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# Hydroxides of transition metals as artificial catalysts for oxidation of water to dioxygen

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## Abstract

Hydroxides of transition metals cations like Fe(III), Co(III), Mn(III), Ru(IV), etc., appear to be efficient artificial catalysts in oxidation of water to $O_2$. The paper describes some catalytic properties of these hydroxides. The hydroxide-based catalysts for the water oxidation can be obtained in three modifications: bulky (individual and binary), supported on the ion exchange resins or conventional oxide supports ($SiO_2$, $TiO_2$, $Al_2O_3$, zeolites), and colloidal catalysts stabilized by starch. The possible mechanism of the catalytic reaction, including the stage of the formation of peroxocomplexes as intermediates is under discussion. Some similarities are drawn between the catalytic properties of hydroxide catalysts and those of the manganese-based oxygen evolving complex of the Photosystem II of green plants. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Transition metals; Artificial catalysts; Dioxygen evolution; Photosystem II; Aqueous solutions; Hydroxides

## 1. Introduction

During the last two decades much work has been done in attempts to create functioning molecular models of the green plants' photosynthesis. The simplest reaction for mimicking the function of the photosynthesis is indeed photocatalytic cleavage of water

$$H_2O \xrightarrow{h\nu} H_2 + \tfrac{1}{2}O_2 \tag{1}$$

A principal scheme of this process is represented in Fig. 1. Since in the typical molecular photocatalytic systems the photons absorbed by a photocatalyst (PhC) are able to drive, like in natural photosynthesis, not more than one electron, they generate only one-electron reducing agents $A^-$, and one-electron oxidants $D^+$. Thus, the very important and unavoidable units of any artificial photocatalytic water-dissociating systems should be catalysts providing two-electron reduction of water to dihydrogen and its four-electron oxidation to dioxygen.

Note that catalysts for oxidation of water to dioxygen are needed also for any other more complicated systems mimicking the function of the natural green plants' photosynthesis (see Table 1).

At the beginning of the work on that kind of artificial photocatalytic systems, there was no knowledge on artificial catalysts of catalytic oxidation of water at all (see, e.g., books [20,41,47] and reviews therein). However, a large progress seems to have been achieved in this area (see reviews [15,17,19,42,43]).

The aim of this paper is to demonstrate some recent trends in design of artificial hydroxides-based catalysts for oxidation of water to dioxygen with the emphasis on the operation of the water oxidation catalysts mainly on the base of Fe and Co.

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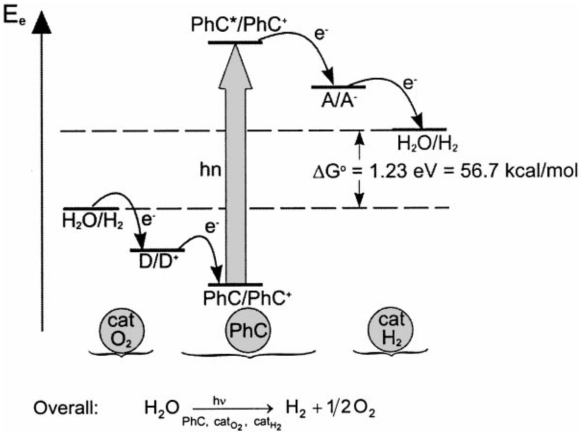


Fig. 1. A principal scheme of photocatalytic cleavage of water into $H_2$ and $O_2$ in molecular systems. PhC is a photocatalyst capable of a charge separation under light quanta; $cat_{O_2}$ and $cat_{H_2}$ stand for catalysts for dioxygen and dihydrogen evolution. $E_e$ is the energy of reacting electrons.

## 2. Artificial catalysts for water oxidation and their general properties

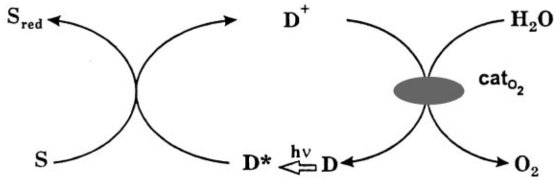
Thermodynamics of water oxidation is known to be very rigid and requires the use of multi-electron transfer to achieve the highest efficiency of solar energy transformation into the energy of synthesized chemical fuel, e.g., the pair of reagents "dihydrogen–dioxygen" as in reaction (1). Fig. 2 depicts some well known thermodynamic peculiarities of oxidation of water through one-, two-, three- and four-electron processes. Evidently, a direct four-electron oxidation without a release of free intermediate of one-, two- or three-electron water oxidation, like oxygen-containing free radicals or non-bound hydrogen peroxide, is highly desirable. Thus, the absence of any free intermediates of water oxidation should be the main demand to any "good" catalyst for the water oxidation.

For finding the artificial catalysts for the water oxidation, three kinds of experiments on catalytic and/or photocatalytic systems are typically provided. These are:

1. "Dark" catalytic oxidation of water by initially *chemically* prepared one-electron oxidants $D^+$:

$$4D^+ + 2H_2O \overset{cat}{\rightarrow} 4D + 4H^+ + O_2\uparrow \qquad (2)$$

   The usual oxidants $D^+$ used in such experiments are $Fe(bpy)_3{}^{3+}$, $Fe(phen)_3{}^{3+}$, $Ru(bpy)_3{}^{3+}$, $Ru(bpy)_2(py)_2{}^{3+}$, $Ce_{aq}{}^{IV}$, $Co_{aq}{}^{III}$. Here and later bpy stands for α,α-bipyridine, phen stands for *o*-phenantroline, py stands for pyridine.
2. Photocatalytic oxidation of water by in situ *photogenerated* one-electron oxidants $D^+$ in "sacrificial" systems according to, e.g., the following scheme:



   In these experiments a substrate S serves as an irreversibly consumed "victim" consuming the light-generating electrons. For the photocatalytic oxidation of water in molecular sacrificial systems, mostly $Ru(bpy)_3{}^{2+}$ or its analogs served as the photocatalyst D. So, the light-generated oxidants $D^+$ appear to be usually also the same species as those mentioned above. No doubts, the chemical nature of the processes of $O_2$ evolution in both cases are also nearly the same.

Table 1
Some processes suggested for photocatalytic conversion of solar energy in artificial systems mimicking plants' photosynthesis[a]

| | Processes | $n$ | $\Delta G^0_{289}$ (kcal mol$^{-1}$) | $\Delta H^0_{289}$ (kcal mol$^{-1}$) | $\Delta G^0_{289}$ (per electron, eV) | $\lambda_0$ (nm) |
|---|---|---|---|---|---|---|
| 1 | $H_2O \rightarrow H_2 + \frac{1}{2}O_2$ | 2 | 56.7 | 68.3 | 1.23 | 1008 |
| 2 | $2H_2O + CO_2 \rightarrow CH_4 + 2O_2$ | 8 | 195.5 | 212.8 | 1.06 | 1176 |
| 3 | $2H_2O + CO_2 \rightarrow CH_3OH + \frac{3}{2}O_2$ | 6 | 167.9 | 173.6 | 1.21 | 1025 |
| 4 | $3H_2O + CO_2 \rightarrow C_2H_5OH + 3O_2$ | 12 | 318.3 | 336.8 | 1.15 | 1077 |
| 5 | $3/2H_2O + \frac{1}{2}N_2 \rightarrow NH_3 + \frac{3}{4}O_2$ | 3 | 81.1 | 91.4 | 1.17 | 1059 |
| 6 | $2H_2O + N_2 \rightarrow N_2H_4 + O_2$ | 4 | 181.3 | 148.4 | 1.97 | 629 |

[a] $n$ is the number of electrons to be transferred, $\lambda_0$ is the "red" threshold for the denoted process at the $n$-quantum process.

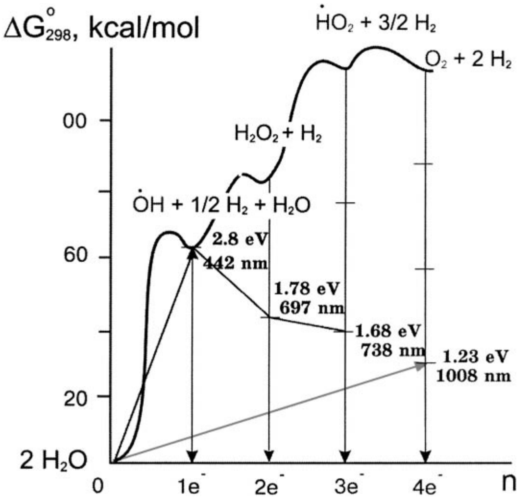


Fig. 2. Energy profile for consecutive reactions of water cleavage. The figures represent the minimum energy and corresponding wavelength of red boundary for light quanta at *n*-quantum mechanism of water cleavage (according to [15,35]).

