The Specific Surface Area and Catalytic Properties of the Calcination Products of δ-FeOOD

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The effect of calcination temperature on the structure, specific area and catalytic activity of samples obtained from δ-FeOOH and δ-FeOOD was studied. It was found that, as a result of dehydratation, the samples differ mainly in specific surface area and in their catalytic properties.

Spezifische Oberfläche und katalytische Eigenschaften der Calcinierungsprodukte von δ-FeOOD

Der Effekt der Calcinierungstemperatur auf die Eigenschaften von Proben aus δ-FeOOH und δ-FeOOD wurde untersucht. Die dehydratisierten Produkte unterschieden sich — bei sehr ähnlichen Strukturen — hauptsächlich bezüglich spezifischer Oberfläche und katalytischer Aktivität.

Introduction

When studying the dehydration process of polymorphous iron oxides[1], our attention concentrated on the physical and catalytic properties of calcination products obtained from oxide deuteroxide and oxide hydroxide of the δ-type. These preparations displayed a strongly differentiated specific surface area and catalytic properties, although their structure was very similar[2].

In this paper, we shall report the results on the correlation between the shapes of the curves, expressing the changes in specific surface area and the catalytic activity of the calcination products obtained at 300 to 600 °C from meta-deuteroxide and hydroxides in the process of violent oxidation of ferrous(II) salts, dried with oxygen[2].

Experimental

Meta-deuteroxide of the type δ-FeOOD was obtained as follows:

Powdered pure iron was dissolved in D_2SO_4 (15 % solution in D_2O). The precipitate was obtained by addition of sodium deuteroxide and was then oxidated with dried oxygen at 55 °C. The oxidated red precipitate obtained from the heavy water solution was filtered, rinsed with D_2O until all accompanying SO_4^{2-} ions were removed and was dried at room temperature over silica gel to constant weight[2].

Meta-hydroxide of the type δ-FeOOH was prepared in the same way from reagents containing hydrogen instead of deuterium.

Chemical analysis proved the δ-FeOOD to contain 0.004 g of non-washed sulphates (loss of weight at 110 °C was 9.8 %), whereas the corresponding δ-FeOOH contained 0.003 g of SO_4^{2-} and 9.2 % H_2O.

The chemical composition determined for both preparations was almost identical: the iron content in δ-FeOOD was 58.8 %, in δ-FeOOH 58.6 %, and the total loss of weight was 14.1 % and 13.5 %, respectively.

The dehydration process and phase transitions[2] were recorded by the DTG and DTA methods (with a MOM, OD-102 Derivatograph).

The specific surface area was measured chromatographically by the thermal desorption of argon[3].

The catalytic properties of the preparations in the water gas shift reaction were tested by the previously described[4] flow method in a microreactor coupled to a gas chromatograph. 500 mg of the catalyst were deluded to a volume of 2 ml with quartz grains, and a gas mixture of $CO:H_2O = 2.5$ was made to pass under atmospheric pressure through the reactor at 350 ± 0.5 °C with a flow rate of 1,500 ml/h. The tests were carried out on the products obtained from δ-FeOOD and δ-FeOOH after 3 h of calcination at 300 to 600 °C, preceded by reduction[4].

Isopropanol decomposition was carried out by impulse technique. An amount of 0.2 g of the oxide was placed in the microreactor coupled with a gas-chromatograph. The carrier gas (N_2) passed through it at a rate of 35.3 ml/min. The reactions were carried out at 300 ± 0.5 °C, the results being the average of 5 injections[1].

Adsorption of pyridine was determined by gas chromatography[5].

Electron-microscopic pictures were taken using the replication method in a Japanese JEM-6 B electron-microscope.

Results and Discussion

Structural, phase, and chemical analyses show that the δ-FeOOD obtained is a pure phase with structural phase and chemical properties[6] close to those of δ-FeOOH. The structure of these preparations was found to be in agreement with literature data[7].

