

# Hydroxocompounds of Fe(III) as colloidal and heterogeneous catalysts for water oxidation to dioxygen. Experimental evidence for a correlation of catalytic activity and the structure of the catalysts

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## Abstract

Catalytic activity of a large set of Fe(III)–hydroxocompounds with various well-defined structures was studied in reaction of the oxidation of water to dioxygen by  $\text{Ru}(\text{bpy})_3^{3+}$  as an one-electron oxidizer. Fe(III)–hydroxocompounds which have the smallest distance between Fe(III) cations and a large amount of the terminal OH groups which should possess rather strong acidic properties are found to have the best catalytic activity. Thus, the catalytic active sites seem to be constructed from two Fe ions inside octahedrons connected by their edges through oxo or hydroxo groups.  $\gamma\text{-FeOOH}$  and a tetrameric complex  $\text{Fe}_4(\text{OH})_{10}(\text{SO}_4)$  appear to be the most suitable materials with the best activity.

*Keywords:* Activity; Hydroxocompounds; Iron; Oxidation; Structure; Water

## 1. Introduction

Water oxidation to dioxygen by one-electron oxidizers, such as, e.g.,  $\text{Ru}(\text{bpy})_3^{3+}$  is known to be accelerated by hydroxide compounds of Ru, Co, Mn, Fe and some other metals ([1,2] and references therein). Up to now Fe-containing compounds were the least popular catalysts for these studies, since in terms of their catalytic properties ( $\text{O}_2$  yields, reaction rate, pH range of catalytic action) they apparently were at a disadvantage in relation to catalysts based on, e.g., Mn(III) or Co(III) [3,4]. On the other hand, hydroxocompounds of iron can be rather conven-

ient for elucidating the nature of both catalytically active species and, probably, the active site of water oxidation, since the composition, structure and physico-chemical properties of Fe(III) hydroxocomplexes appear to have been studied more profoundly than those of any other mentioned catalytically active ions [5]. One could also expect that studies on the elucidation of the structure of the catalytically active sites of artificial catalysts for water oxidation can provide some information on the structure of the active site of the natural Mn-based water oxidase too, since the expected mechanisms of water oxidation in all cases seem to be the same or similar.

In this paper we report on the synthesis and investigation of the catalytic properties of several

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hydroxocompounds of Fe(III) of a known composition for the water oxidation. The compounds under study are in colloidal or heterogeneous states as well as those immobilized on various supports.

## 2. Experimental

### 2.1. Reagents

We used  $\text{Fe}(\text{NO})_3 \cdot 9\text{H}_2\text{O}$  of 'pure' and starch 'pure for iodometry' grade.  $\text{Ru}(\text{bpy})_3(\text{ClO}_4)_3$  synthesized according to [6] was used as the oxidizer of water. Pyrophosphate buffers were prepared by addition of  $\text{HNO}_3$  to a 0.1 M solution of  $\text{Na}_4\text{P}_2\text{O}_7$  to obtain a required pH value. Borate buffers were prepared from  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ .

Hydroxocompounds of Fe(III) used as heterogeneous catalysts were obtained by well known procedures [7], [8], [9], and [10] for  $\text{NaFe}_3(\text{OH})_6(\text{SO}_4)_2$ ,  $\text{Fe}_4(\text{OH})_{10}(\text{SO}_4)$ ,  $\alpha\text{-FeOOH}$  and  $\gamma\text{-FeOOH}$ , respectively.

### 2.2. Synthesis of colloidal catalysts

We have used various synthesis procedures:

#### Procedure 1

202 mg of ferric nitrate dissolved in 25 ml of water were heated in a water bath at 353 K for 30 min. meanwhile pH was changing from 2.2 to 1.5 Fe concentration in the colloid obtained was  $2 \cdot 10^{-2}$  M.

#### Procedure 2

125 mg of starch were added to 25 ml of boiling water, then the mixture was cooled to 353 K and 202 mg of ferric nitrate were added. The mixture was left at the same temperature for 30 min. The starch content in the colloid was 0.5 wt.%, that of iron was  $2 \cdot 10^{-2}$  M.

#### Procedure 3

125 mg of starch were dissolved in boiling water. Then, the mixture was cooled to room temperature and 40.4 mg of ferric nitrate were added.