The tested irreversibly reduced substrate S was $S_2O_8{}^{2-}$, some complexes of $Mn^{III}$, etc. (see, e.g., [15,17,19,20,41–43,47]).

3. Promotion of water oxidation carried on the surface of semiconductor photocatalysts ($TiO_2$, as a rule). Typically, the systems under study appear to be also the sacrificial systems, where surface light-generated holes $h^+$ serve as primary one-electron oxidants $D^+$.

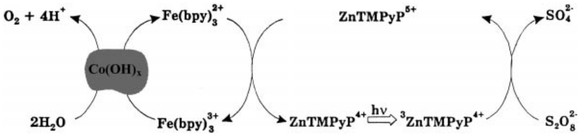
So, in all the above cases the reaction of catalytic oxidation of water to dioxygen can be generalized by reaction (2).

The respective studies have resulted in finding a sufficiently wide variety of artificial catalysts for reaction (2). In addition to natural enzyme “Water oxidase”, operating in the oxygen evolving Photosystem II (PS II) of green plants and based presumably on a cluster manganese compound of $Mn_4O_xL_y$ type, where L are some organic ligands (see, e.g., [19,40]), the found artificial catalysts can be arranged into main groups:

1. Simple and mixed heterogeneous metal oxides (usually partly hydrated or hydroxilated): $RuO_2$, $IrO_2$, $MnO_2$, $M^{II}M^{III}_2O_4$ ($M^{II}$=Cu, Ni, Fe; $M^{III}$=Co, Fe, Cr, Al).
2. Microheterogeneous or heterogeneous simple and mixed hydroxides, both colloidal and surface-stabilized, of Fe(III), Co(II,III), Mn(III,IV), etc.
3. Complexes of Fe(III), Co(II,III), Ru(III,IV), Mn(III,IV), etc., with organic ligands, including water-soluble porphyrines and phthalocyanines.

Remarkably, only a very particular set of transition metals like Fe, Co, Ni, Ru, Ir, Mn, Cu which are capable of having a wide set of consecutive oxidation states, appears to be involved in catalysis of water oxidation through reaction (2).

Curiously, till now there have been no observations of either chemical or sacrificial photocatalytic oxidation of water in artificial systems with oxidized form of porphirines or phthalocyanines as one-electron oxidizers $D^+$ that mimicks natural photosynthesizing center where the oxidized forms of chlorophyll or its dimers operate as such oxidizers. An artificial system of the latter type was suggested in [18] and consisted of a water-soluble Zn-substituted porphirin $ZnTMPyP^{4+}$ (photocatalyst) – $S_2O_8{}^{2-}$ (sacrificial oxidant) – $Fe(bpy)_3{}^{2+}$ – $Co^{2+}$ (the latter two are known as starting compounds for creating the water-oxidizing catalysts). The scheme of water oxidation in this system can be represented as:



In this scheme, $Fe(bpy)_3{}^{2+}$ complexes served as an electron relay between the oxidized form of the photocatalyst and a cobalt hydroxide catalyst. Moreover, this relay operated at two consecutive steps: a “light-driven” stage at pH 3.3 for accumulation of $Fe(bpy)_3{}^{3+}$ under visible light illumination, and a “dark” stage at pH 12 for the dioxygen release. Evidently, in this scheme, the intermediate electron donor $Fe(bpy)_3{}^{2+}$ allows: (i) to use a short-lived oxidized porphyrin radical for the generation of a sufficiently stable one-electron oxidant $Fe(bpy)_3{}^{3+}$ and (ii) to separate in time the processes of the oxidant photogeneration and of the catalytic water oxidation.

Operating sacrificial photocatalytic systems with water-soluble porphirines of Zn and some other metals without an intermediate electron relay have been reported too and contained, e.g., also $S_2O_8{}^{2-}$ as the sacrificial oxidant and $IrO_x$ as the water-oxidizing catalyst [2,22,34]. Unfortunately, these systems appeared to be not very well reproduced by other research groups.

Studies on artificial catalysts of water oxidation have demonstrated that, despite the "unusual" nature of this process, the found catalysts behave in many respects as conventional catalysts. So, e.g., parameters identifying the properties of catalysts for water oxidation are the same as those of catalysts for the "convential" catalytic processes. The principal parameters are:

1. *Selectivity*. A non-100% value of the selectivity originates from a fact that typically a part of the strong oxidant $D^+$ can be consumed for the oxidation of organic or other compounds present in the system.
2. *Activity* (the turnover rate of the active center of the catalysts). It was found that usually this value increases rapidly with the increase of pH and can reach the value of $10^3\,s^{-1}$ or even more.
3. *Stability* (the turnover number per the catalyst life time). A finite value of this parameter originates from a deactivation of the catalyst, the deactivation seems to result typically from creation of, e.g., some non-active crystalline modifications of polymeric oxohydroxides of the catalytically active metals.

For providing the dioxygen evolution in photocatalytic systems, of the most importance is, indeed, the value of selectivity of artificial catalysts for water oxidation, since the low selectivity can follow in an immediate destruction of the usually extremely complicated molecular photocatalytic systems. It is well known that selectivity of the natural Water Oxidase enzyme in Photosystem II equals nearly 100%. This means that in the native conditions, all photogenerated strong oxidants (their primary forms are oxidized pheophytine or chlorophyll molecules) do not oxidize the organic surrounding at all. On the contrary, most of the artificial water oxidation catalysts have much lower value of the selectivity. Nevertheless, the selectivity of the best artificial catalysts on the base of Co- and Fe-hydroxides at neutral and slightly basic water solutions can approach 95%.

It was also found, that selectivity of some artificial catalysts can remain the same when the catalytically active species are stabilized by such easily oxidizable substrates as lipid membranes [29,30] and even some carbohydrates like cyclodextrine or starch [12,13,29,30,43]. Thus, artificial catalysts can also be very selective in oxidation of water. According to current opinion, a lower apparent selectivity in case of oxidants $\mathrm{Ru(bpy)_3}^{3+}$, $\mathrm{Fe(bpy)_3}^{3+}$, etc., originates from non-stability of ligands of these metallocomplexes rather than from an oxidation of some other surrounding compounds.

A lot of work has been done in order to improve artificial catalysts for water oxidation and to establish the mechanism of their action. The most important question is, indeed, whether there exist some intermediate products of water oxidation ($\dot{O}H$, $H_2O_2$ or $H\dot{O}_2$) which evolve in the free state into solution bulk during the catalysis. Hopefully, even in the very first work on example of partly hydrolyzed Fe–bpy complexes as such catalysts it was found that at least in presence of these iron compounds there is no sufficient formation of above free intermediates [9]. This conclusion followed directly from the fact that at pH 4 the creation of $\dot{O}H$ or $H_2O_2$ in the free state is not possible when $\mathrm{Fe(bpy)_3}^{3+}$ with the oxidative redox potential $E^0=+1.0\,V$ (here and later vs. NHE) is used as the oxidant (see Fig. 2 and also [35]).

For studies on the elementary mechanism of the water oxidation catalyst action, another interesting question is elucidation of the very step of the first appearance of O–O bond for the future dioxygen molecule.

Nowadays, there is a lot of speculations on the nature of this step. For example, a large list of schemes of the water oxidation over the natural Water Oxidase enzyme is compiled in reviews [19,40]. Usually, in the old papers, the O–O bond is suggested to be formed during a "synchronous" transfer of several electrons. Such synchronous transfer was discussed in many early theoretical works on the catalytic oxidation of water and implies a preliminary accumulation of several oxidizing equivalents inside the catalyst active center.

Usually, catalytically active metals of different nature are assumed to follow different mechanisms of O–O bond formation, i.e., the stage of the oxidation of water molecules to an intermediate peroxide species. Pt-metal oxides as well as Mn- and Ru-containing complexes as catalysts of water oxidation were reviewed in [32,40]. In the present paper we discuss mostly the catalytic properties of iron and cobalt hydroxides and the mechanism of reaction (2) in their presence.

