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NOVEL CATALYST FOR DIHYDROGEN EVOLUTION FROM WATER BASED ON RHODIUM COMPLEXES WITH POLYETHYLENEIMINE

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Catalytic activity of homogeneous and heterogeneous rhodium complexes with polyethyleneimine or ethylenediamine at various Rh : N ratios has been studied in the reaction of water reduction to dihydrogen by V^{2+}_{aq} and Cr^{2+}_{aq} and the applicability of these catalysts for photocatalytic evolution of H_2 from water is discussed.

Исследована каталитическая активность гомогенных и гетерогенных комплексов родия с полиэтиленимином и этилендиамином при различных соотношениях Rh : N в реакции восстановления воды до водорода под действием V^{2+}_{aq} и Cr^{2+}_{aq} .Показана возможность использования изученных катализаторов для фотокаталитического выделения водорода из воды.

The elaboration of highly-effective catalysts for dihydrogen evolution from water by strong one-electron reductants (R) is one of the main problems to be solved for the development of photocatalytic converters of solar energy into the energy of a chemical fuel, e.g. hydrogen /1/. The known catalysts for H_2 evolution of non-biological origin are, as a rule, either stabilized noble metal sols or supported metals of the platinum group (of e.g. Ref. /1/). Little is known about metal complex catalysts for the reaction

$$2R + 2H_2O \longrightarrow 2R^+ + 2OH^- + H_2\uparrow$$

$$(\text{or } 2R + 2H^+ \longrightarrow 2R^+ + H_2\uparrow) \qquad (1)$$

Apparently, a rather promising subject to develop metal complex catalysts for reaction (1) are rhodium compounds, used in many homogeneous catalysts for hydrogenation and dehydrogenation of various organic compounds /2, 3/. Some data are known about H_2 evolution from water and about the reverse reaction of its oxidation to water in the presence of a dinuclear carbonyl-acetylacetonato rhodium complex /4, 5/ or metallic rhodium /6/. We have discovered the catalytic activity of Rh complexes with polyethyleneimine (PEI) and its low-molecular analog ethylenediamine (en) for reaction (1) with R = V^{2+}_{aq} and Cr^{2+}_{aq}.

EXPERIMENTAL

PEI (molecular mass 30000, 33% branching) was prepared at the Department of Chemistry, Moscow University. Complexes Rh-PEI with Rh : N = 1 : 4 (I – "yellow") and Rh : N = 1 : 2 ratios (II – "red") were prepared by mixing ethanol solutions of $RhCl_3 \cdot 3H_2O$ and that of PEI at a constant concentration of $RhCl_3$ (3×10^{-2}M) and various concentrations of PEI. After 6 h incubation at 298 K, the precipitate formed was separated, thoroughly washed by distilled water and ethanol from $RhCl_3$, washed by acetone and dried. The yellow complex $[Rh(en)_2Cl_2]$ Cl (III) was prepared by a known method /8/. The red complex $Rh(en)Cl_3$ (IV) was prepared by mixing ethanol solutions of $RhCl_3 \cdot 3H_2O$ and of en at the ratio Rh : en = 1 : 1; the product precipitate was thoroughly washed from $RhCl_3$ with ethanol, washed with acetone and dried. Apparently, samples I and III are individual compounds, whereas II and IV always contain noticeable admixtures of compounds with various numbers of coordinated ligands, in particular, of I and III, respectively /7/.

VSO_4 and $CrSO_4$ were prepared via the reduction of $VOSO_4$ and $K_2Cr_2O_7$ in 1 N H_2SO_4 by amalgamated zinc, according to known methods /9, 10/. Kinetic studies were performed in a temperature-controlled reactor ($T = 298 \pm 0.5$ K), supplied with a magnetic stirrer in a flow of argon. The reactor was loaded by the catalyst in a solution of H_2SO_4, evacuated to 10^{-2}Torr and filled with argon, then, through a buret, a solution of the reductant was added. The experiment was carried out at pH = 0 and 2.

The amount of evolved H_2 was measured by volumetric and GLC methods.

Reaction (1) with $R = V^{2+}$ or Cr^{2+} without catalyst (or photoactive light) does not occur at any detectable rate even in a strongly acidic medium, but in the presence of compounds I–IV in the same systems, H_2 evolves rather rapidly (Fig. 1) and after completion of the process, its amount corresponds to the stoichiometry of reaction (1). H_2 evolution in the presence of I or III for $R = V^{2+}$ proceeds with a distinct induction period. The addition of new portions of R into all samples upon completion of H_2 evolution, leads to renewed evolution of H_2 at practically the same rate, with I and III no induction periods being observed.

