).

For thermoanalysis, a Mettler TA 4000 system was used, equipped with a microbalance M3 and Mettler Graphware TA 72.5. The furnace was a Mettler TG 50, controlled by the Mettler Processor TC-11. Samples of approximately 20 mg were heated to 1000 °C at a rate of 5 °C $\min^{-1}$ in a nitrogen flow.

For transmission electron microscopy (TEM) , the samples were dispersed in doubly distilled water by ultrasound. Afterwards a drop was transferred to a carbon-coated bronze mesh and dried. Then the samples were examined in a Hitachi H-600-2 electron microscope and micrographs were taken.

Temperature-programmed reduction (TPR) was carried out in a standard apparatus under the following conditions: heating from 30–600 °C upon linear increase of the temperature at a rate of 10 °C $\min^{-1}$

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and pure hydrogen as reducing agent at a flow rate of 60 ml min^{-1}.

The reduction activity of the samples in the reaction of I_2 with hydroxyl groups in hexane in an inert atmosphere, as described elsewhere [8, 9] was used as a measure of the amount of OH groups on the surface.

Infrared spectra were recorded on a "Perkin–Elmer" spectrometer Model 9830 in the range 400–4000 cm^{-1} using a pellet of KBr.

The catalytic activity of the samples in the WGSR was evaluated on the basis of the reaction rate (mol m^{-2} h^{-1}), measured in a gradientless flow-circulation system, described elsewhere [10], under the following conditions: feed composition 5 vol% CO and 95 vol% Ar at a space velocity of 3000 h^{-1} and temperature interval 360–420 °C.

3. Results and discussion

Table I lists the results of the chemical analysis of the samples and some physical characteristics. The chemical analysis of the iron content in the air-dried and in the calcined Sample 2 (Fe(II)AD and Fe(II)C, respectively), carried out by means of oxidative hydrolysis of Fe(II), shows that the iron content is very close to the stoichiometric one for FeOOH or Fe_2O_3 respectively. By comparison, Sample 1, obtained by hydrolysis of Fe(III), has a lower iron content both in the air-dried and in the calcined form. Sample 1 possesses a higher specific surface area and it remains higher even after reduction, i.e. in the operating form of the catalyst. The density of Sample 2, obtained by oxidative hydrolysis, is higher than that of Sample 1.

The data, obtained by TEM (Fig. 1), show that the Fe(II)AD sample is a typical α-FeOOH (Fig. 1a) with a rather broad size distribution. The Fe(II)C sample shows the same size distribution (Fig. 2b). The prisms possess a distinctly grainy appearance; therefore, the product is a porous dehydrated phase. The actual crystallites are much smaller than the initially formed prisms, but they are still highly orientated. The Fe(III) AD sample has an amorphous appearance and represents, in fact, aggregates of many small crystallites of about 5–6 nm in diameter (Fig. 1c). The Fe(III)C sample has the same appearance; only the crystallites are somewhat larger.

The analysis of the samples by the X-ray diffraction method confirms the result obtained by TEM. The Fe(II)AD sample is α-FeOOH and the Fe(II)C sample is α-Fe_2O_3. The crystallite size of the α-Fe_2O_3 is of the order of 200–280 nm, which is in agreement with the results obtained by TEM. The two forms of Sample 1 (air-dried and calcined), can be interpreted better by means of a densitometer trace (Fig. 2). Comparison with the densitometer traces of α-FeOOH and α-Fe_2O_3 p.a. Merck, used as references, proves that α-FeOOH and α-Fe_2O_3 are formed in the samples with a very small size of the crystallites, which again is consistent with TEM results.

The comparison of the TG curves of the dry samples (Fig. 3a and b) shows that the total loss of weight in the range from 25–1000 °C is 20.87% for Sample 1 and 13.76% for Sample 2. The calculated loss, according to stoichiometry, from α-FeOOH to α-Fe_2O_3 is 10.14%. This difference shows that the quantity of water, above the stoichiometrically calculated amount for Sample 1, is 10.73%, while for Sample 2 it is 3.62%. It should be noted, also that after calcining of the samples at 400°C, a much larger quantity of water remains in Sample 1. This last and very essential result will be commented upon later. The well-crystallized α-Fe_2O_3, obtained from Sample 2, has only a small amount of water, which is difficult to liberate (only at about 700 °C). The finely dispersed α-Fe_2O_3, obtained from Sample 1, easily liberates the adsorbed water (at about 570 °C) and thereafter begins the sintering of the samples.