## 3. Preparation and modifications of hydroxide catalysts and their properties

Hydroxides are well known as the simplest compounds formed by highly charged cations not only in neutral and basic, but also in acidic water solutions. Hydroxides of many metals are widely used as sorbents, ion exchangers, collectors of admixtures, etc. However, so far they did not find an extensive application as catalysts and were practically not studied in performance of catalytic processes. At the same time, some properties of hydroxides are highly attractive for catalysis in general and for the catalytic oxidation processes in water solutions in particular. These properties are the following:

1. As a rule, the hydroxides have a developed surface, and thus many of their active sites are accessible for the reactants.
2. In aqueous solutions, the hydroxide surface is strongly hydroxylated, so the hydroxides can be considered as compounds with the greatest affinity to the aqueous medium.
3. Hydroxides are polynuclear compounds, which favor the occurrence of multi-electron and multi-stage complex processes.
4. The absence of easily oxidizable ligands in hydroxides decreases considerably a possibility of side processes often diminishing the selectivity of the water oxidation and hampering studies of the oxidation reaction mechanisms.
5. Hydroxides allow wide opportunities for producing the catalysts in various forms: bulky, supported and colloidal ones.

*Bulky hydroxides*. In reaction (2), where trisbipyridine complex of ruthenium(III), $Ru(bpy)_3^{3+}$, was used as oxidant $D^+$, the bulky hydroxides of Fe(III) and Co(III) were studied most thoroughly, both individual and mixed ones [26]. The catalysts under discussion were produced by ammonia precipitation from solutions of individual salts $FeCl_3$ and $K[Co(NH_3)_2(CO_3)_2]$, or of their mixtures with salts of Cu(II), Al(III), Ti(IV), Sn(IV), Si(IV) and Ce(IV). After precipitation, the samples were dried at temperature not exceeding 400 K. At higher temperatures, the hydroxides convert into oxides and their catalytic action decreases considerably.

Catalysts containing from 20 to 40 wt.% Fe or Co were tested in a wide pH range 5–12. For this purpose, the phosphate, pyrophosphate and borate buffer solutions as well as water solutions of pure NaOH were used [26]. Since reaction (2) is accompanied by a side process of bpy oxidation and, in addition, proceeds in a 1 s time range, for the catalysts characterization there were used mostly the $O_2$ yields, i.e., the selectivity in respect to reaction (2) calculated by the stoichiometry of this reaction at a complete consumption of the oxidant. The amount of $O_2$ formed was determined in a vacuum setup or directly in a solution with the use of the Clark's electrode.

It was found that among the cations listed above only Fe-, Co- and Cu-hydroxides show a catalytic activity in reaction (2). Amorphous FeO(OH) appeared to be more selective than the cobalt hydroxide, and for the binary Fe–Co samples an increase in the catalytic action was observed as compared to individual hydroxides (Fig. 3); this increase appeared to be only slightly depending on the catalyst components ratio. All Co-containing binary catalysts obtained from mixtures with the cations listed above in the whole pH region exhibit an increase of selectivity in comparison with the single-component CoO(OH), the effect of Ti(IV) and Sn(IV) ions being somewhat less pronounced than that of the other metals. An addition of

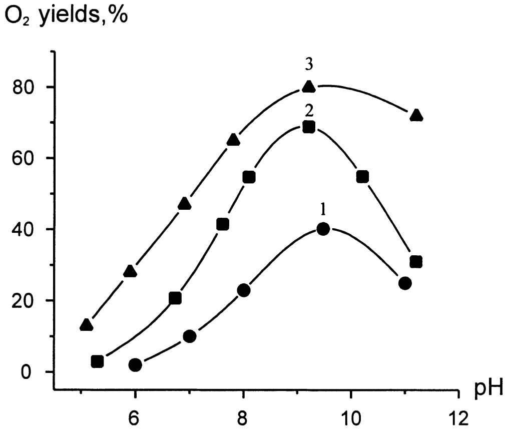


Fig. 3. The $O_2$ yields vs. pH of the solution at the oxidation of water by $Ru(bpy)_3^{3+}$ in the presence of CoO(OH) (1), FeO(OH) (2), and binary hydroxide of Fe–Co (3).

the same ions appeared to affect the catalytic properties of the iron-containing samples in a more complicated way: introduction of Ti, Sn, Si or Al cations results in a decrease of selectivity, while introduction of Cu or Ce(IV) cations — results in an increase of selectivity.

A thermogravimetrical analysis evidences that the binary compounds under study are not a mechanical mixture of two hydroxides. They are amorphous materials, in which the ions of inactive metals enter the nearest coordination surroundings of the catalytically active Fe or Co ions with a high probability. This is confirmed by the EXAFS spectroscopy on the Fe atoms. It follows from these data too that the length of Fe–O, Fe–OH and Fe–Fe bonds changes in the binary iron-containing hydroxides. This may be connected with a modification of the structure and electron properties of the initial hydroxide in the presence of the second component.

The electron-microscopy studies showed that except of pure cobalt hydroxide, consisting of rather large particles up to 30 nm in size, all other iron- and cobalt-containing samples, which demonstrate quite different $O_2$ yields, represent the entities composed of hydroxide nanoparticles slightly varying in size (7–10 nm). This is evidenced in the lack of any correlations between the catalytic properties of hydroxides and their specific surface area. No correlations were found also between the $O_2$ yields and the total amount of the surface hydroxyl groups, which are the most probable substrates for the water oxidation reaction. For example, Co–Sn and Co–Ce samples contain 0.35 and 1.30 mM $g^{-1}$ of the surface $OH^-$ groups, respectively, while the $O_2$ yields for both catalysts are equal and comprise 60%. One can assume that for manifestation of catalytic activity in the reaction of water oxidation, the high acidity of hydroxyl groups is more important than the total amount of these groups on the catalyst surface. From the EXAFS data, in the binary iron hydroxides, the second cationic component affects mainly the length of Fe–OH bond. It is quite probable that its shortening leads to a strengthening of the acidic properties of $OH^-$ group coordinated to the active site, and hence favors its oxidation in the catalytic process. Thus, there should exist a correlation between the $O_2$ yields and the acidic properties of hydroxyls coordinated to the catalytically active ion. In this case, a correlation is expected between the $O_2$ yields and the length of the Fe–OH bond. Such correlation is, indeed, observed experimentally (Fig. 4).

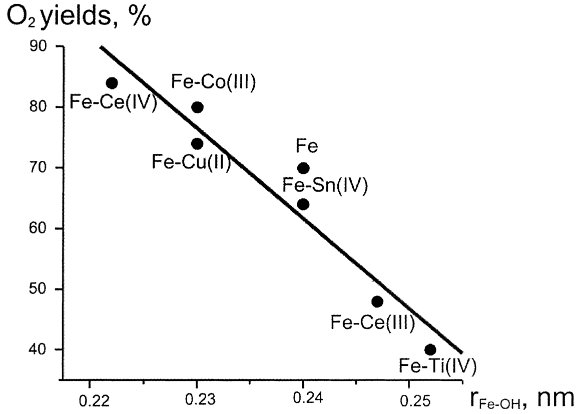


Fig. 4. The $O_2$ yields at the oxidation of water by $Ru(bpy)_3{}^{3+}$ vs. the length of bond $r_{Fe–OH}$ in the binary iron hydroxides. The concentration of $Fe(bpy)_3{}^{3+}$ is $2\times10^{-3}$ M, pH 9, 20 mg of catalyst in 10 ml of the solution.