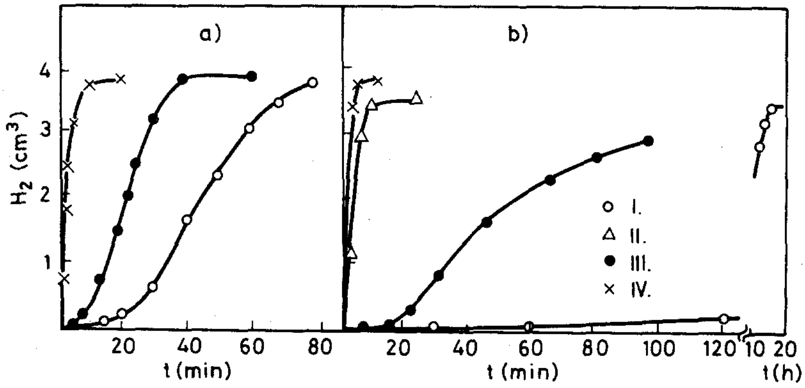

Fig. 1. Kinetics of hydrogen evolution by V^{2+} (1.5×10^{-2} M) in the presence of compounds I–IV at pH = 0 (a) and pH = 2 (b) for 20 cm^3 of solution with 10^{-5} mol (in metal) catalyst

At pH = 0, the activity is significantly higher for II and IV than for I and III, respectively. The drop of acidity to pH = 2 decreases the rate of H_2 evolution, especially for I. After more than 60 cycles of H_2 evolution (per each metal atom), we failed to observe any noticeable deactivation of the catalysts. During the reaction, catalysts I and III do not undergo any noticeable changes, whereas particles of catalyst II blacken immediately after starting the reaction, and in the solution of IV a black suspension is formed (apparently, dispersed metal rhodium). Catalyst III is likely to be active in its homogeneous state.

No definite conclusions on the mechanism of action of the catalysts can be drawn at present. Nevertheless, one should pay attention to the significantly higher catalytic activity of the coordinatively less saturated II and IV (Rh : N = 1 : 4) in the case of both the polymeric ligand and its low-molecular analog. It is most likely that this difference in catalytic activity is associated either with much easier coordination of water (and/or H^+) to the central ion of the catalyst in compounds II and IV as compared with I and III, or with much easier reduction of the central rhodium ion to lower oxidation states for II and IV. The formation of Rh(I) and Rh(0) compounds or even metallic rhodium for compounds II and IV, is proved by the above mentioned change in the catalyst state, whereas the catalytic action of I and III cannot be associated with such deep reduction of rhodium ions.

It is of great interest to establish the nature of induction period for I and III when catalytically active structures are formed. This period is probably associated either with the necessity to reorganize the coordination sphere of the complexes or with the formation of intermediates (e.g., hydrides /11/) of low-valent rhodium. The induction period can also be attributed to the slow reduction of rhodium ion from its initial oxidation state to a catalytically active state. The latter is confirmed by the absence of any noticeable induction periods for $R = Cr^{2+}$ for which the rate constants of reduction of the initial catalyst species may be higher, as Cr^{2+} is a stronger reductant than V^{2+} (E° vs. N.H.E. is -0.41 V and -0.26 V, respectively /12/).

It should be noted that the observed effect of pH on the rate of H_2 evolution can be attributed not only to the mass action law (eq. (1)), but also to the probable labilization of ligands in strongly acidic solutions due to the partial protonation of amine groups, which leads to the formation of cooredinatively less saturated structures with higher catalytic activity.

Structure and mechanism of the action of catalysts I–IV are under study, however, their applicability in weakly acidic solutions and in photocatalytic systems seems to be possible. We have observed considerable evolution of H_2 in a "classical" homogeneous photocatalytic system (6×10^{-4} M tris(bipyridyl) ruthenium(II) (photocatalyst), 10^{-1} M methyl viologen (intermediate acceptor, whose reduced form acts as R) and 2×10^{-1} M ethylenediaminetetraacetic acid (irreversible donor of electrons) (cf. Ref. /1/)) at pH = 5 during its irradiation by blue light in the presence of 2×10^{-5} mol of compound II per 20 cm^3 of solution.

The catalytic activity of rhodium compounds with PEI in reaction (1) is maintained when a partially cross-linked PEI (anionite AN-221) is used as a macroligand. This permits to prepare practically useable catalysts in the form of granules. A high catalytic activity in reaction (1) was also observed for ruthenium compounds with PEI. High catalytic activities can also be predicted for compounds of the macroligand studied with other platinum group ions.

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