Co(II,III) hydroxides supported on zeolite acting as an efficient and robust catalyst for catalytic water oxidation with $Ru(bpy)_3^{3+}$

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Abstract

A novel highly efficient and stable for many cycles catalyst (1%Co-ZSM-5(17)) for water oxidation was developed using the method of polycondensation for stabilization of oxo/hydroxo complexes of cobalt (II, III) and nanosize Co_3O_4 in zeolite channels. In a weak-alkaline medium (pH 8.0, 9.2, 10.0) in the presence of a one-electron oxidant $(Ru(bpy)_3^{3+})$, the catalyst provided the yield of oxygen as high as 56, 73 и 78 % of the stoichiometric quantity, respectively. Catalysts based on ZSM-5 zeolite exhibited higher catalytic activity as compared to the catalysts based on the MOR, BEA, Y. Inspection of the electron states of cobalt in the Co-containing zeolite-based catalysts using TPR-H_2 and UV-Vis DR techniques revealed that α-$Co(OH)_2$-like polynuclear clusters and hydrocomplexes stabilized in the zeolite channels were most active to catalytic oxidation of water, while their transformation to Co_3O_4-like clusters/nanoparticles and Co^{2+} oxocomplexes, respectively, during thermal treatment led to some decrease in the catalyst efficiency. Coarsening of Co_3O_4-like clusters/nanoparticles caused the further decrease in the system efficiency. The minimal activity was observed with the catalysts containing predominantly isolated Co^{2+}_{Oh} ions. The result obtained indicates a kind of at least polynuclear structure of the catalytically active center Co_nO_x, where $n > 2$.

Keywords: water splitting, one-electron oxidants, cobalt hydroxides, zeolite, oxygen evolution reaction

1. Introduction

Development of photocatalytic systems based on the transformation of solar to chemical energy is the key challenge in transition to the use of alternative energy sources with zero carbon balance [1]. In these systems, photoinitiated electron transfer from donor molecules to molecules of the electron acceptor is accompanied by the formation of energy saturated compounds such as, for example, carbohydrades in natural photosynthesis (I) or molecular hydrogen in water photodecomposition (II). Of interest are the systems with H_2O as the electron donor and CO_2 or H_2O as the electron acceptor:

$$6H_2O + 6CO_2 \longrightarrow C_6H_{12}O_6 + 6O_2\uparrow \qquad \text{(I)};$$

$$2H_2O \xrightarrow{h\nu} 2H_2\uparrow + O_2\uparrow \qquad \text{(II)};$$

The processes of carbon dioxide fixation (I) and complete water splitting (II) differ considerably but, even so, the reaction of water oxidation (III) is the limiting stages in both processes:

$$2H_2O + 4Ox^+ \xrightarrow{h\nu} 4H^+ + 4Ox(red) + O_2\uparrow \qquad \text{(III)},$$

where Ox+ is a one-electron oxidant generated under the action of visible light, and Ox(red) is its reduced specices. This reaction needs successive transfer of four electrons and four protons from two water molecules. However, the photocatalysts, which are excited upon absorption of unit light quantum, are only capable of generating one-electron oxidants. Therefore, a catalyst for water oxidation should be used to provide accumulation of the necessary quantity of oxidative equivalents and stabilization of intermediate products of water oxidation [2].

It is known now with certainty that some oxo/hydroxo compounds of Co(III) can catalyze water oxidation [3-8]. The efficiency of these catalysts decreases as their crystallites grow in size, and the maximal efficiency is observed with the particles less than 4 nm in diameter [9]. The reaction is conducted in weak-alkaline media where cobalt hydroxides tend to coagulate and to form bulky particles [10]. Therefore, the stabilization of highly effective nanosize particles (less than 4 nm in size) needs the presence of stabilizing ligands [11, 12]. This approach makes it possible to create colloidal systems that are appropriate for studying the reaction mechanism [7, 12]. Heterogeneous catalysts are of more practical interest. In these catalysts, the nanosize particles are stabilized using a support; the support not only prevents coarsening of the particles of Co(III) hydroxo compounds but also changes their electron structure due to

the interaction with the support surface. The typical supports are oxides of silicon [13] or aluminium [14], oxidized carbons [15, 16, 17], nitrogen doped carbon nanotubes [18], polyoxometallates [7, 19,20] and the other oxide materials [21].