For the next step 1 M NaOH was introduced dropwise to give a pH of ca. 10–11. Then, the solution was diluted to 25 ml. The contents of iron and starch were  $4 \cdot 10^{-3}$  M and 0.5 wt.%, respectively.

### 2.3. Synthesis of immobilized catalysts

$\text{Fe}_3(\text{CO})_{12}$  (a starting reagent for the synthesis of immobilized catalysts) was obtained by the procedure described in [11]. The supports  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$  or  $\text{SiO}_2$  were preliminarily vacuumed under heating.

#### Procedure 1

Iron carbonyl was adsorbed on  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  from hexane solution and then unadsorbed complexes were washed out with an excess of solvent [12]. The catalyst was aged in air at ambient temperature.

#### Procedure 2

On  $\text{SiO}_2$  iron carbonyl was deposited by impregnation with hexane solution followed by the solvent distillation under vacuum [12].

### 2.4. Measurement of the surface hydroxyl group concentration

10.0 ml of water and 10.0 ml of 0.02 M NaOH were added to 50 mg of catalysts, stirred for 30 min, then filtered. 15.0 ml were sampled from the filtrate and titrated with 0.02 M solution of HCl by potentiometry on a glass electrode.

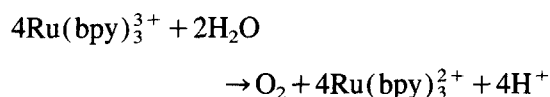
### 2.5. Optical and $\text{O}_2$ measurements

UV–VIS spectra were recorded with a Specord UV–Vis (Karl Zeiss, GDR) spectrophotometer. pH was measured with ionometer I-135 (USSR).  $\text{O}_2$  concentration was monitored with the Clark electrode with Monitor II Beckman (UK).

#### Catalytic reaction performance

20 ml of 0.05 M buffer and a sample of colloidal solution (or 30–50 mg of heterogeneous catalyst) were introduced in a 25 ml glass reactor and bub-

bled with argon during 10–15 min at 298 K. Then, under continuous stirring and argon bubbling, the fresh solution of oxidizer was introduced to give a concentration of  $1 \cdot 10^{-3}$  M. The reactor was plugged with a stopper with the Clark electrode and no gas phase was left between the stopper and solution. The catalyst selectivity towards  $O_2$  ( $O_2$  yield) was calculated in relative % from the stoichiometric yield of reaction:



The preliminary experiments have shown, that the spectra of  $Ru(bpy)_3^{3+}$  solutions are not changed when colloidal starch is added. This is evidenced in the fact that the chosen oxidizer is not able to react with pure starch under conditions of this study (see also [13,14]).

### 3. Results and discussion

#### 3.1. Catalytic properties of colloidal Fe(III) hydroxides

Alkalization of Fe(III) salt solutions even at pH 3 results in precipitation of a hydroxide. In the presence of starch, like at hydrolysis of Mn(III) [13] or Co(III) [14] complexes, a transparent and stable solution can be obtained even at pH 12. The absorbance spectrum of sample 1 (see

Table 1) is presented in Fig. 1 (curve 1). The spectrum shape of the colloids does not change when the starch concentration is varied from 0.1 up to 1 wt.%. However, addition of the colloidal catalyst to the pyrophosphate buffer, where the reaction is carried out, leads to an appreciable change of its spectrum (curve 2, Fig. 1). As for the Co(III) colloids, we rationalize such a phenomenon in terms of partial dissolution of the colloid particles due to their interaction with the buffer yielding pyrophosphate complexes of Fe(III). This is accompanied by a change in the absorbance spectra. The changes in the spectrum become less pronounced at higher pH or when pyrophosphate buffer is replaced with the borate one.

