

## CATALYTIC OXIDATION OF WATER TO DIOXYGEN BY Ru(bpy)<sup>3+</sup> IN THE PRESENCE OF MIXED IRON AND COBALT HYDROXIDES

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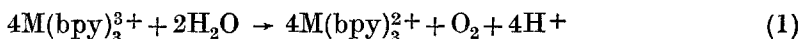
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The catalytic activity of Co(III) and Fe(III) hydroxides as well as of their mixtures produced by co-precipitation with hydroxides of some highly charged transition and non-transition metals has been studied over the pH range from 5 to 11. In some cases mixed hydroxides demonstrate an increase in efficiency of the catalytic action.

В диапазоне pH 5—11 изучена каталитическая активность гидроксидов Co(III) и Fe(III) и их смесей, полученных соосаждением с гидроксидами некоторых высокозарядных переходных и непереходных металлов. В ряде случаев для смешанных гидроксидов обнаружено увеличение эффективности действия катализатора.

We have recently reported [1] on the catalytic action of some mixed oxides of the spinel type in the reaction of water oxidation:



where M is Ru or Fe, bpy is bipyridyl. It has been suggested that when immersed in water, the surface of spinels is hydroxylated rather quickly and, thus, the catalytic action can be provided by compounds similar to hydroxides of the corresponding metals rather than by the spinels themselves. In this work the catalytic activity of Co(III) and Fe(III) hydroxides as well as of their mixtures with transition and non-transition metal hydroxides in reaction 1 has been studied.

### EXPERIMENTAL

All reagents used in experiments were of chemically pure grade. Ru(bpy)<sub>3</sub>(ClO<sub>4</sub>)<sub>3</sub> was prepared as described in [2]. 0.02 M phosphate and 0.02 M borate buffer solutions were used to achieve pH 5–8 and pH 8–11, respectively.

Mixed hydroxides were prepared by co-precipitation by ammonia (1 : 1) from acid solutions of salts at pH of complete deposition of the precipitate.

Freshly precipitated samples were dried at 60 °C and washed thoroughly from  $\text{Co}^{3+}$  and  $\text{Fe}^{3+}$  ions until no qualitative reactions occurred in washings. The precipitates were then kept in air at 110 °C for 4–5 h.

The quantitative chemical analysis of samples was carried out complexometrically or spectrophotometrically using standard procedures. Prior to tests, the catalysts were powdered thoroughly to less than 0.01 mm fractions. Reaction 1 was carried out by adding the oxidant  $\text{Ru}(\text{bpy})_3^{3+}$  to the catalyst suspended in a buffer solution or in alkali upon vigorous agitation by a magnetic stirrer.

Because we have found a strong adsorption of evolved dioxygen on these heterogeneous catalysts, the experiments were performed in vacuum, and chromatographic analysis of  $\text{O}_2$  evolved was made [1] 15 min after mixing the solutions, i.e. by the time of complete termination of reaction 1. In order to have standard test conditions, all experiments were carried out at room temperature using a  $2 \times 10^{-3}$  M concentration of  $\text{Ru}(\text{bpy})_3^{3+}$  and a catalyst sample of ca. 20 mg per 10  $\text{cm}^3$  of the solution.

## RESULTS AND DISCUSSION

The yields of  $\text{O}_2$  (in % of the stoichiometric value expected in reaction 1) are listed in Tables 1 and 2. They were obtained for samples containing ca. 30 wt. % of Fe (Table 1) and ca. 20 wt. % of Co (Table 2). The change in the content of the active component (calculated for the above metals) from 20 to 40% almost did not affect the yields of  $\text{O}_2$  measured.  $\text{Ti}^{\text{IV}}$ ,  $\text{Sn}^{\text{IV}}$ , and  $\text{Al}^{\text{III}}$  hydroxides were inactive in such conditions. In the presence of  $\text{Ce}^{\text{IV}}$  hydroxide, traces of oxygen (< 1% at pH 9) were observed. Over the whole range of pH, iron hydroxide was more efficient than cobalt hydroxide, in contrast to homogeneous solutions in which the efficiency of  $\text{Co}^{\text{III}}$  and  $\text{Fe}^{\text{III}}$  was about the same [3]. A maximum activity of Fe hydroxide was observed at pH 8–9.