A wide variety of the aluminosilicate supports [22] makes them applicable for stabilization of oxo/hydroxo compounds of transition metals and allows the size of catalytically active species and electron state of the active component to be finely adjusted. It was shown with oxides MnO_x as an example that their stabilization on the zeolite support NaY [23] provided a high efficiency of the catalyst for water oxidation (TOF 0.44-1.67 mmol $O_2 \cdot mol^{-1}$ $Mn \cdot s^{-1}$). In the present work we used zeolites with different topology and modulus (Si/Al ratio) for stabilization of oxo/hydroxo compounds of Co (II,III). Variations in the methods for the catalyst synthesis (impregnation of H-zeolite with a Co salt solution, polycondensation of the active component in the zeolite channels via hydrolysis of hydrated Co(II) cations under controlled conditions) the state of the active component to change considerably. From literature data [24], polycondensation is an optimal method for stabilization of one-dimensional nanoclusters of CoO and $CoAl_2O_4$ in channels and mesopores of H-ZSM-5 zeolite, while the size, localization and electron state of cobalt cations in the oxo/hydroxo compounds may be controlled via intentional choice of the NH_4OH/M^{2+} ratio and variations in the content of the active metal in the zeolite; that has been demonstrated earlier with Cu(II) cations stabilized in H-ZSM-5 [25]. However, data on the influence of the said parameters on the state of cobalt ions stabilized in the zeolite matrix are unavailable in literature.

Development of high-effective catalysts for water oxidation with the one-electron oxidant $Ru(bpy)_3^{3+}$ based on hydroxo/oxo compounds of Co needed systematic studies of the influence of synthetic parameters (morphology and modulus (Si/Al ratio) of the zeolites, quantity, the NH_4OH/M^{2+} ratio and supporting procedure of the active component) on the composition, structure and localization of the oxo/hydroxo complexes of Co, characterization of catalytic behavior of the prepared samples, as well as revealing of the correlation between physicochemical and catalytic properties of the catalysts. The aim of this article is an ~~aims at identification~~elucidation of these relationships.

2. Materials and methods

Chemicals and materials

The following reagents were used: $Ru(OH)Cl_3$ (pure), H_2SO_4 (high pure), HNO_3 (high pure), $HClO_4$ (high pure), NaOH (Panreac), $NaClO_4$ (high pure), Na_2HPO_4 (analytically pure), NaH_2PO_4 (analytically pure), $CoCl_2 \cdot 6H_2O$ (pure). All the solutions were prepared with deionized water obtained using a Milli-Q (Millipore) treatment system.

Complex $Ru(bpy)_3(ClO_4)_3$ as the oxidant was prepared by oxidizing $Ru(bpy)_3(ClO_4)_2$ with PbO_2 [26]. Complex $Ru(bpy)_3(ClO_4)_2$ was synthesized from $Ru(OH)Cl_3$ using the known procedure [27]. From UB-Vis data obtained at λ=452 nm (ε=14 000) using Agilent Cary 60, USA, there was no more that 5 % of the initial two-valent complex in the prepared oxidant.

Catalyst preparation

Co-ZSM-5 catalysts were prepared by polycondensation of hydrated Co(II) ion in the zeolite pores [21], some of the synthetic parameters were optimized [22] in order to stabilize oxo/hydroxo clusters of transition metals. The zeolite, after its incipient wetness impregnation with a cobalt chloride solution, was treated with the solution of ammonia at the required concentration at room temperature for 24 hours. The modified samples were filtered, washed with distilled water and dried in air to obtain free flowing sample, then at 120 °C for 2 hours. The resulting samples were calcined at 500 °C for 4 hours.