A stable colloid of a hydroxocompound of Fe(III) can be prepared without a stabilizer, as well, if only a fresh solution of ferric nitrate is heated in a water bath. The initial pH of solution equal to 2.2 decreases to 1.5 during this procedure. The shape of final spectrum (see curve 3 of Fig. 1) coincides with that of the starch stabilized colloid obtained in an alkaline medium, though its intensity is considerably lower; this is to be expected, since in acidic solutions the concentration of hydroxocomplexes should be far lower than in the alkaline ones. Indeed, taking the colloid obtained in acidic medium and possessing spectrum 3, adding 0.5 wt.% of starch and then NaOH to give a pH of 10–11 (sample 4, Table 1), will obviously give a spectrum coinciding with spectrum 1. If

Table 1  
 $O_2$  yields with regard to pH and the nature of buffer obtained in solutions with Fe(III) hydrolyzed under various conditions

Sample no.	Fe(III) hydrolysis conditions			Catalyst composition		Catalyst pH $O_2$ yield (%)			
	pH	Temperature (K)	Starch admixture	[Fe(III)] (M)	Starch (%)	pH 7.5	pH 9.0		
						Pyrophosphate buffer	Pyrophosphate buffer	Borate buffer	
1	10–11	295	+	$4 \cdot 10^{-3}$	0.5	10	5–7	50	55
2	10–11	295	+	$4 \cdot 10^{-3}$	0.1	10	25	53	60
3	2.2	350	–	$2 \cdot 10^{-2}$	–	1.5	33	62	74
4	2.2	350	–	$2 \cdot 10^{-2}$	0.5	10	48	65	73
5	2.2	350	+	$2 \cdot 10^{-2}$	0.5	1.5	16	63	71

Conditions of the catalytic experiments:  $[Fe] = 2 \cdot 10^{-4}$  M,  $[Ru(bpy)_3^{3+}]_0 = 1 \cdot 10^{-3}$  M, 0.05 M buffer.

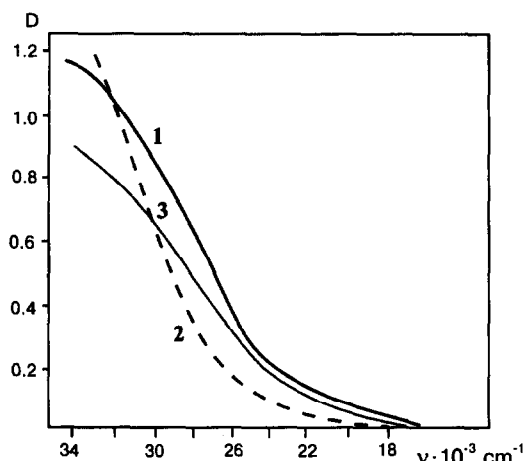


Fig. 1. Absorbance spectra of the solutions of hydrolyzed Fe(III): 1 –the sample 1 of Table 1:  $[\text{Fe}] = 4 \cdot 10^{-3} \text{M}$ , 0.5% of starch; optical length 0.1 cm; 2 –the same solution is diluted by 10-fold with 0.05 M pyrophosphate buffer, pH 7.5, optical length 1.0 cm; 3 –the sample 3 of Table 1:  $[\text{Fe}] = 4 \cdot 10^{-3} \text{M}$ , optical length 0.1 cm.

ferric nitrate is hydrolyzed in acidic medium in the presence of starch (sample 5, Table 1), then the spectrum of the obtained colloid is similar to that without starch, but is slightly less in intensity.

At pH 7.5, the  $\text{O}_2$  yields over various colloids prepared in both acidic and basic media (samples 2, 3, 4, 5) are essentially different, but are approximately the same at pH 9, being similarly higher in the borate buffer, than in the pyrophosphate one. We failed to reveal any distinct correlations between the catalytic properties of colloids and their spectra or their ability to dissolve in the pyrophosphate buffer, since after dilution with the latter the spectrum changed noticeably only in the case of samples 1 and 5 at pH 7.5.

In solutions of hydrolyzed ferric salts the products of initial hydrolysis with a low molecular weight coexist with hydroxide polymers of high molecular weight containing hundreds of Fe(III) ions [5,15]. We have supposed, that the smallest initial hydroxocompounds containing only a few iron atoms should be the most efficient in the catalysis, such as is the case for Mn- and Co-containing colloidal catalysts stabilized with starch [13,14]. However, to establish a reliable relationship between the content of the active species in the colloid and their catalytic properties is difficult. For this reason, we have synthesized and tested in

the oxidation of water the activity of the Fe(III) compounds specially prepared from either hydroxopolymer or low-molecular hydroxocomplexes of a known structure.