Additional information on the effect of structural factors on the catalytic properties of hydroxides in the reaction of water oxidation was obtained on a set of Fe(III)-hydroxocompounds with various well-defined structures: α- and γ-FeO(OH) as well as $NaFe_3(OH)_6(SO_4)_2$ and $Fe_4(OH)_{10}(SO_4)$ complexes (see Fig. 5 and [14]). Of the best activity in this range appeared to be γ-FeO(OH) as well as an $Fe_4(OH)_{10}(SO_4)$ complex. On the contrary, α-FeO(OH) and a $NaFe_3(OH)_6(SO_4)_2$ complex are almost inactive in the catalysis of water oxidation. Again, no correlations were found between the $O_2$ yields and the overall concentration of hydroxyl groups on the external catalyst surface in aqueous solution. For example, the contents of $OH_{surf}{}^-$ for amorphous FeO(OH) and γ-FeO(OH) are nearly the same, but the $O_2$ yields are 41 and 93%, respectively. However, the active compounds were found to be distinguished from the inactive ones with the following particular features:

1. The distance between Fe(III)-cations in the active $Fe_4$-complexes is smaller than that in the $Fe_3$-complexes (0.30 and 0.36 nm, respectively, see Fig. 5).
2. A great number of hydrogen bonds can promote the formation of strong acid sites. Such H-bonds are formed in the structures of both γ-FeO(OH) and

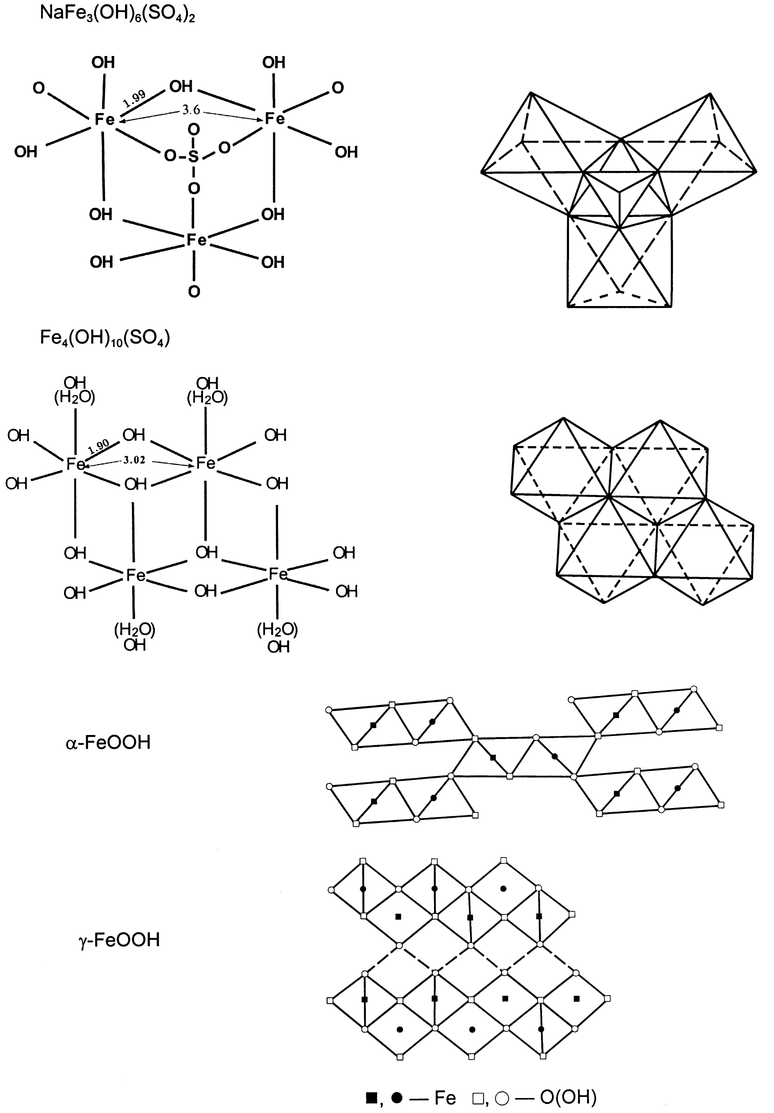


Fig. 5. Molecular and crystalline structures of some Fe-hydroxide compounds tested as water oxidation catalysts. The figures show the interatomic distances measured by EXAFS spectroscopy [14].

$Fe_4(OH)_{10}(SO_4)$ [6], which both provide the high $O_2$ yields. Moreover, the same H-bonds were observed in the case of $RuO_2{\cdot}nH_2O$, which is known to be the most active catalyst in the water oxidation reaction [39].

3. γ-FeO(OH) and $Fe_4$-compounds have a layered structure in contrast to the "framework" structure of α-FeO(OH) and $Fe_3$-compounds [6]. The layered structure undoubtedly helps in holding the reagents (both the oxidants and $H_2O$ or $OH^-$) in the reaction center.

*Colloidal catalysts*. Several methods were developed for the synthesis of colloidal hydroxides of Fe(III), Co(III) and Mn(III) stabilized by polyvinyl alcohol or water-soluble starch to obtain stable-in-time and transparent colloidal solutions. An evident advantage of systems on the base of such samples over heterogeneous ones is the absence of sufficient light scattering, so colloidal catalysts may appear convenient for studying the reactions under the action of light.

The catalytic properties of the hydroxides-based colloids proved to be similar in many respects to those of bulky samples. For example, the $O_2$ yields in the binary Fe–Ce colloid appeared much higher, and in the Fe–Al or Fe–Ti colloids much lower than in the colloid containing only FeO(OH). Note that a mechanical mixture of independently prepared sols of Fe-hydroxide and those of another metal had the properties of an individual Fe-hydroxide colloid [10]. As in the case of suspended hydroxides, the rate of water oxidation depends on the nature of the used buffer and increases with increasing pH [8,10,12–14]. Moreover, for both kinds of the catalysts, the $O_2$ yields increase to a great extent in the presence of perchlorate salts.

At the same time, the colloidal catalysts have some essential distinctions and peculiarities. First of all, it turned out that, in contrast to the bulky samples, in the colloidal state, FeO(OH) is considerably less efficient than CoO(OH), and addition of various cations to the latter one practically did not affect its catalytic properties, probably because a mechanical rather than a chemical mixture of the hydroxides is formed in the latter case [10].

In the manganese hydroxide colloids stabilized with polyvinyl alcohol, the size of the colloidal particles proved to be greater than that stabilized with starch (11 and 4 nm, respectively), but this does not affect the catalytic properties. On keeping, the size of colloidal particles may grow without any change in their activity and selectivity [12]. A spectrophotometric study of the colloidal catalysts revealed that the shape of their spectra (Fig. 6) depends on pH and temperature of the synthesis, on the starch concentration, and on the nature of buffer anions [12–14]. One can assume that in colloidal hydroxides an equilibrium exists between the highly active polymer molecules of hydroxide with a minor extent of polymerization (the oligomers formation) and the high-molecular compounds exhibiting a weak (or no) catalytic action. This is confirmed by the fact that the buffer solutions with a strong complexing agent (e.g., phosphate, pyrophosphate anions) dissolve the most active part of colloidal catalysts FeO(OH) [14] and CoO(OH) [13]. This dissolving of the colloids shows up in the change of their absorption spectra and further in reducing the catalytic activity of the colloids. On the other hand, when the colloidal cobalt hydroxide is predominantly fixed on the surface of, e.g., $Al_2O_3$, this increases both the $O_2$ yields and the catalyst resistance against dissolving under the action of a buffer [13].

The studies of the catalytic properties of the starch stabilized colloidal manganese hydroxides in various degrees of the metal cation oxidation (II, III, IV)

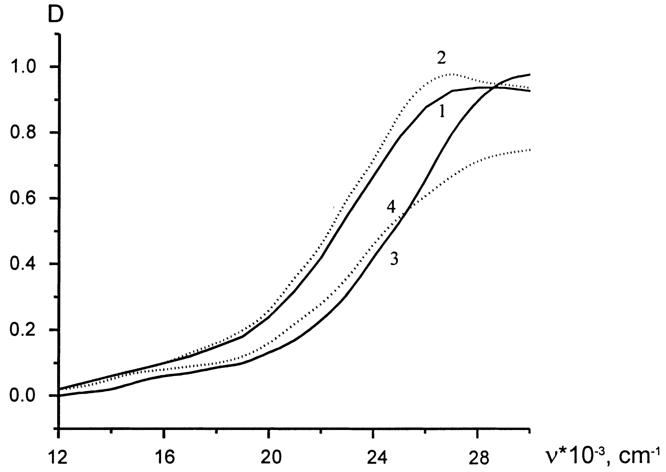


Fig. 6. Absorption spectra of the colloidal Co(III)-hydroxide catalysts in the presence of 0.01% (1, 2) and 0.5% (3, 4) starch. The temperature of the catalyst synthesis is 300 K (1, 3) and 350 K (2, 4), the cobalt concentration is $5\times10^{-4}$ M, the light path is 1 cm.

demonstrated that the Mn(II) and Mn(IV) colloids containing no noticeable amounts of Mn(III) ions are practically inactive in the reaction of water oxidation, and the colloid of MnO(OH) hydroxide is close to that of CoO(OH) in its catalytic properties [12].

*Supported catalysts*. Two kinds of supports were tested for the catalysts preparation: ion exchange resins and conventional inorganic supports like $SiO_2$, $TiO_2$, $Al_2O_3$ and zeolites.