Five series of Co-ZSM-5 catalysts were prepared by this method. In the first series, the NH_4OH/Co^{2+} (α) ratio was varied (3, 6, 10, 15, 20, 30) by varying the ammonia concentration at the constant cobalt content (1 wt %). H-ZSM-5 zeolite with Si/Al=17, 95 % crystallinity and no more than 0.09 wt % of Fe impurity was used for the preparation. From ^{27}Al NMR data, there was no more than 10 % of extralattice Al^{3+} complexes [28].

In the second series, the cobalt content was carried (0.1, 0.5, 1 and 2 wt %) at the constant NH_4OH/Co^{2+} (α) ratio equal to 6; H-ZSM-5 zeolite with Si/Al = 17 was used.

In the third series, the silica ratio of H-ZSM-5 (from Khimkontsentrat, Russia) was varied as 17, 30 and 45 at the cobalt content equal to 1 wt % and NH_4OH/Co^{2+} ratio (α) to 6. H-ZSM-5 zeolites with Si/Al = 30 and 45 comprised no more than 0.6 wt % of extrinsic Fe cations [26].

In the fourth series, the chemical composition and structure of Y, MOR, BEA zeolites were varied at the Co content of 1 wt % and $\alpha = 6$.

Catalysts of the fifth series was prepared for comparison; they were prepared by impregnating H-ZSM-5(17) with the solutions of cobalt (II) chloride and hexaammoniate of cobalt (II) chloride.

In the paper, the catalysts are symbolized as n%Co(α)-Z(s) where n is the cobalt content (wt %); α is the NH_4OH/Co^{2+} ratio; Z is the structural type of zeolite (ZSM-5, Y, MOR, BEA); s is the silica ratio of zeolite (Si/Al ratio calculated on the basis of the data of X-ray fluorescence analysis). The composition and textural properties of the catalysts are shown in Table 1.

Catalyst characterization

UV-Vis DR spectra were acquired with $BaSO_4$ as the reflectance standard at 11000–53000 cm^{-1} using a UV-2501 PC spectrophotometer from Shimadzu equipped with a diffuse reflectance unit ISR-240 A. The spectra are plotted in the Kubelka-Munk function, F(R∞), – wave number coordinates.

Temperature programmed reduction of Co-ZSM-5 with hydrogen (TPR-H_2) was experimentally studied using a flow setup equipped with a thermal conductivity detector. A catalyst sample (100 mg of 0.25–0.50 mm fraction) was mixed with 100 mg of quartz granules of the similar size. The sample was kept in flowing oxygen (30 cm^3/min) at 500 °C for 30 min in order to remove adsorbed water, then cooled to room temperature and kept in flowing argon (30 cm^3/min) in order to remove oxygen from the catalyst pores. To record the TPR-H_2 curve, a hydrogen-argon mixture (10 vol % H_2) was passed at the rate of 30 cm^3/min through the catalyst sample heated from 20 °C to 800 °C at the rate of 10 °C/min. The formed water was frozen out at -60 °C in a trap. The hydrogen uptake was calibrated relative to the quantity of hydrogen consumed for reduction of CuO at identical conditions.

The TPR-H_2 tests were carried out to evaluate the activation energies for~~of~~ cobalt oxide particles reduction by hydrogen when the heating rate was varied: 5, 10, and ~~15~~ 15 °C/min. We calculated the activation energy (E_a) as a slope of the line plotted by the equiation ~~using linearization of the dependence~~ [29]:~~of~~

$$2\,LnT_m - Ln\,\beta = \frac{E_a}{RT_m} + C$$:~~(2LnT$_{max}$-Lnβ) from 1/T$_{max}$ [29],~~ [O1]

~~w~~here β is~~denoted~~ the rate of temperature increase, C i~~was~~ a constant relevant to the experimental condition, T_{max} is~~was~~ the temperature maximum in the TPR-H_2 profile registered at different β (5, 10, and 15 °C/min), ~~and~~ R ~~was~~ is the gas constant.