The phase transitions, accompanying the calcination of δ-FeOOD and δ-FeOOH, were recorded by means of a derivatograph. The respective changes in the DTG curves are shown in Fig. 1.

It is apparent from these curves (Fig. 1) that the dehydration process sets in at 60 °C and lasts up to 300 °C. The DTA curve shows a deep endothermic peak, related with a loss in weight of about 10 %,

with its maximum at 150 °C (δ-FeOOH) or at 160 °C (δ-FeOOD). A slight maximum is observed next, originating from crystallization of the α-phase. The slight shift in the endothermic maximum in the case of δ-FeOOD compared to δ-FeOOH is presumably related with the *Curie* point, which in the former case lies at 180 °C and in the latter at 175 °C[2,6]. A new hematite phase is formed in the temperature range from 300 to 950 °C and thus no loss in weight is observed[9,10,13]. The differentiated dehydration rate of δ-FeOOH and δ-FeOOD favours the
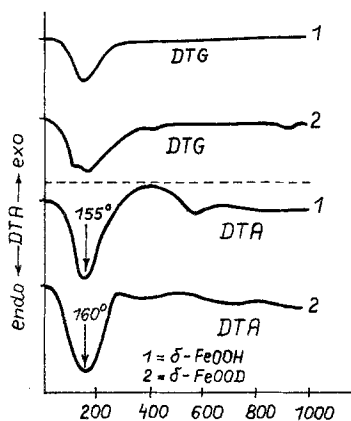

Fig. 1. DTG and DTA curves of samples δ-FeOOH and δ-FeOOD

formation of a different morphology of the samples very markedly influencing the specific surface area and catalytic properties[4].

In order to compare the morphology of the surface of the reaction products of these δ-FeOOD and δ-FeOOH, obtained under similar conditions, we give some electron-microscopic pictures (Figs. 2a-d). It can be generally concluded from them that the preparations obtained from δ-FeOOH are of a fine grain type (Figs. 2a, b) and consist of loose or conglomerated (after calcination) spherical particles, whereas the preparations originating from δ-FeOOD form compact lumps with visible single spherical particles of iron oxide Figs. 2c, d).

The surface area of preparations obtained by calcination of δ-FeOOD in comparison to that of the preparations obtained from δ-FeOOH is surprisingly large. The differences amount to about 150 to 160 % (Table). These differences are still present in the reduced preparations, immediately before the reaction of CO conversion with water vapour. The curves showing the conversion degree of the water vapour gas shift reaction run similarly (Table 1). In this case the catalytic

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properties of the preparations obtained from δ-FeOOD are, in the whole range investigated, by about 100% higher than those of the preparations obtained from δ-FeOOH. In the water gas shift reaction, the best results are exhibited by the preparations obtained by
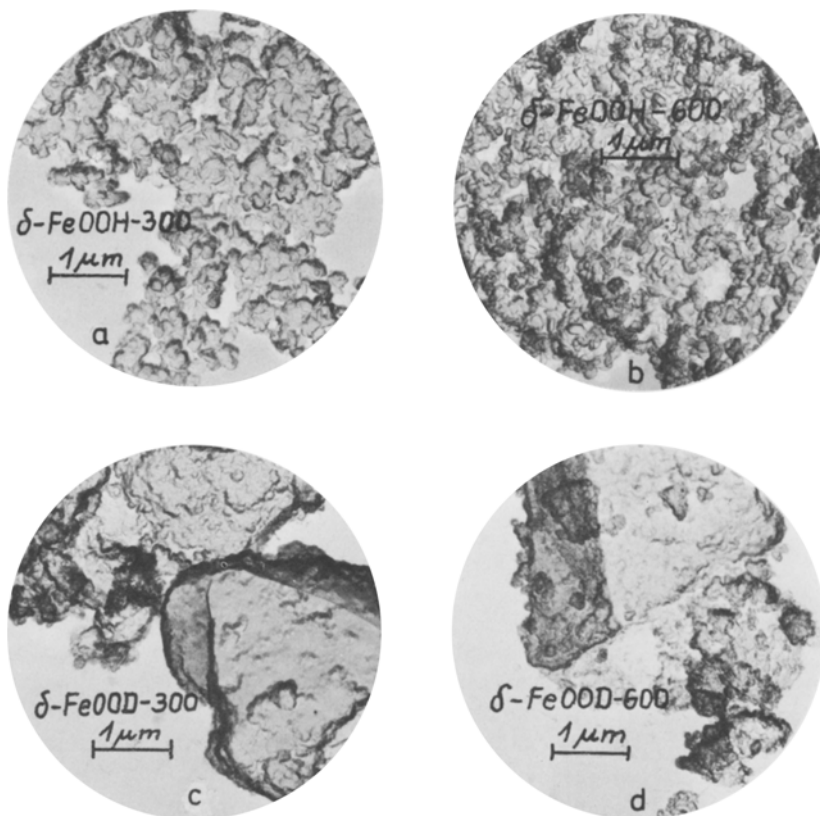