Table 1  
Yield of  $\text{O}_2$  as a function of pH for iron-containing catalysts

Catalyst	pH of solution							
	5	6	7	8	9	10	11	
							buffer	NaOH
FeOOH	0	0	18	57	70	—	—	30
Fe—Ce	—	2	34	69	84	44	30	50
Fe—Co	10	14	39	71	80	—	18	72
Fe—Al	0	0	14	25	65	—	—	69
Fe—Sn	0	0	2	35	61	57	33	—
Fe—Ti	0	0	0	30	39	33	—	—

Table 2  
Yield of O<sub>2</sub> as a function of pH for cobalt-containing catalysts

Catalyst	pH of solution						
	5	6	7	8	9	10	11
							buffer
Co <sub>2</sub> O <sub>3</sub> ·nH <sub>2</sub> O	0	0	15	22	40	—	26
Co—Fe	10	14	39	71	80	18	72
Co—Ce	0	10	38	67	60	18	—
Co—Al	10	20	48	70	65	—	75
Co—Sn	—	15	37	60	60	27	56
Co—Ti	—	10	45	57	44	28	—

At pH 11 the yield of oxygen in buffer solutions was lower than in NaOH solutions, which was also observed earlier for homogeneous solutions [4].

In all experiments we observed evolution of CO<sub>2</sub> resulting from side reactions of bipyridyl oxidation. Unfortunately, we failed to find any relation between the amounts of CO<sub>2</sub> and O<sub>2</sub> evolved.

The experimental data suggest that the activity of the catalysts studied (to be more precise, their efficiency since we measured only the yield of O<sub>2</sub> but not the rate of its formation) depends to a large extent on the concentration of their hydroxy groups. When using the procedure of "non-mixed" catalyst preparation, hydrated oxides, namely amorphous FeOOH and crystalline Co<sub>2</sub>O<sub>3</sub>·nH<sub>2</sub>O are produced [5]. Calcination of the same samples producing M<sub>2</sub>O<sub>3</sub> leads to the decrease of O<sub>2</sub> yields from 70% down to 40% for Fe<sub>2</sub>O<sub>3</sub> at pH 9 and has almost no influence on the efficiency of cobalt-containing catalyst (40 and 35%, respectively).

For mixed cobalt-containing catalysts with the metals that produce hydroxides saturated with OH<sup>-</sup> groups (Al(OH)<sub>3</sub> and MO(OH)<sub>2</sub>, where M = Ce<sup>4+</sup>, Ti<sup>4+</sup>, Sn<sup>4+</sup>) an increase in efficiency compared to non-mixed hydroxides is observed over the whole range of pH's. On the contrary, the effect of the same hydroxides on the catalytic properties of iron-containing samples appeared to be less unambiguous. For example, over the whole range of pH's studied the efficiency of iron-containing catalysts decreases in the presence of Ti hydroxide and increases in the presence of Ce or Co hydroxides. Even more complicated is the influence of Sn and Al hydroxides: the activity of Fe hydroxide does not change at pH 9 but falls sharply in a more acid region.

It is as yet untimely to make any definite conclusions about the nature of the effect of the second component on the efficiency of mixed catalysts because the data presented in the tables have been obtained in standard conditions when equal amounts of the catalysts were used. As a rule, a decrease of this amount affected in one-to-one manner the yield of O<sub>2</sub>, whereas its increase did not lead to any noticeable changes in the O<sub>2</sub> yield. Moreover,

one can assume that for some of the samples studied the homogeneous process that occurs without O<sub>2</sub> evolution [4] still made an appreciable contribution to the process of the oxidant reduction. In fact, the average volume concentration of active components estimated from the geometrical surface area of the sample (ca. 100 cm<sup>2</sup>) is about 10<sup>-6</sup> M, which corresponds to the lowest active concentration of these components in its homogeneous solutions. Therefore, it is not clear at the moment whether the influence of the second component results from a change in the structure of the catalytically active centers themselves or from a change in the surface structure of the hydroxide as a whole. It is necessary to carry out a more detailed study of the properties of the hydroxide surfaces in question and, in particular, of their adsorptive ability with respect to the reagent (oxidant) under these particular experimental conditions. One can assume that this latter property, which is of primary significance in heterogeneous catalysis, varies over wide ranges in mixtures of various metal hydroxides and is responsible for the high activity of non-mixed Fe hydroxide.

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