~~Here, the calculated slope of the plot related to the E_a/R, where E_a was activation energy.~~

Catalyst testing for water oxidation by $Ru(bpy)_3^{3+}$

Catalysts were tested for water oxidation (WO) with complex $Ru(bpy)_3(ClO_4)_3$. The oxygen yield was recorded using a Clark electrode (764080 Dissolved Oxygen Probe, Germany) in line with an oxygen meter (HI 2004 edge, Germany). A plastic reactor mounted in a jacketed vessel and thermostated with a thermostat (TEPMEX VT-8-02) was used for the experiments. A catalyst sample (50–300 mg) was immersed in 24 mL buffer solution (0.06 M borate buffer at pH 9.2, 10.0 or 0.06 M phosphate buffer at pH 7.00); the reactor was blown through with argon until the oxygen meter showed zero oxygen, then thermostated at 298 K for 15 min. After mixing and argon blowing was stopped, the aqueous solution (1 mL) containing 24 mg of $Ru(bpy)_3^{3+}$ was added. The reactor was plugged hermetically during 1–2 s, stirring turned on, and the oxygen yield started recorded.

The oxygen yield was calculated by formula:

$$Y\% = \frac{[O_2]}{0.25 \times [Ru(bpy)_3^{3+}]^0} \times 100$$

where $[O_2]$ is the equilibrium concentration registered by oxygen meter after the reaction, $[Ru(bpy)_3^{3+}]_0$ is the initial concentration of oxidant.

3. Results and discussion

Electron state of cobalt cations in n%Co(α)-Z(s) depending on the synthetic conditions

UV-Vis DR spectra (Fig. 1) were acquired with the air-dry and calcined catalysts prepared by polycondensation and containing 1 wt % of a transition metal. The absorption fundamental edge (AFE) seen as the absorption at the UV region (>37500 cm^{-1}) is characteristic of H-ZSM-5 zeolite [24]. The absence of bands of H-ZSM-5 in the visible region of the spectrum allows the electron state of cobalt cations in the Co-ZSM-5 catalyst to be reliably interpreted. In the UV-Vis DR spectra of 1%Co(*α*)-ZSM-5 prepared at varied NH_4OH/Co^{2+} ratio in the range of α = 3–30, a multiplet absorption

band with maxima at 14300–15300–16100 cm^{-1} and a broad asymmetric band at 17500–19000 cm^{-1} (Fig. 1A) is observed. The band energies correspond to the d-d transition of the cations with the tetrahedral (Co^{2+}_{Td}) and octahedral (Co^{2+}_{Oh}) ligand surroundings [30], respectively. However, energies of d-d transitions of Co^{2+} complexes with oxygen-containing and ammonia ligands differ only slightly that makes it difficult to interpret the ligand nature in the coordination sphere based on the absorption bands in the UV-Vis DR spectra. From literature data [26, 31, 32], two d-d transitions ($^4T_{2g}$ — $^4T_{1g}$ and $^4T_{1g}(P)$ — $^4T_{1g}$) at 8100 and 19000 cm^{-1} appear in the spectra of $[Co(H_2O)_6]^{2+}$ and $[Co(H_2O)_5(OH)]^+$ with the octahedral ligand coordination and at 9000 and 21000 cm^{-1} in the spectra of $[Co(NH_3)_6]^{2+}$. Similar phenomena are characteristic of tetragonal complexes of Co^{2+}: a multiplet at 16450 – 18600 – 22250 cm^{-1} (d-d transitions $^4A_{2g}$ — $^4B_{1g}$, $^4T_{1g}(P)$ — $4E_g$, $^4T_{1g}(P)$ —$4A_{2g}$) for $[Co(H_2O)_4]Cl_2$ and at16000 – 18000 – 19200 cm^{-1} (d-d transition $4T_1(P)$ —$4A_2$) for $[Co(NH_3)_4]^{2+}$ [30]. Analysis of the state of Co^{2+} cations is made even more difficult due to possible interaction between the active component and the support that may occur in heterogeneous systems to shift absorption bans by 1000–2000 cm^{-1}.