### 3.2. Catalytic properties of Fe(III) hydroxides

For the study, we have selected  $\alpha$ - and  $\gamma$ -modifications of FeOOH as well as amorphous FeOOH. All these species present polymeric oxo-hydroxocomplexes of different crystalline structure. Evidently, all FeOOH modifications (including colloidal) are related by origin and possess a common chemical composition and molecular structure determined by that of the polymer [5]. So, they should have similar catalytic properties. However, this is not confirmed experimentally. In the presence of  $\alpha$ -FeOOH the  $\text{O}_2$  yields are rather low (Table 2). Colloidal catalysts prepared in acidic medium (see, e.g., sample 4, Table 1) appear to be more selective than amorphous hydroxide. The latter seems to be a result of the presence, in the colloidal catalysts, of considerable amounts of high activity low-molecular hydroxocomplexes besides the high-molecular polymer. Among the modifications of the bulk FeOOH,  $\gamma$ -FeOOH was found to be the most selective (Table 2).

Table 2  
Dependence of  $\text{O}_2$  yields on pH of the reaction media obtained over Fe-containing heterogeneous catalysts

No	Catalyst	pH					
		6	7	7.5	8	9	10
1	FeOOH (amorph.)		25	40	40	41	40
2	$\alpha$ -FeOOH			<5		16	
3	$\gamma$ -FeOOH	8	34	55	78	93	92
4	$\text{Fe}_4(\text{OH})_{10}(\text{SO}_4)$	27	57	81	86	84	87
5	$\text{NaFe}_3(\text{OH})_6(\text{SO}_4)_2$			0		5	8
6	$\text{Fe}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$			<5		11	15
7	$\text{Fe}_3(\text{CO})_{12}/\text{TiO}_2$			<5		12	15
8	$\text{Fe}_3(\text{CO})_{12}/\text{SiO}_2$					30	40

Conditions of the catalytic experiments: 30–50 mg of the catalyst in 20 ml of 0.05 M pyrophosphate buffer,  $[\text{Ru}(\text{bpy})_3^{3+}]_0 = 1 \cdot 10^{-3} \text{M}$ .

Table 3  
Some structural parameters of tri- and tetrameric ferric sulfates obtained by the EXAFS method

Chemical bond	Bond length (Å)	
	NaFe <sub>3</sub> (OH) <sub>6</sub> (SO <sub>4</sub> ) <sub>2</sub>	Fe <sub>4</sub> (OH) <sub>10</sub> (SO <sub>4</sub> ) <sub>4</sub>
Fe–O	1.99	1.90
	3.6	3.72
Fe–S	3.22	no
Fe–Fe	3.6	3.02

### 3.3. Catalytic properties of low-molecular hydroxocompounds of Fe(III)

Hydrolysis of Fe(III) sulfates in a small excess of alkali produces a set of hardly soluble basic sulfates [16], among them trimeric NaFe<sub>3</sub>(OH)<sub>6</sub>(SO<sub>4</sub>)<sub>2</sub> [7] and tetrameric Fe<sub>4</sub>(OH)<sub>10</sub>(SO<sub>4</sub>) [8] compounds have been the most intensively studied. O<sub>2</sub> yields obtained over these heterogeneous catalysts are presented in Table 2 as functions of the pH of the reaction solution. With the trimeric complex, the dioxygen yields are insignificant. On the contrary, the tetrameric complex appears to be the most efficient catalyst among all iron containing catalysts for water oxidation known to us. Both the substances have been studied with IR and EXAFS methods and found to be different in their structure. Details of this study will be published elsewhere [17]. In Table 3, some EXAFS data on the structure of these complexes are presented.

NaFe<sub>3</sub>(OH)<sub>6</sub>(SO<sub>4</sub>)<sub>2</sub> ('jarosite') represents a network of Fe octahedrons connected through OH tops. It is easy to reveal in this structure a cyclic triad of Fe octahedrons coordinated to SO<sub>4</sub><sup>2-</sup> tetrahedron (Fig. 2a); this structure is confirmed by X-ray technique [18].