Co- and Fe-containing samples were supported on both cationite and anionite resins [8]. After the ion exchange of Co(III) and Fe(III) salts with the resins, the samples were treated with a NaOH solution in order to produce hydroxocompounds on the surface of the supports. The binary Co catalysts were prepared with the same method from the solutions of a mixture of corresponding salts. The content of Co in the catalysts was 0.5 wt.%; the content of the other metals (Fe(III), Al(III), Ce(IV), Sn(IV), Ti(IV)) was ca. 1 wt.%.

The Co-hydroxide supported on the cationite resin appear to be more selective than the bulky one almost over the whole range of pH studied. When using the anionites containing various amino groups or pyridine, at the water oxidation, the catalyst samples provided large amounts of $CO_2$ instead of $O_2$. Like for bulk Co-hydroxide, the $O_2$ yields for the supported binary catalysts are higher than those for an individual supported hydroxocompound. Moreover, Sn(IV) and Ti(IV) ions cause considerably lesser effect than the other ions.

The cationite-supported Fe-containing samples were found to be inactive over the whole range of pH studied. One can suggest that this kind of support prevents the formation of hydroxocompounds in sufficient amounts.

Some conventional oxide supports were tested to prepare the hydroxide catalysts containing Fe(III), Co(III), Ru(IV) and Mn(II,III,IV) [11,14]. The bulky hydrated oxides of ruthenium and manganese in the reaction of water oxidation were described in [21,32], while the supported ones were produced and studied for the first time by us. An essential factor of such catalysts synthesis consists in hydrolysis of corresponding salts in the presence of a support at constantly high pH of 10–11. Therewith, the catalytically active ions (with the 1 wt.% and lower content) convert quantitatively into hydroxides which became chemically fixed on the support surface. After filtration, the samples were dried at 373 K. Further calcination at 500 K resulted in many cases in a considerable increase of the activity and selectivity.

$RuO_2 \cdot nH_2O$ is widely considered to be one of the most active catalysts of water oxidation [32,39]. However, in the supported state, the ruthenium and cobalt hydroxides appeared to be similar both in their activity and selectivity. In a series of Mn-containing samples, no catalysts were obtained having only one fixed oxidation state (II,III or IV) of the manganese cation, in contrast to the colloidal solutions. Nevertheless, the catalysts with the prevailing content of Mn(III) exhibit the best catalytic properties.

In spite of the distinctions in the valence state and chemical properties of the catalytically active ions, the results obtained point to obvious similarity in the nature of the catalysts under study. This is indicated by a partial reduction of Co(III)-, Ru(IV)-, Mn(III)- and Mn(IV)-hydroxides both in the course of their synthesis and on prolonged aging of the catalysts on air as well as by an activation and reactivation of the catalysts (after their long storage) via calcination at 500 K. In addition, the influence of supports is similar in many respects. For example, for the Co and Ru catalysts the most active samples are obtained on the same supports (NaA, $TiO_2$, $\alpha$-$Al_2O_3$), while the less active ones' catalysts are obtained with the use of $\gamma$-$Al_2O_3$ and $SnO_2$. For the Mn-based catalysts, NaA and $\alpha$-$Al_2O_3$ appeared to be the advantageous supports as well. However, in general the effect of a support proved to be unclear in many respects. For example, the catalysts with similar activity are obtained on the supports with the specific surface area differing by a factor of 5 (the cases of NaA and $\alpha$-$Al_2O_3$). Yet, the same support (e.g., $\gamma$-$Al_2O_3$ or $TiO_2$) may a contradictory effect on the catalytic properties of the surface hydroxides Co and Ru (highly active) and manganese (low active) [11].

One of the reasons of such support action may be the formation of the surface hydroxide particles with different sizes. Actually, it was found by X-ray method that on the $TiO_2$ surface, cobalt hydroxide forms particles of 30 nm size, while on NaA — not more than of 2 nm. However the catalytic properties of these samples proved to be identical. Moreover, the effect of the support nature may be leveled under the action of a buffer solution, in which the water oxidation reaction proceeds. For example, in the phosphate buffer, the catalysts on the base of α- and $\gamma$-$Al_2O_3$ may differ in activity by two times, while in the pyrophosphate buffer they become identical [11].

It is important that at pH of 6–9 the activity and selectivity of the catalysts under study is considerably lower in a non-buffered medium than in the buffer solutions. Since the buffers used contain the complexing anions, their effect may be caused by the two reasons: firstly, by the formation of new active sites because of a break of bridging bonds in a polymeric molecule of the hydroxide, and, secondly, by an activation of the active site due to the formation of a complex with the catalytically active ion.

Hydrolysis of multivalent ions is known to be a very complicated process, and equilibria at particular stages of such hydrolysis can be achieved very slowly. Thus, as a rule, the catalytic properties of the hydroxides depend greatly on the conditions of their synthesis and are badly reproduced. However, upon immobilization, the initial hydroxide particles are rapidly bound to the oxide surface, whose chemical nature is close to their one. In this case, it becomes possible to stabilize hydroxocompounds of a definite composition and structure, which form either at the moment of precipitation or upon calcination at given temperature. A chemical binding with the support surface seems to protect these structures against the further slow processes which are characteristic for the formation of bulky hydroxides. This allows to obtain rather reproducible and active catalysts of water oxidation.

Therefore, the heterogeneous and microheterogeneous water oxidation catalysts of the hydroxide nature are similar with conventional catalysts in many respects. Actually, their main characteristics are activity and selectivity. At the same time, some distinguishing features are revealed too. Firstly, the absence of habitual correlations between the catalytic properties and the size of the catalyst particles (their geometric surface area), i.e., occurrence of the reaction is highly probable not only on the catalyst surface, but perhaps, in its volume too. Secondly, this is also an indisputable effect of equilibria of the complexes formation, as in the case of homogeneous catalysts. Of importance is that the use of microheterogeneous (colloidal) catalysts opens new opportunities for finding the reaction intermediates and for a more detailed study of the reaction mechanism, which will be shown below.

## 4. Possible mechanism of the hydroxide catalysts operation at the water oxidation

A thorough investigation of the reaction kinetics of water oxidation by $Ru(bpy)_3{}^{3+}$ complex with the use of Clark's electrode based on the $O_2$ release into the solution showed that all studied catalysts, regardless of their modification (heterogeneous or microheterogeneous) and of the nature of the catalytically active ion (Co, Fe, Mn, Ru), seem to act by the same mechanism [7]. This is evidenced by the kinetic regularities which are found to be common for all catalysts: the extremal (with a maximum) dependencies of the $O_2$ yields and of the reaction rate on both pH and the catalyst and oxidant concentrations, a strong effect of the buffer nature, and a retarding action of the product of the oxidant reduction, $Ru(bpy)_3{}^{2+}$, which is decreased by addition of perchlorate anions.

A general reaction scheme of water oxidation by $Ru(bpy)_3{}^{3+}$ is considered, which explains the main kinetic regularities, observed at the experiments is given below.

The first stage of reaction (2) is obviously a coordination of the oxidant with the catalyst active site containing a rather acidic $OH^-$ group, through the mechanism of ion exchange:

$$M^{III}\text{–}OH + Ru(III) \rightleftarrows M^{III}\text{–}O^- \cdots Ru(III) + H^+ \quad (1)$$

Here Ru(III) stands for an oxidant, while $M^{III}$–OH group is included in the composition of a polymer molecule of 3-valence metal hydroxide. For the ruthenium hydroxide catalysts, $Ru^{IV}$–OH is expected to be the initial state.

The reduced form of the oxidant, Ru(II), can co-ordinate similarly with the same active site and thus may cause its inhibition:

$$M^{III}\text{–}OH + Ru(II) \rightleftarrows M^{III}\text{–}O^- \cdots Ru(II) + H^+ \quad (2)$$

The stage of the active site oxidation (transfer of the first electron) may follow inside the ionic complex of Ru(III) with the catalyst:

$$M^{III}\text{–}O^- \cdots Ru(III) \rightarrow M^{IV}{=}O^{2+} + Ru(II) \quad (3)$$

There is a general opinion [5,33] supported by the quantum-chemical calculations [16] that namely this stage is a rate-limiting (rate-determining) one for the water oxidation.