Two experimental observations should be analyzed for identification of the complex compositions. First, in the spectrum of the impregnated sample 1%Co(*0*)-ZSM-5-IWI prepared by incipient wetness impregnation of the zeolite with the $CoCl_2$ solution without further treatment with ammonia contains bands at 14300-15300-16100 (multiplet) and 17500-21200 cm^{-1} with maxima close in energy to those of $[Co(H_2O)_4]^{2+}$ and $[Co(H_2O)_6]^{2+}$ [28], respectively. Hence, the multiplet at 14300-15300-16100 cm^{-1} relates to nanoparticles of a salt with the structure close to $[Co(H_2O)_4]Cl_2$ localized in the pore structure of the zeolite. A broad band at 17500-21200 cm^{-1} is assigned to isolated $[Co(H_2O)_6]^{2+}$ cations in the zeolite cation-exchange positions formed through ion exchange with zeolite protons during the impregnation with cobalt chloride at pH 3.5. Cations $[Co(H_2O)_6]^{2+}$, which are characterized by the absorption band at 19500 cm^{-1}, were identified earlier in the spectra of hydrated Co-ZSM-5 prepared by wet ion exchange with solutions of $Co(NO_3)_2$, $CoCl_2$ and $Co(CH_3COO)_2$ [33-35].

Second, two weakly resolved multiplet at 14300-15300-16100 cm^{-1} and 16000-17500-18500 cm^{-1} are observed in the spectrum of 1%Co(*24*)-ZSM-5-IWI prepared by the impregnation with water-ammonia solution of $[Co(NH_3)_6]^{3+}$ with the ratio NH_4OH/Co^{2+} = 24 (the spectrum is not presented) that results in apparent violation of intensity ratios in both multiplets. The former multiplet energy (14300-15300-16100 cm^{-1}) relates, as discussed above, to Co^{2+}_{Td} cations. Since Co^{2+} ammines are easily

destroyed to $Co(OH)_2$ in water, it is reasonable to suppose that Co^{2+}_{Td} cations are involved in $Co(OH)_2$. The latter multiplet energy corresponds almost ideally to the energy of d-d transition $^4T_1(P) - {}^4A_2$ to $[Co(NH_3)_4]^{2+}$ (16000 – 18000 – 19200 [28]). On the other hand, the said absorption bands can be assigned to ammine complexes of Co^{3+} with different coordination spheres, for example: $[Co(NH_3)_5Cl]^{2+}$ (18720, 21350, 27500 cm^{-1} [28]), $[Co(NH_3)_4Cl]^{+}$ (15900, 21000, 24940 cm^{-1} [**Ошибка! Закладка не определена.**~~28~~]) and $[Co(NH_3)_3Cl_3]$ (15800, 17500 cm^{-1} [28]). Note that multiplet 16000-17500-18500 cm^{-1} is observed in the spectrum of the sample dried at 120 °C but absorption bands at 11000 cm^{-1} (weak), 18000 - 21000 cm^{-1} and 25000-33000 cm^{-1} (intense) in the spectrum of the impregnated sample. The presence of bands with the energy characteristic of $[Co(NH_3)_6]^{3+}$ (13000, 21200, 29600 cm^{-1} [28]) indicates the formation of complexes $[Co(NH_3)_4]^{2+}$ and/or $[Co(NH_3)_{6-x}Cl_x]^{(3-x)+}$ from $[Co(NH_3)_6]^{3+}$ in the course of drying. Thus, sample 1%Co(*24*)-ZSM-5-IWI there are hydroxide-like nanoparticles which comprise Co^{2+}_{Td} cations in the zeolite pore space and various ammine complexes $[Co(NH_3)_4]^{2+}/[Co(NH_3)_{6-x}Cl_x]^{(3-x)+}$ in the cation positions of the zeolite.