Fe<sub>4</sub>(OH)<sub>10</sub>(SO<sub>4</sub>) is amorphous, as a rule, and hard to test with conventional X-ray analysis. We found its structure to be similar to that of aluminite, Al<sub>4</sub>(OH)<sub>10</sub>SO<sub>4</sub>. The structure of the latter was

discovered with X-ray diffraction analysis [19]. The structural unit of the tetrameric iron compound appears to be a cluster of four Fe octahedrons connected with their edges through OH groups (Fig. 2b). SO<sub>4</sub><sup>2-</sup> groups are not combined in the first coordination sphere of iron, but form H-bonds with coordinated OH and H<sub>2</sub>O ligands. EXAFS data confirm this structure rather well (Table 3). Thus, the main structural difference of the studied trimeric and tetrameric iron compounds is the manner of SO<sub>4</sub><sup>2-</sup> ion coordination and of the link between the neighbor Fe octahedrons through either edge or top (Fe–Fe distances are 3.0 and 3.6 Å, respectively). To exclude a possible unfavorable effect of coordinated sulfates we tested other low-molecular iron complexes, not containing SO<sub>4</sub><sup>2-</sup> ion, in the water oxidation.

### 3.4. Properties of supported hydroxocomplexes obtained from Fe<sub>3</sub>(CO)<sub>12</sub>

It is known reliably now [20], that a solid iron carbonyl, Fe<sub>3</sub>(CO)<sub>12</sub>, has a cyclic structure, that is, the iron atoms are situated at triangular tops (see Fig. 2c). Earlier we studied adsorption of this carbonyl on some supports, such as Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and SiO<sub>2</sub>.

This iron carbonyl is known to be adsorbed on the surface of Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> as isolated and spatially separated trinuclear complexes or their dimeric surface agglomerates, due to formation of strong chemical bonds with the surface [12]. On the contrary, SiO<sub>2</sub> surface possesses no sites capable to react with the iron carbonyl, and this carbonyl is deposited here as microcrystals [12]. One can expect that hydrolysis of iron carbonyl so immobilized should lead to formation of the amorphous Fe(III) hydroxide species on the SiO<sub>2</sub> surface while on the Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> surfaces Fe(III) hydroxo complexes with, possibly, a trimeric structure should be formed. Hence, these samples should differ in their catalytic properties. In fact, the Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>-based samples exhibit no significant catalytic effect, like this is the case for the trimeric iron sulphate. On the contrary, the catalytic efficiency of the SiO<sub>2</sub> supported catalyst