Further, the generated “oxene” group interacts with a hydroxyl group coordinated to the adjacent M-cation in the hydroxide composition. Such interaction results in the formation of O–O bond corresponding to oxidation of a water molecule by two electrons with the simultaneous two-electron reduction of one of the M-cations and coordination of peroxide group to another (see Section 5):

$$\mathrm{M^{IV}{=}O + HO{-}M^{III} \rightarrow M^{II} + M^{III}{-}OOH} \qquad (4)$$

Note that the polynuclear structure of hydroxides should favor these processes.

Therefore, at stages (2) and (4), the two-electron oxidation of water occurs, while only one electron is transferred to the oxidant molecule. A theoretical analysis of the activation energy of the $O_2$ photosynthetic release presented in [28] showed that thermodynamically the above consequence of steps of the water oxidation is the most advantageous.

The next stage of the reaction is the formation of free $O_2$ molecule. Oxidation of water to free (non-coordinated) hydrogen peroxide through two consecutive one-electron transfers is extremely unfavorable in energetical respect [16,28,35]. On the contrary, oxidation of $H_2O_2$ to $O_2$ is equally feasible both as an one-stage oxidation (with transfer of two electrons) and as a two-stage oxidation (with transfer of one electron at each stage). The choice of the most favorable way should be determined by the nature of the catalytically active ion as well as by composition and structure of its closest surroundings. For example, some quantum-chemical calculations show that in the framework of the chosen models in case of Fe [16] and Mn [28], the two-stage oxidation of the coordinated peroxide moiety is more favorable, while in case of the Co-containing catalyst this is an one-stage oxidation [16] by reactions (5) and (6):

$$\mathrm{M^{III}{-}OOH + Ru(III) \rightarrow M^{IV}{-}OOH + Ru(II)} \qquad (5)$$

$$\mathrm{M^{IV}{-}OOH \rightarrow M^{II}{+}O_2{+}H^+} \qquad (6)$$

The catalytic cycle is closed in this case by the stage of the catalyst re-oxidation:

$$\mathrm{2M^{II}{+}2Ru(III){+}2(H)OH{\rightarrow}2M^{II}{-}OH\ \ ({+}2H^+)} \qquad (7)$$

From the above scheme it follows that not only oxidation–reduction processes but also the acidic–alkaline equilibriums are responsible for a strong pH dependence of the reaction kinetics. The quantum-chemical calculations show [27] that for lowering the activation barriers, the protons which are released in the process of water oxidation should not evolve to the bulk of the solution as free ions. Therefore, in the oxygen-evolution center of the green plant’s Photosystem II some protein-bound groups with definite basic properties should exist. In our opinion, one of the reasons of high efficiency of hydroxides in the water oxidation reaction may consist also in the existence of the hydroxide surface sites with various acidic properties, among which the releasing protons can easily find the place with appropriate $pK_a$.

Thermodynamically, the most advantageous is indeed the synchronous four-electron water oxidation to $O_2$ ($\Delta G^0_{298} = 1.23\,\mathrm{eV}$), but kinetic feasibility of a synchronous transfer of four electrons seems to be very questionable. On the other hand, the kinetically more probable oxidation of water with two electrons to free (non-coordinated) $H_2O_2$ requires a very strong oxidant with the oxidative electrode potential of 1.78 V, which exceeds greatly the standard oxidative electrode potential of the pair $\mathrm{Ru(bpy)_3}^{3+}/\mathrm{Ru(bpy)_3}^{2+}$ (1.26 V). This contradiction is removed by an assumption that the formed $H_2O_2$ molecule remains coordinated to the active site of the catalyst, as shown in stage (4). This assumption is indeed confirmed by some quantum-chemical calculations [16,28].

Our studies seem to demonstrate that of a high importance should be also the structure of the forming peroxocomplex since the peroxoligand can co-ordinate in an either terminal or bridging position. Indeed, when studying the kinetics of the water oxidation in a colloidal solution of Co(III) hydroxide stabilized by starch [36] by the stopped flow method, we detected optically an intermediate which, according to both the position of its absorption band (560 nm) and an extinction coefficient ($10^2\,\mathrm{M^{-1}\,cm^{-1}}$), can be identified as a bridge-type peroxocomplex Co(III) [3]. The rate constant of this intermediate disappearance (ca. $2\,\mathrm{s^{-1}}$ at room temperature) is several orders of magnitude less than the effective rate constant of the rate-limiting stage (3) which is larger than $10^3\,\mathrm{s^{-1}}$. So, this intermediate seems cannot participate in the formation of the $O_2$ molecule. Moreover, it has long been known [45] that oxidizing elimination of $O_2$ from the bridge-type cobalt peroxides is impossible, since all the known oxidants are able to oxidize such peroxides by one electron only with the formation of bridge-type superoxides. Similar distinctions were found in the oxidation properties of copper peroxides: the terminally coordinated peroxogroup can be oxidized to $O_2$, while the bridging one, as in the case of cobalt peroxides, seems to be a rather strong oxidant [31]. Hence, one can assume that disappearance of the intermediate found in [36] occurs in a side reaction of an oxidant ligands oxidation:

$$\begin{aligned}&\mathrm{M^{III}\text{–}OOH + HO\text{–}M^{III}}\\&\quad\rightarrow \mathrm{M^{III}\text{–}(O_2{}^{2-})\text{–}M^{III} + H_2O}\end{aligned} \tag{8}$$

$$\begin{aligned}&\mathrm{M^{III}\text{–}(O_2{}^{2-})\text{–}M^{III} + Ru(bpy)_3{}^{3+}}\\&\quad\rightarrow \mathrm{2M^{III}\text{–}OH + Ru(bpy)_2(bpy_{oxidized})}\end{aligned} \tag{9}$$

The presence of stage (9) explains the fact that even for the most selective hydroxide catalysts of oxidation of water by $\mathrm{Ru(bpy)_3{}^{3+}}$, the reported $O_2$ yields did not exceed 95%. Note that use of colloidal catalysts to find an interesting intermediate by conventional spectrophotometry, cannot be applied to suspensions.

It should be noted that all kinetic regularities for the heterogeneous and microheterogeneous hydroxide catalysts of water oxidation appear to coincide. This confirms the presence of ion exchange stages (1) and (2) and allows to calculate their equilibrium constants [36].

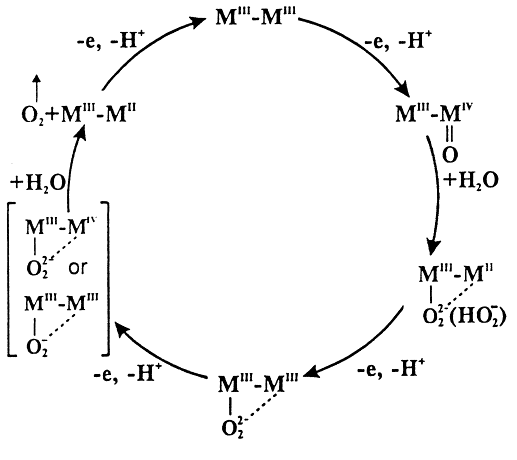
## 5. Molecular model for the dioxygen evolution

In spite of the traditional interest to the problem of oxidation of water to oxygen, the concepts of the molecular structure of the key catalytic centers and process intermediates for this reaction remain to be rather hypothetical and speculative. The greatest attention in this respect was given to the Photosystem II with the Water Oxidase enzyme. The modern models of this enzyme are based on the concept of polynuclear structure of the catalytic center. The final stage of the process is usually described as a synchronous transformation of the manganese-containing polyhedrons with evolution of $O_2$, e.g., as a conversion of "adamantane"-like $Mn_4O_6$ complex to $Mn_4O_4$ cubane complex [4]. Transformation of the cubane structure in the course of coordination of two water molecules and their oxidation to $O_2$ were considered in [46]. The paper [40] presents an excellent review of the present status of molecular modeling of the initial structure of the dioxygen-evolving center of the Photosystem II and the main process intermediates. A possible molecular mechanism of $O_2$ evolution in the Photosystem II was considered in [37] on the basis of the extended Hückel quantum chemical calculations. It was concluded that tri- and tetra-coordination of a peroxide moiety could promote its two electron oxidation to dioxygen.

Recently [23], the abstraction of H-atom from the manganese coordinated water molecule by tyrosil radical was proposed as a key step of the dioxygen evolution in the Photosystem II. This mechanism was used as a basis for the model quantum-chemical calculation [44] of the consecutive formation of intermediates $S_0$, $S_1$, $S_2$, $S_3$, $S_4$ of the Kok's cycle. The calculation was done by the method of the density functional; as in the model the adjacent cations of Mn and Ca were considered as active center, to which the hydroxyl groups and water molecules are coordinated. This calculation was aimed, in particular, at elucidating the role of $Ca^{2+}$ cations in the Photosystem II.