Let us compare UV-Vis DR spectra acquired with the samples prepared by polycondensation and impregnation. First, in the spectra of air-dry samples prepared by polycondensation in the presence of ammonia, the band at 17500 – 21200 cm^{-1} is shifted towards lower wave numbers (approximately, 1000 cm^{-1}) and increases in intensity with an increase in the NH_4OH/Co^{2+} from 0 to 15 and then changes in non-linear manner at NH_4OH/Co^{2+} = 20 and 30. Unlike a.b. 17500 – 21200 cm^{-1}, the triplet band energy is practically independent of NH_4OH/Co^{2+} in the range of 6 to 30, and the apparent change in its intensity is accounted for by overlapping with the band at 17500 – 21200 cm^{-1}. The said spectral features indicate the presence of Co^{2+}_{Td} (14300-15300-16100 cm^{-1}) and Co^{2+}_{Oh} (17500-21200 cm^{-1}) cations. The polycondensation includes the following chemical processes occurring in micro- and mesopores of the zeolite: (1) hydrolysis of $[Co(H_2O)_6]^{2+}$ cations resulting from the local changes in pH upon addition of the ammonia solution; (2) polycondensation of $[Co(OH)]^{+}$ to $[Co_2(OH)]^{3+}$, $[Co_4(OH)_4]^{4+}$ and $Co(OH)_2$ [36]. Thus, Co^{2+}_{Td} and Co^{2+}_{Oh} cations are constituents of polynuclear hydroxoclusters. As the NH_4OH/Co^{2+} ratio increases, ligands $H_2O(OH)$ are substituted for by NH_3 in the coordination sphere of Co^{2+}_{Oh} cation that leads to gradual decrease of $[Co_x(OH)_y]$-like clusters in size and, at the limit, to their complete dissolution and formation of ammonia complexes $[Co(NH_3)_n]^{2+}$, the complete dissolution is observed at a high ammonia concentration at NH_4OH/Co^{2+} ratio no less than 18. Complexes

$[Co(NH_3)_n]^{2+}$ exchange with protons of the zeolite and are stabilized in its cation positions. When the NH_4OH/Co^{2+} ratio increases from 3 to 30, the proportion of $[Co(NH_3)_n]^{2+}$ increases, d-d transition at ca. 19500 cm^{-1} and a multiplet at 16000-17500-18500 cm^{-1} being characteristic of $[Co(NH_3)_6]^{2+}$ and $[Co(NH_3)_4]^{2+}$, respectively. Thus, samples of 1%Co(α)-ZSM-5 prepared both at low (α=3) and high (α=30) ratio NH_4OH/Co^{2+} contain hydroxide-like polynuclear species and isolated $[Co(NH_3)_n]^{2+}$ cations. The energy of the observed triplet in the visible range of spectra of 1%Co(α)-ZSM-5 agrees with absorption bands in the spectrum of α-$Co(OH)_2$ with the mixed coordination of Co^{2+} cations and structural formula $[(Co^{2+}_{Oh})_{1-x}[Co^{2+}_{Td}]_{2x}(OH)_2]^{2x+}$ [36]. This spectrum contains broad bands at 16000 cm^{-1} (Co^{2+}_{Td}) and 17500-21000 cm^{-1} (Co^{2+}_{Oh}) unlike the spectra of α-$Co(OH)_2$ and β-$Co(OH)_2$ with Co^{2+}_{Oh} cations (triplet at 19000-20000-21200 cm^{-1} and a broad band at 19000-21200 cm^{-1}, respectively) [35, 38]. Hydroxide α-$Co(OH)_2$ with the mixed coordination of Co^{2+} ions is defect in respect of hydroxide anion; therefore the charge of $[(Co^{2+}_{Oh})_{1-x}[Co^{2+}_{Td}]_{2x}(OH)_2]^{2x+}$ is compensated by anions of acid residues [35, 39, 40], e.g. Cl^- in the case under consideration. It was suggested earlier that Co-ZSM-5 comprises oligomers oxohydroxide $[CoOH\text{-}CoO]^+$ identified with the triplet at 14500-16100 cm^{-1} in UV-Vis DR spectra [33], the hydrolysis of $[Co(H_2O)_6]^{2+}$ inside the channels followed by polycondensation (oxolation/olation) at the thermal treatment being considered as the main reason for the formation of the oxohydroxides. Baes et al. [31] discussed the presence of oxide-like clusters CoO_x (with the so-called extralattice oxygen) in Co-ZSM-5 prepared via solid-phase ion exchange; they suggested that CoO_x-like clusters comprise both Co^{2+}_{Td} and Co^{3+}_{Td} cations. The latter are identified as the shoulder at 24000 cm^{-1} in the UV-Vis DR spectrum.