The infrared spectra of the two samples confirm once again the conclusions from the TEM and DTG studies. It has been observed that there is an intensive absorbance characteristic for the bending vibration of the hydroxyl groups OH at 1627 cm^{-1} and for the stretching vibration of the OH groups and the coordinated water at 3400 cm^{-1}.

The TPR of the samples (Table I) shows the two expected reduction peaks: the α-peak, corresponding to reduction of Fe_2O_3 to Fe_3O_4 and the β-peak, corresponding to reduction of Fe_3O_4 to Fe°. The α-peak of reduction to the operating form of the catalyst Fe_3O_4 for Sample 1 has an area which is twice as large. The total sum of the peak areas, related to that of iron, also remains higher for Sample 1.

An estimation of the reduction activity and reactivity of the hydroxyl groups in the samples may also be obtained chemically by means of the reaction of I_2 in organic solvent in an inert atmosphere [8, 9]. It can be seen from the data listed in Table I that the value obtained for Sample 1 is higher than that for Sample 2.

The detailed study of the physicochemical properties of the samples shows that the α-Fe_2O_3, obtained

TABLE I Physico-chemical properties of the samples

Sample	Iron content[a] (wt %)		Surface area[a] (m^2 g^{-1})		Density[b] (g cm^{-3})	TPR		Reduction activity[c] (mmol$_{I_2}$ gat^{-1}$_{Fe}$)
	AD	C	C	R		α-peak (%)	β-peak (%)	
1 Fe (III)	56.2	57.7	130	14	3.75	22	78	9.1 ± 0.1
2 Fe (II)	59.1	66.5	80	6	4.00	11	89	6.8 ± 0.1

[a] AD, air dried; C, calcined; R, reduced.
[b] The density has been measured after calcination at 400 °C.
[c] The reduction activity refers to reduced samples.