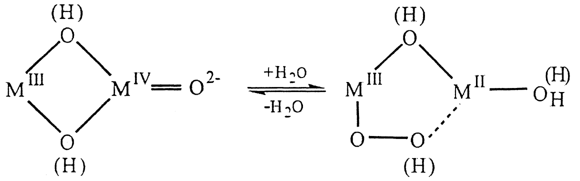
The scheme considered in [44] bears some similarities to the scheme we proposed earlier in [16]. Our scheme was obtained on the basis of quantum-chemical calculations by the NDDO/MC method for the reaction of water oxidation catalyzed by hydroxides of transition metals. In [16], a tetranuclear Fe(III) hydroxocomplex and a binuclear Co(III) complex were chosen as the simplest models of the catalyst active centers. The intermediates of the consecutive one-electron oxidation, followed by their deprotonation, were calculated. Efficiently, it amounted to the removal of H atom from M–OH group with further separation of hydrogen atoms from the coordinated hydroxyls at the next stages of the process, in close analogy to the scheme in [44]. However, it should be remembered that, according to the Kok's terminology, in the case of hydroxides $S_1$ is the initial structure but not $S_0$, as in the Photosystem II [44].

In spite of the oversimplified model used, a set of important conclusions follows from the above calculations. First of all, the results of the quantum-chemical calculations allowed to propose a whole closed cycle of the water oxidation in the presence of hydroxide-like species of transition metals:



This cycle corresponds to that discussed in Section 3 and appears to be common at least for the two different model systems discussed (both binuclear Co(III) and tetranuclear Fe(III) complexes). Thus, one can hope that it is valid for many other hydroxo compounds of catalytically active transition metals as well. Of the top importance is that this scheme assumes the creation of O–O bond just *after the first oxidation* of the initial form of the reaction center (i.e., of $M^{III}$–$M^{III}$) with only one electron. This is a sequence of two-electron reduction of a virtually created $M^{IV}$ form of the active ion (the stage (4)).

Secondly, the calculations show that the active site of the water oxidation catalyst should contain at least two metal atoms. Although only one metal atom is involved in the redox transformation (in the above scheme it corresponds to the transformations III→IV→II→III), the second atom is necessary for stabilizing an intermediate structure with $O_2^{2-}$ (or $HO_2^-$) moiety. Otherwise, the mononuclear $M^{II}$–$O_2^{2-}$ (or $M^{II}$–$HO_2^-$) fragment, formed after the first oxidation step, should most probably participate in an energy-consuming reaction with a water molecule yielding free (non-coordinated) $\dot{O}H$ radicals and the starting structure of the catalytic site. A stabilization of these intermediates of the oxidized water molecules is achieved through interaction with the second metal atom which remains at the starting oxidation degree. Note that the stabilization via equilibrium of the type



obviously needs a binuclear structure most probably created from the metal ions of the same nature; otherwise the nearly equipotential equilibrium (X) will be shifted to one side, thus making an obstacle for the catalytic cycle to occur. It is of the top importance that namely nearly equipotential rearrangement (X) serves, according to the calculations in [16], as the widely discussed but still experimentally non-identified step of O–O bond formation at the oxidation of water to dioxygen.

Third, in the model under discussion, the external driving force for the process of the water oxidation with formation of a dioxygen molecule appears to consist in the consecutive one-electron oxidation steps rather than in a synchronous multi-electron oxidation, which is generally discussed for the process of $O_2$ evolution. With that, during some steps, an one-electron oxidation forces a transfer of two electrons from a ligand ($H_2O$, $OH^-$, $HOO^-$) to the metal cation. The evaluated energy values necessary for each oxidation step appear to be comparable with the oxidative potentials of one-electron oxidants used in the artificial water oxidation system ($E^0$=1–1.5 V).

Note that the $M^{IV}$=$O^{2-}$ intermediates obtained in the quantum-chemical calculations [16] are not totally hypothetical structures since for most of them their real chemical analogs are known to exist. For example, the highly active ferryl groups $Fe^{IV}$=$O^{2-}$ are known to be included in the active sites of some enzymes containing both heme and non-heme iron [24].

Thus, the quantum-chemical analysis appeared to be a very important tool for understanding and studying the mechanism of very complicated multi-electron redox reactions, for which even sophisticated instrumental methods of experimental investigation fail to produce a detailed information.

## 6. Conclusions on the hydroxide catalysts for water oxidation

Artificial catalysts of hydroxide nature for the water oxidation differ dramatically in general composition from a manganese cluster of the oxygen releasing center of the green plants' Photosystem II, except the polynuclear structure of the prostetic group of the enzyme. Nevertheless, a number of peculiarities, characterizing the water oxidation in the presence of hydroxides, coincide with the available findings on the natural Water Oxidase enzymes. Among them one can mention the following:

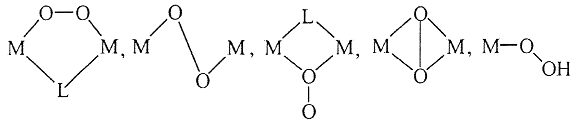
1. Ability of the hydroxide catalysts to exclude the one-electron transfers with the formation of energetically disadvantageous oxidation products (non-coordinated free radicals), despite the use of an one-electron oxidant.
2. Coordination of intermediate products of water oxidation like $H_2O_2$ to the active site, which enhances greatly the process energetics as a whole.
3. A possibility to prevent the release of protons into the bulk of the reaction solution and thus to affect positively the reaction energetics.
4. A promoting action of some cations in the binary hydroxides, which can be connected with some structural changes in the active site and may occur similarly to the action of $Ca^{2+}$ cations in the native Photosystem II.
5. A promoting (or inhibiting) action of the buffer anions, which is similar to the action of chlorides (or fluorides) on the Photosystem II.

The above features testify that the hydroxide catalysts may be considered in many respects as a functional analog of the dioxygen evolving center of the native Photosystem II.

Manifestation of the catalytic action in the reaction of water oxidation necessitates, as follows from the above, participation of the cations of those metals, which are able to exist in a set of more or less stable states with consecutive oxidation degrees differing by a unit. Among such metals are Fe, Co, Mn (oxidation degrees II, III and IV), Ru (those III, IV, V) and Cu (I, II, III). For the catalytically active ions studied, the catalytic activity and selectivity (up to 95%) do not practically depend on their nature (with the exception of the less active copper-containing samples), since one can find the terms of the catalyst synthesis or their modification to obtain the samples with high catalytic efficiency. For example, for iron these are γ-FeO(OH) and $Fe_4(OH)_{10}(SO_4)$.

Indeed, the reported data on the artificial hydroxide-based catalysts for water oxidation cannot be considered as completed ones and a further investigation is required to prove the data obtained. We hope, however, that already now they are able to help in comprehending more clearly the catalytic properties of both synthetic and natural catalysts for water oxidation. For example, these allow to formulate some specific demands to metallocomplexes considered as possible catalysts for oxidation of water to $O_2$:

1. First of all, one should have, indeed, a correspondence of the redox-potentials of the oxidants and the states of the reaction center to the needed redox transformations of the coordinated water molecules to be oxidized.
2. Existence of "free" co-ordinative sites or labile ligands which can be easily substituted by $H_2O$ or $OH^-$ is necessary to provide oxidation of water in the first coordination sphere of the catalytically active cation.
3. The ligands surrounding the redox-active metal ions should not be strong bases or electron donors. Otherwise one can observe oxidation of the ligands rather than that of $H_2O$ molecule. Moreover this kind of the ligands decreases an effective positive charge on the metal cation and thus diminishes the oxidative potential as well as the acidity of coordinated $H_2O$ ($OH^-$) molecule.
4. If the starting metallocomplex is mononuclear, it should have an ability to create dimers in solution.
5. The distance M–M inside the active center has to allow creation of a –O–O-moiety. The possible options of the core structure of such –O–O-containing complexes (at least when their creation through oxygenation of metallocomplexes) could be:However, note that according to our experience, the only last structure with a termal peroxointermediate is leading to formation of $O_2$ molecules at the water oxidation.