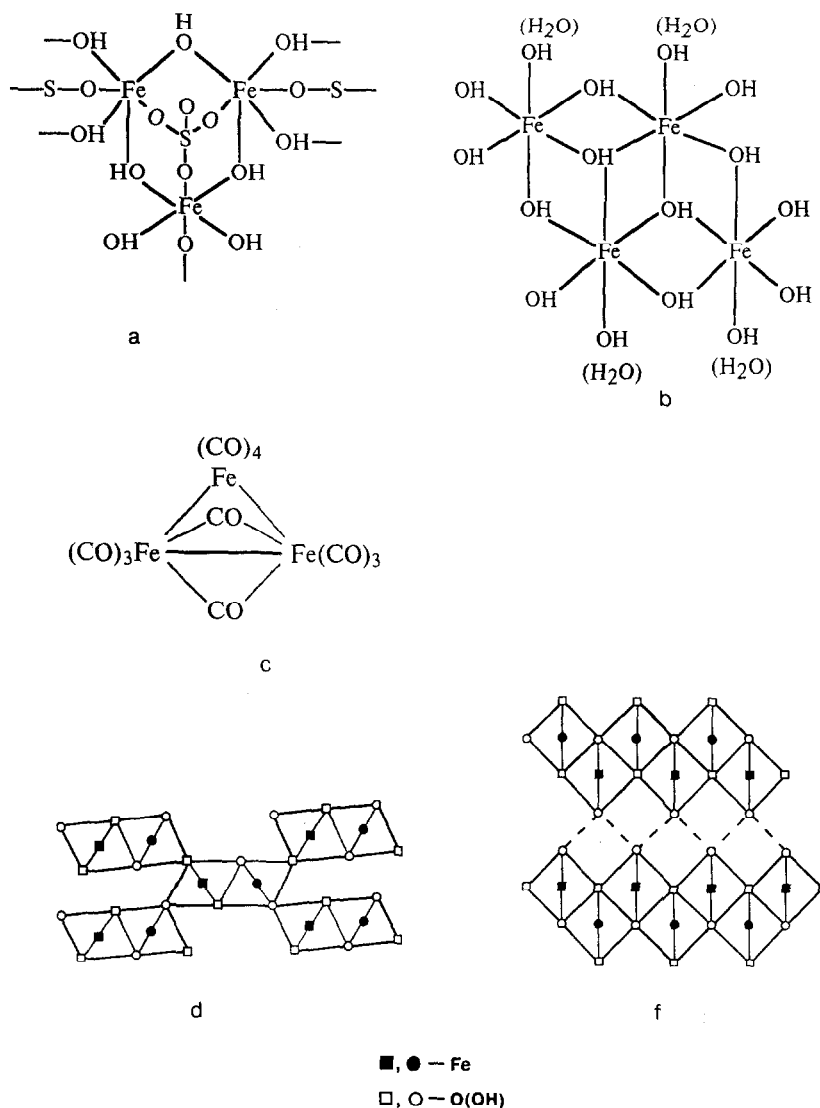


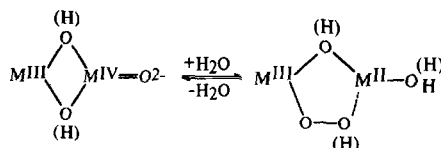
Fig. 2. Molecular (a, b, c) and crystalline (d, e) structures of heterogeneous Fe-containing catalysts under study: a –  $\text{NaFe}_3(\text{OH})_6(\text{SO}_4)_2$  [18]; b –  $\text{Fe}_4(\text{OH})_{10}(\text{SO}_4)$  [19]; c –  $\text{Fe}_3(\text{CO})_{12}$  [20]; d –  $\alpha\text{-FeOOH}$  [5]; e –  $\gamma\text{-FeOOH}$  [5].

coincides with that of amorphous  $\text{FeOOH}$  (Table 2).

### 3.5. Relationship of catalytic properties with the catalyst structure

At the moment, there is no generally accepted concept concerning the mechanism of the catalytic action of both natural and synthetic catalysts for water oxidation, though the first attempt to elaborate such concept was made recently in our quantum-chemical study [21]. This study has

supported the expected catalytic efficiency of di- and oligonuclear hydroxocompounds of transition metals having three consecutive oxidation states, e.g. II, III, and IV, that is the case for iron, cobalt, and manganese. The same calculations evidence in a necessity for the catalytic site to have two



Scheme 1.  $M^n$  is the ion of the catalytically active metal in oxidation state  $n$ .

Table 4  
Concentration of the surface hydroxyl groups and O<sub>2</sub> yields at pH 9 obtained over Fe-containing heterogeneous catalysts

Catalyst	OH <sub>surf</sub> <sup>-</sup> (mmol/g)	O <sub>2</sub> yield (%)
FeOOH (amorph.)	0.50	41
α-FeOOH	<0.1	16
γ-FeOOH	0.45	93
NaFe <sub>3</sub> (OH) <sub>6</sub> (SO <sub>4</sub> ) <sub>2</sub>	4.7	5
Fe <sub>4</sub> (OH) <sub>10</sub> (SO <sub>4</sub> )	2.6	84

Conditions of the catalytic experiments are the same as in Table 2.

neighboring metal ions, since the formation of O–O bond in the water oxidation should, on the basis of the calculations, take place in a very specific intramolecular rearrangement as depicted in Scheme 1.

The main distinction of the water oxidizing catalysts of a hydroxyl nature is that initially they already contain the substrate to be oxidized, e.g. coordinated hydroxyl groups. Moreover, for the colloidal and heterogeneous catalysts, their surface in water solutions is obviously covered by a layer of H<sub>2</sub>O molecules and their moieties. For the catalyst in a crystalline form, the hydroxylation of the surface makes the surface more amorphous. This phenomenon was observed experimentally, when a crystalline form of RuO<sub>2</sub> · nH<sub>2</sub>O (one of the most efficient catalysts of the water oxidation) was studied [22].