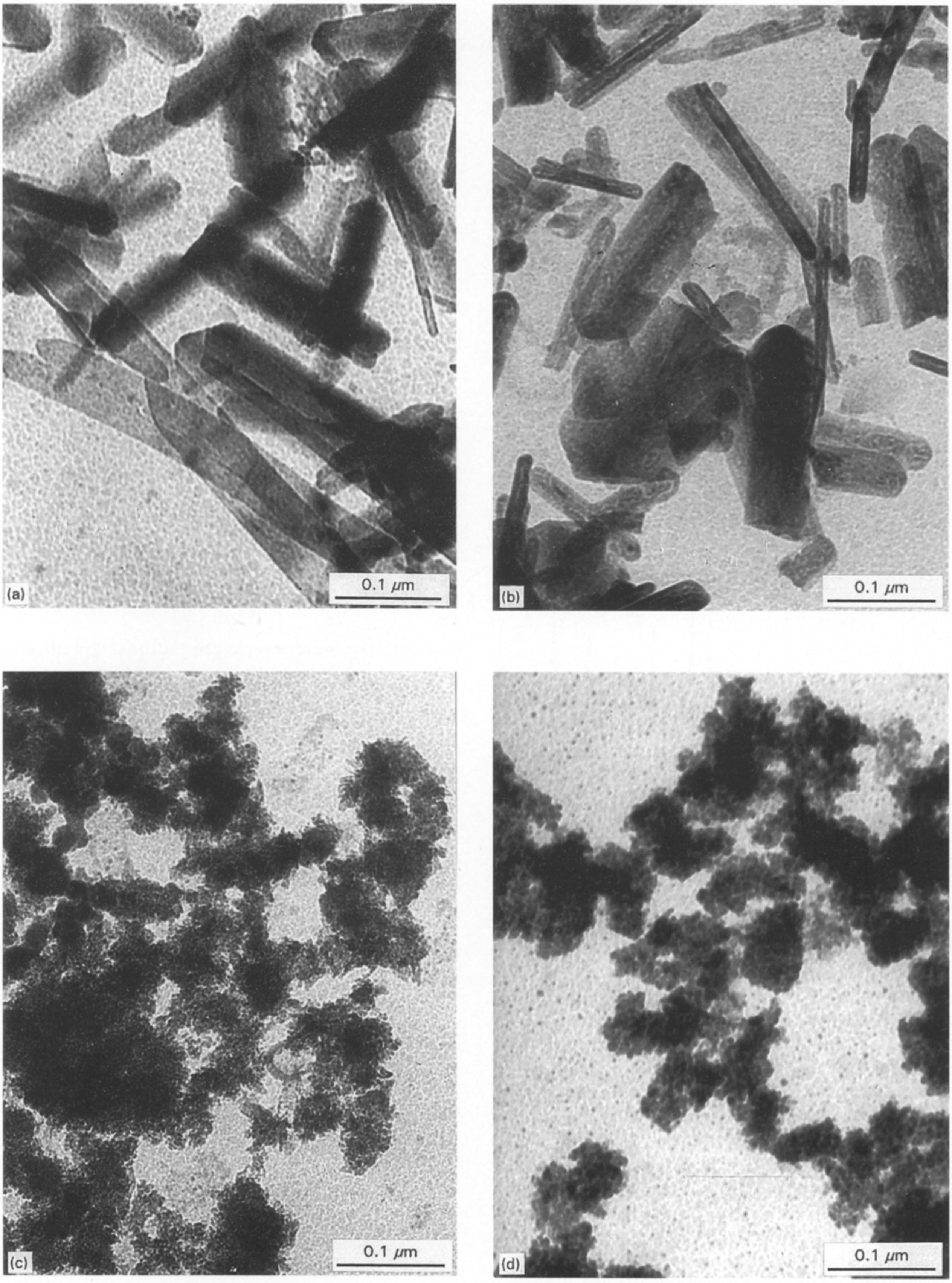


Figure 1 Transmission electron micrographs of the samples: (a) Fe(II) AD; (b) Fe(II) C; (c) Fe(III) AD; (d) Fe(III) C.

from ferrihydrite (Sample 1), is substantially different from Sample 2, prepared from α-FeOOH upon oxidative hydrolysis of Fe(II). The important point in this case is to note the differences in the degree of hydration of the two samples, the higher reduction activity and the higher amount of OH groups of Sample 1.

As was found in our previous studies, the formation of the well-crystallized phase of α-FeOOH during the oxidative hydrolysis of Fe(II) is due to the intensive combination of the initial hydrolysate aggregates by means of oxidatively hydrolysed Fe^{2+} [2, 3]. The ferrihydrite phase, obtained during the hydrolysis of