## 7. On the Water Oxidase enzyme and its genesis

Mn-containing cluster of the natural Water Oxidase enzyme in Photosystem II of green plants seems to remain to be the most efficient system for water oxidation to $O_2$. A good deal of efforts has been made to elucidate the reason of its high activity. However, the mechanism of its action is not yet completely revealed (see, e.g., reviews [40]). One can assume, that extremely high efficiency of this enzyme can be provided, e.g., by both optimal arrangement of Mn ions in the Mn-containing cluster and $OH^-$groups coordinated to Mn ions as well as the strong acidity of these $OH^-$-groups. However, the strong acidity of hydroxyls may result not only from the structural peculiarity of the oxygen-evolving center. Unlike the artificial transition metal hydroxide catalysts, where the catalytically active ion is surrounded by ligands of one type ($H_2O$ and its fragments), the catalytically active site of the natural Water Oxidase enzyme possesses probably an optimal composition of the coordination sphere of the manganese cation involving other than $OH^-$-ligands, e.g., functional groups of protein molecules. Such a surrounding may help to retain a high effective positive charge on the Mn ions in the water oxidation process and, thus, to provide an efficient deprotonation of the coordinated $H_2O$ and $OH^-$-groups.

The above data on hydroxocomplexes of iron can be regarded as experimental evidences in a relationship between the catalytic properties of ferric hydroxocompounds in the oxidation of water to $O_2$ and molecular (crystalline) structure of these compounds. Not only the nature and the number of the redox-active metal cations in the catalyst reaction center is important but also a mutual location of both these cations and coordinated $OH^-$-groups. Their location in a position bounded by edges of the metals' coordination octahedra containing O- or OH-ligands seems to be the most profitable for the catalytic oxidation of water.

This is of importance to understand why numerous artificial polynuclear Mn-containing compounds with a known structure suggested as the models for the $O_2$ evolving center of the Photosystem II appear to be not catalytically active, as a rule.

Note that the above mentioned quantum-chemical calculations allow also to explain numerous failure in reproducing the manganese dioxygen-evolving enzyme of Photosystem II by direct synthesis of multinuclear manganese clusters even with suitable location of Mn ions. Indeed, it is easy to find that in most of synthesized manganese complexes the coordination sites needed for performing the rearrangement of the mentioned type (X) are blocked by electron-donor ligands other than OH or $H_2O$ that makes an obstacle for the water oxidation to occur, but facilitates oxidation of the coordinated organic ligands.

It is of interest that the above data on the very high catalytic activity of the mentioned tetrameric iron(III) complex allow also to express simultaneously a hypothesis on the origin and/or genesis of the four-manganese active sites in the natural water oxidases. Indeed, according to the long-term experience with Fe(III) hydroxides it was found, that at the small iron cations concentration, the mononuclear and binuclear iron hydroxocomplexes arized as primary particles at the hydroxides nucleation appear to be extremely thermodynamically non-stable in the processes of iron hydroxides formation and tend to oligomerize.

The same situation seems to take place in Nature when selecting the catalytically active sites for the plant photosynthesis during evolution of the life. Small oligomeric manganese hydroxocomplexes appeared also to be smallest from the growing manganese hydroxopolymers successfully stabilized by native ligands. One may suggest that at the earliest stages of the green plants evolution, the Water Oxidase enzyme existed as only a small oligomer of a manganese (or mixed manganese–iron) hydroxide captured by the green plant's precursor directly from the natural waters, which have everywhere a variety of dissolved cations. No doubt, the needed catalytic ability should be revealed by even the primary precursors of the enzyme, since otherwise the probability of evolutionary design of the very complicated prostetic group is obviously negligible (indeed, otherwise the time consuming evolution was not able to proceed in the absence of the valuable properties of the evolution intermediates). At the later stages of the evolution, this oligomeric cluster has been optimized in order to enhance efficiency of the enzyme. Note, that the modern data do not contradict a "double" dimeric structure of the active center (see, e.g., Fig. 7 and [40]).

Note, that a di- and tetra-meric composition have also some other non-heme enzymes of the line of oxidoreductases (e.g., the methane mono-oxygenase on

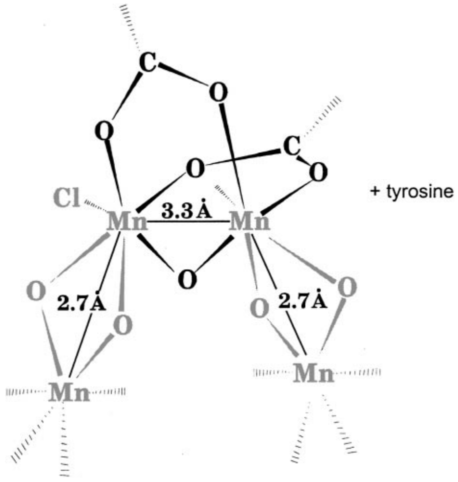


Fig. 7. An example of modern EXAFS data on the structure of the Water Oxidase enzyme in Photosystem II (see, e.g., [40]).

the base of dimeric iron-hydroxide, some bacterial hydrogenases on the base of iron–sulfur clusters, etc.). The origin of the Nature's choice of these structures can perhaps be the same.

Thus, the genesis of the Water Oxidase enzyme in the Photosystem II is undoubtedly related with the *captured oligomeric hydroxocomplexes* of Fe, Co, Mn, Ni and Cu with their future optimization in size and surrounding and stabilizing ligands via evolution of the life. Nevertheless, despite iron is distributed in nature much more widely than manganese, the Nature has chosen namely manganese for constructing the Photosystem II.

Why Nature has chosen namely Manganese, not iron or cobalt, as a main compounds for the Water Oxidase enzyme in the Photosystem II? One can imagine that there were several important reasons for that:

1. Mn is an easily available element, being the second in availability after Fe (e.g., in sea bottom concretions Mn is the first).
2. $Mn^{2+}$ does not hydrolize up to pH 9 which makes it possible for these cations to penetrate easily the lipid membranes of the photosynthesizing organisms and to be bound with these membranes.
3. The first step of one-electron oxidation of $Fe^{3+}$ or $Co^{3+}$ hydroxides needed more strong oxidants than that of $Mn^{3+}$ hydroxides (see Table 2).
4. However, in our opinion, one of the most important reason seems to be the proximity of oxidation potentials for various oxidation degrees which is characteristic only for the manganese cations (Table 2) and its complexes, that distinguishes principally this chemical element from the other mentioned metals. As a result, many redox reactions of Mn compounds are accompanied by redox disproportionation of Mn ions. Note that closeness of the electrochemical potentials at the transition of catalytically active ion from one oxidation state to another seems to lead to the smoothing of the energy relief of the reaction and hence to its optimization. Moreover, the availability of a large set of oxidation states of Mn (from +2 to +7) makes possible to perform water oxidation according different parallel mechanisms that increases the reliability of the enzyme operation and ensures selectivity of 100%. This particular property seems also actively used by Nature at the design of the Photosystem II.

Table 2
Oxidation potentials for the consecutive redox pairs of the bulk oxohydroxides of metals active in the reaction of oxidation of water to dioxygen [1,25,38]

| Redox pair | $E^0$ (V) | | | |
|---|---|---|---|---|
| | Fe | Co | Mn | Ru |
| III/II | 0.27 | 0.87 | 1.0 | |
| IV/III | >1.0 | 1.48 | 1.01 | 0.9 |
| IV/II | – | 1.18 | 0.9 | 0.0 |
| V/IV | | | | 1.15 |

## 8. Conclusions

The presented short overview on the modern achievements in the development of artificial hydroxide-type catalysts for water oxidation demonstrates that now numerous, both experimental and theoretical data, are available in order to create a non-contradictory version of the structure and possible mechanism of operation of such catalysts. Of importance is that the recent studies do not demand a synchronous transfer of many oxidative equivalents to provide advantageous multielectron oxidation of water molecules. On the contrary, there is a very natural explanation of the first most important step of

O–O bond creation through a change of the oxidation state of a redox-active transient metal ion by only two electrons.

In future some research work for molecular or structurally organized photocatalytic systems of water cleavage may be undertaken, coupling of the artificial water oxidation catalysts with the one-electron oxidants of the porphirines type easily generated by light seems to be of importance. Note that till now the respective attempts have failed, may be due to absence of a suitable relay between the oxidants and the catalyst active center. Quite probable, that electron relays like tyrosine molecules which couple the water-oxidizing system in natural photosynthesis are really needed.

Of large interest should be also development of "hybrid" systems containing semiconductor nanoparticles as the photocatalysts joined with an extended electron transfer chain.

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