Fig. 2. Electron-microscopic pictures of the calcination products of δ-FeOOH (*a*, *b*) and δ-FeOOD (*c*, *d*)

calcination at 300 °C. Application of higher temperatures results in a rapid decrease in catalytic activity caused by the changes in surface texture[12, 14].

In order to confirm the nature of the differences between the surfaces of calcination products δ-FeOOH and δ-FeOOD, their catalytic activity was measured in a model reaction of isopropanol decom-

Table 1. Characteristics of some physical and catalytic properties of the products of calcination of δ-FeOOH and δ-FeOOD

	Calcination temperature [°C]	Specific surface area [m²/g]		Pyridine adsorption × 10⁴ [mVal/g]	Degree of conversion [%]		Selectivity [%]	
		before reduction	after reduction in 350 °C		CO + H₂O [350 °C]	isopropanol [300 °C]	dehydrogen.	dehydrat.
δ-FeOOH	300	91.8	13.8	27.2	23.6	53.8	71.9	—
	400	42.3	17.7	19.1	19.6	50.8	67.2	—
	500	17.4	14.4	10.5	17.1	42.1	71.0	—
	600	14.7	—	—	14.5	29.2	55.1	—
δ-FeOOD	300	225.3	23.7	29.8	45.3	70.2	15.0	85.0
	400	106.2	23.1	22.6	38.6	44.1	28.0	72.0
	500	53.8	22.4	11.9	29.8	50.2	62.0	38.0
	600	41.0	—	—	27.4	—	—	—

position, which is known to occur on acid centres according to an electronic mechanism[1]. Thus the selectivity of this reaction depends largely on hydroxylic groups, containing convertible hydrogen. From our results, the preparations obtained from δ-FeOOD are distinctly more active in isopropanol conversion than the analogical preparations obtained from δ-FeOOH. It is also easy to see that the calcination products of δ-FeOOH catalyze, first of all, the dehydrogenation process, whereas the respective calcination products of δ-FeOOD are more apt to catalyze dehydration of isopropanol.

The capacity of these preparations to adsorb pyridine is closely related to their activity. The calcination products of δ-FeOOD adsorb slightly more pyridine than those originating from δ-FeOOH. The increased adsorption of pyridine as well as the activity in the dehydratation process of isopropanol in the case of preparations originating from δ-FeOOD is thus determined by the larger numbers of hydroxylic groups remaining on the surface of the calcination products of δ-FeOOD in comparison to δ-FeOOH. The process leading to water and propylen in this reaction will mainly occur on centres of the active surfaces formed by polarisation of the OH groups. We can relate dehydrogenation of isopropanol (where the calcination products of δ-FeOOH are more highly active) to the surface texture and interphase space. The differentiated catalytic properties should also be in relation with the magnitude of the specific surface area (biographically different preparations carrying at least two kinds of catalytically active sites). The role of these binary active centres occuring on the surface of iron oxide has been discussed extensively in another paper[1].

Acknowledgments

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