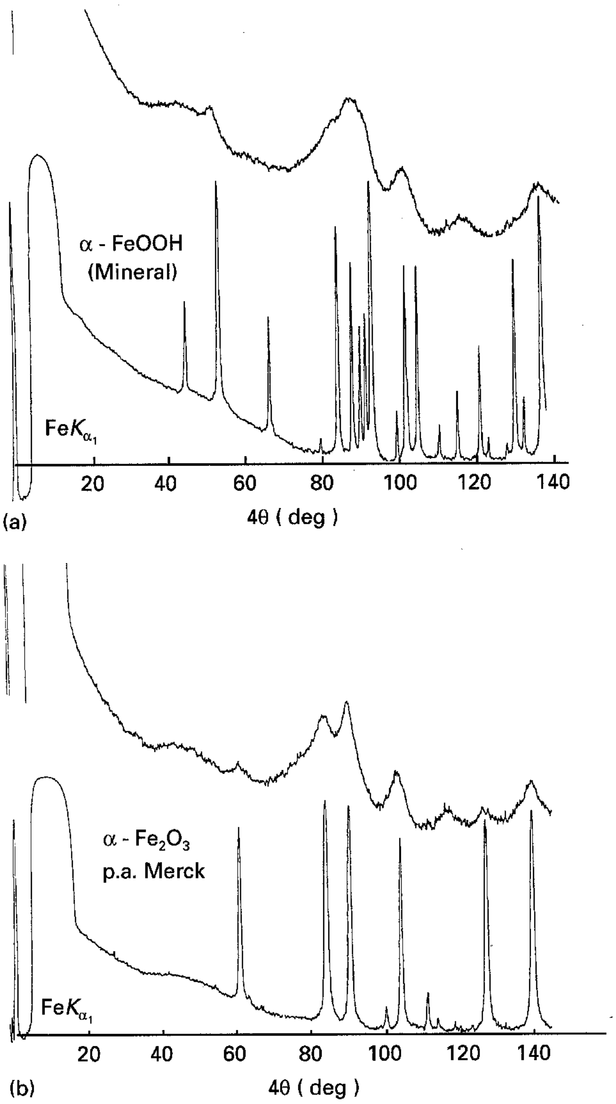


Figure 2 XRD patterns of the samples: (a) Fe(III) AD; (b) Fe(III) C.

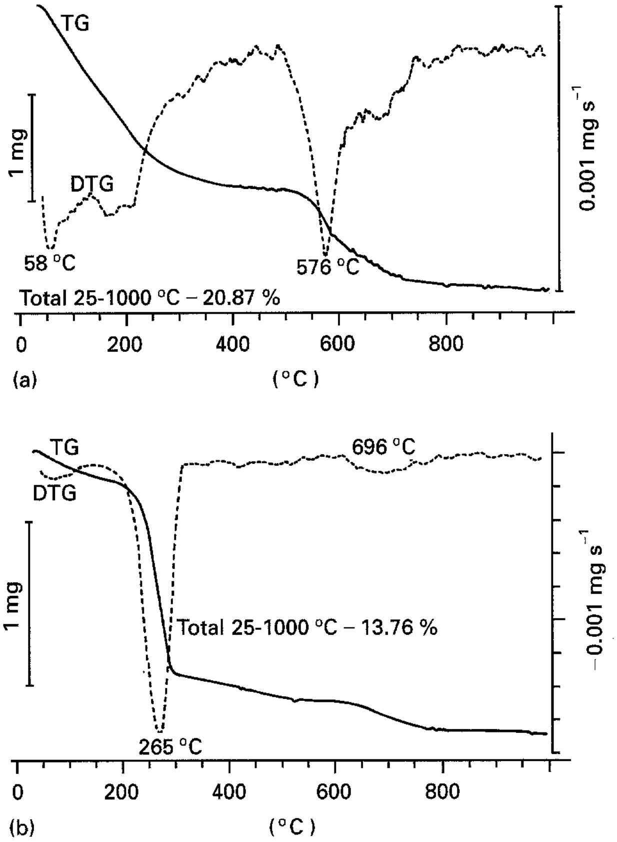


Figure 3 DTG curves of the samples: (a) Fe(III) AD; (b) Fe(II) AD.