Second, a weak absorption at 27500-32500 cm^{-1} is observed in UV-Vis DR spectra of air-dry samples 1%Co(*α*)-ZSM-5 (Fig. 1A). The band energy corresponds to the d-d transition in the structures with Co^{3+} cations in octahedral surrounding (Co^{3+}_{Oh}) of oxygen-containing (24700 cm^{-1} [30]) and/or ammonia (29550 cm^{-1} [30]) ligands, as well as ligand-to-metal charge transfer band (CTB L-M) of polynuclear complexes of Co^{2+} with bridging ligands [30]. In view of the fact of the symbate increase in intensity of the mulriplet band at 14500-15300-16100 cm^{-1} (Co^{2+}_{Td}) with the intensity of band 27500-32500 cm^{-1} (Co^{3+}_{Oh}), it is reasonable to suppose that Co^{2+}_{Td} and Co^{3+}_{Oh} cations are comprised in the same compounds, for example polynuclear hydroxo complex of cobalt (II,III) with the structure close to the defect α-$Co(OH)_2$. Unfortunately, it is hardly possible to correlate directly the intensity of the band at 27500 cm^{-1} with the

content of Co^{3+}_{Oh} catalytic activity of 1%Co(*α*)-ZSM-5 to water decomposition because CTB L-M of hydroxo/oxo clusters of Co^{2+} and extralattice species with Cl^--modified Al^{3+} ions may appear at the same spectral region. We observed earlier the band at 27500 cm^{-1} in the spectra of Cu-ZSM-5 prepared by polycondensation [22].

Third, we cannot exclude that the 1%Co(*30*)-ZSM-5 sample prepared at a high NH_4OH/Co^{2+} ratio comprises isolated $[Co(NH_3)_6]^{3+}$ ions which give a low-intense band at 13000 cm^{-1}, a band at 21000 cm^{-1}, and a shoulder at 30000-33000 cm^{-1} (d-d transitions ^1A_g - $^1T_{1g}$ and ^1A_g -$^1T_{2g}$ [28]). In the spectrum of 1%Co(*24*)-ZSM-5-IWI prepared by impregnation with a water-ammonia solution of $[Co(NH_3)_6]^{3+}$ (dark cherry colored) at NH_4OH/Co^{2+} = 24 and dried at 25 °C these bands also were observed but disappeared after drying at 120 °C to indicate the removal of NH_3 ligands from the coordination sphere of Co^{3+} cations. This is consistent with the ability of $[Co(NH_3)_6]^{2+}$ to be gradually oxidized by air oxygen to $[Co(NH_3)_6]^{3+}$ [41]. EPR technique was used [32] to observe the formation of $[Co^{3+}(NH_3)_{x-1}(O_2^-)]^{2+}$ adducts through interaction of Co^{2+} in Co-ZSM-5 with ammonia at room temperature in oxygen-containing atmosphere. Hence, Co^{3+}_{Oh} cations can form via intraspheric electron transfer from Co^{2+} to O_2 at the stage of polycondensation of hydrolyzed $[Co(H_2O)_5(OH)]^+$ ions in concentrated ammonia solutions.