Thus, such hydrolytic and amorphization processes could be expected to level the surface properties of hydroxides (oxides) of the same composition, but different crystal structure. However, in the case of iron-containing catalyst this seems not to occur.

As shown earlier, the catalytic properties of α- and γ-FeOOH differ from each other and from those of amorphous FeOOH. Moreover, we failed to find any correlations between the O<sub>2</sub> yields and the overall concentration of hydroxyl groups on the external catalyst surface in aqueous solution (see Table 4). Thus, NaFe<sub>3</sub>(OH)<sub>6</sub>(SO<sub>4</sub>)<sub>2</sub> and α-FeOOH, which have the highest and the lowest concentrations of surface OH groups, respectively, show similar, low selectivities. Probably,

the hydroxylation affects only the overall amount of the surface hydroxyl groups, while the particular properties of these groups depend on the catalyst structure even under the mentioned conditions.

The results obtained allow us to draw the following conclusions on the effect of the catalyst structure on the properties of hydroxyls and, thus, on the O<sub>2</sub> yields in the water oxidation:

(1) The oxidizing OH groups should be located not far from each other, since, if the opposite were true, O–O bonds (in a dioxygen molecule to be created) can hardly be formed. When OH groups are bound to different Fe ions, the distance between such hydroxyls is determined by the distance between Fe ions which coordinate these hydroxyls. Hence we can explain the high O<sub>2</sub> yields obtained on Fe<sub>4</sub>(OH)<sub>10</sub>SO<sub>4</sub> by the fact, that here Fe octahedrons are connected along the edge and Fe–Fe distance is shorter than in NaFe<sub>3</sub>(OH)<sub>6</sub>(SO<sub>4</sub>)<sub>2</sub>, where the octahedrons are connected through the tops (Table 3). In the other words, the distance between the transition metal ions involved into the catalytic site should be optimal, perhaps, in order to perform the rearrangement (1) predicted by the quantum-chemical calculations [21].

(2) Oxidation of OH groups should proceed with the lowest energy consumption. Our quantum-chemical calculations show that oxidation of the end hydroxyls is more favorable thermodynamically than that of the bridge ones [21]. The structure of highly active tetramer and γ-FeOOH (see Fig. 2) provides a higher concentration of the end hydroxyls on their surface if compared to the low active trimer or α-FeOOH.

(3) The surface hydroxyls should exhibit rather strong acidic properties [23]. Acidity of OH groups can depend on various factors (e.g., on the effective charge on the metal ion, which coordinates hydroxyls, the composition of its coordination sphere, a mutual effect of the ligands, etc.). A structural factor of note is the large number of hydrogen bonds, which can promote the formation of strong acid sites. Such H-bonds are formed in the structures of both γ-FeOOH and

$\text{Fe}_4(\text{OH})_{10}(\text{SO}_4)$ , which both provide high  $\text{O}_2$  yields. The acid sites can expand the pH region of the catalyst action towards acidic pH in comparison to amorphous or colloidal hydroxides. Moreover, the same H-bonds were observed in the case of  $\text{RuO}_2 \cdot n\text{H}_2\text{O}$  already mentioned above [22].

#### 4. Conclusion

The above data can be regarded as experimental evidence for a relationship between the catalytic properties of ferric hydroxocompounds in the oxidation of water to  $\text{O}_2$  and the molecular or crystalline structure of these compounds. It is clear that not only is the nature and the number of the redox active metal cations of importance, but also the location of these cations in the catalyst reaction centre. Their location in a position bounded by edges of the metals coordination spheres containing O or OH ligands seems to be the most profitable for the catalytic oxidation of water, because particularly this location creates the optimal distance between the catalytically active ions of the reaction centres. In addition, location and, consequently, the properties of the hydroxyls to be oxidized should have a strong effect too. The above results seem to be the first experimental evidence of such idea, that seems to be of importance for synthesis of polynuclear Mn-containing compounds suggested to be the models for the  $\text{O}_2$  evolving center of the Photosystem II. It is well known, that the most of the models presented up to now, as a rule, do not appear to be catalytically active.

The reported results cannot be regarded as complete and, indeed, further investigation is required to prove the data obtained. We hope, however,

that they will contribute to a clearer comprehension of the catalytic properties of both synthetic and natural catalysts for oxidation of water.

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