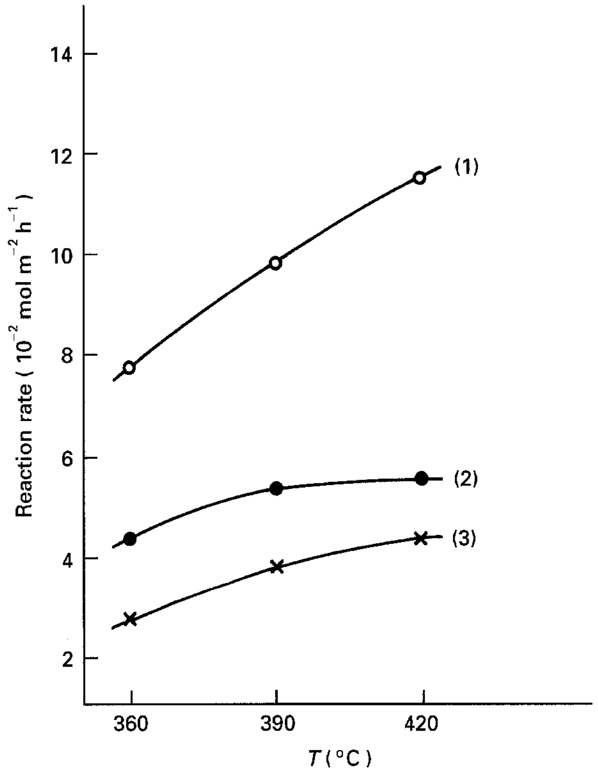
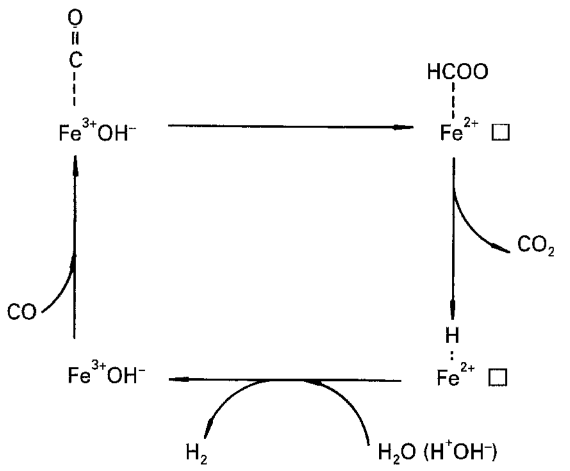


Figure 4 Catalytic activity in WGSR (rate of reaction as a function of temperature at partial pressure of water vapour of 149.4 mm Hg) for the samples (1) Fe(III), (2) Fe(II), (3) commercial catalyst.

Fe(III), has a very low crystallinity and a high degree of hydration, including the adsorption water and a large quantity of hydroxyl groups. In addition to this, the smaller amount of water in Sample 2 is localized in tunnel pores, i.e. difficult to evolve, while in Sample 1 the water is only weakly bound.

These investigations prove that some of the properties of the initial precursors are retained to a certain degree in the α-Fe_2O_3 samples prepared from them. On the basis of the established differences in the physico-chemical properties of the two samples of α-Fe_2O_3, obtained in different ways from Fe(II) and Fe(III), the differences in their catalytic activity for the WGSR could also be explained (Fig. 4).

According to modern concepts, the WGSR proceeds via two basic mechanisms: oxidation–reduction and an associative mechanism [11]. It has been accepted that over iron oxide (high-temperature) catalysts, the mechanism is oxidation–reduction. In previous studies [12, 13] it was found that upon promotion of the iron oxides with cobalt in addition to the α-Fe_2O_3, a certain amount of γ-Fe_2O_3 is stabilized in them. Upon the formation of the operating magnetite phase of the catalyst, the stabilization of some quantities of structures similar to γ-Fe_2O_3 also proceeds. An increased amount of active hydroxyl groups and occluded water is contained in these structures, which could participate in the reaction via the associative mechanism [11] according to scheme I.



A characteristic feature of this mechanism is the participation of active hydroxyl groups, OH, from the surface of the catalyst in the formation of surface formate complexes, and enhanced electron transfer in the interchanging valency states Fe^{2+} and Fe^{3+}. The possibility of participation of carbonate and bicarbonate intermediate complexes, instead of the formates, is also under discussion [14, 15], which does not alter the mechanism substantially. The higher catalytic activity in the WGSR observed for Sample 1 (Fe(III)) in comparison to Sample 2 (Fe(II)) could be explained by the presence of active hydroxyl groups in the former. As a result of this, there exists a possibility for the WGSR to proceed in Sample 1 (Fe(III)) both via the oxidation–reduction and the associative mechanisms. This conclusion is based upon the experimentally observed higher reaction rate over Sample 1 (Fe(III)) at lower temperatures.

The present study provides evidence to conclude that the formation of iron oxide catalysts from precursors, leading to the formation of structures containing an increased amount of active hydroxyl groups, is a reliable criterion for the selection of catalysts active for the WGS reaction.

Acknowledgement

This work was partially supported by the National Foundation for Scientific Research, Bulgaria.

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Received 25 October 1993
and accepted 17 July 1994