When air-dry 1%Co(*a*)-ZSM-5 catalysts are calcined in air at 500 °C (Fig. 1B), defect α-$Co(OH)_2$-like clusters are transformed to oxide-like clusters with the electron structure similar to that of spinel with Co^{2+}_{Td} (14400-16000 cm^{-1}) and Co^{3+}_{Oh} (24500-32500 cm^{-1}) cations, while isolated Co^{2+}_{Oh} ions (19000-21000 cm^{-1}) are still in cation positions of the zeolite. The calcined catalyst 1%Co(*24*)-ZSM-5-IWI was an only sample containing isolated Co^{2+}_{Oh} (d-d 19000 cm^{-1}, the spectrum is not presented) but not Co_3O_4–like clusters. Temperature genesis of α-$Co(OH)_2$-like clusters in channels of 1%Co(*a*)-ZSM-5 is consistent with transformations characteristic of bulk hydroxide α-$Co(OH)_2$. For example, thermal decomposition of α-$Co(OH)_2$ at 300 °C results in the formation of Co_3O_4 in air and CoO in argon [42]. On the other hand, FTIR studies indicate the formation of CoO from oligomers clusters $[CoOH\text{-}CoO]^+$ in the course of thermal treatment of Co-ZSM-5 [33]. Literature data on changes in the oxidation degree of Co^{2+} to Co^{3+} during oxidative treatment are somewhat contradictory. Some researchers suggest that Co^{2+} is oxidized to Co^{3+} during thermal treatment of Co(II)-containing materials [31, 37] but the others deny the oxidation of Co^{2+} to Co^{3+} at below 450 °C [21, 32, 33].

Co_3O_4-like clusters containing Co^{2+}_{Td} cations (triplet at 14400-15300-16000 cm^{-1}) and Co^{3+}_{Oh} (24500-32500 cm^{-1}), and isolated Co^{2+}_{Oh} cations (19000-21000 cm^{-1}) were observed in the other series of catalysts n%Co(*6*)-Z(s) prepared using H-ZSM-5 with different silicate ratios and the other type zeolites (BEA, MOR, Y), as well as with different cobalt contents. UV-Vis DR studies of these catalysts revealed that an increase in the silica ratio (from 17 to 45, no illustration) leads to an increase in the proportion of Co_3O_4-like clusters in the calcined catalysts 1%Co(*6*)-Z(s) (where s = 17, 30 and 45), the proportion of isolated Co^{2+}_{Oh} ions being naturally decreased. This trend is natural because the increase in the silica ratio results in a decrease in the cation exchange positions in ZSM-5 zeolite, which are necessary for binding the isolated Co^{2+}_{Oh} ions [26]. Note that there is a trend to the formation of CoO-like species apart from Co_3O_4-like clusters in the calicned samples of 1%Co(*6*)-ZSM-5(30) and 1%Co(*6*)-ZSM-5(45). The latter clusters give absorption bands at 13200 and 21000 cm^{-1} [30]. The maximal proportion of the CoO-like clusters is characteristic of 1%Co(*6*)-ZSM-5(30).

In calcined catalysts 1%Co(*6*)-Z-5(s) prepared using zeolites with different topology, the proportion of Co_3O_4-like clusters increases in the series ZSM-5 > BEA > Y >> MOR. Absorption bands at 14500-15300-16100, 18500-19900 and 27500 cm^{-1} are assigned to these clusters. Note that 1%Co(*6*)-MOR was an only catalyst where the quantity of isolated Co^{2+} ions was more than that of Co_3O_4 clusters; seemingly, the ions were stabilized in cation positions of the zeolite (18900 cm^{-1}). Again, this as an only sample that became pink colored upon addition of ammonia solution (for polycondensation of Co^{2+} ions) that may indicate stabilization of β-$Co(OH)_2$ [43] and/or isolated Co^{2+}_{Oh} ions [28]. The blue-and-green color of all the other n%Co(α)Z(s) samples, before they were calcined, is characteristic of α-$Co(OH)_2$ comprising Co^{2+}_{Td}, Co^{2+}_{Oh}, and Co^{3+}_{Oh} cations [35, 41]. Similar to above discussed 1%Co(*6*)-ZSM-5, air-dry samples based on Beta and Y zeolites gave differently intense a.b. at 14400-15000-15900, 16200-17500-18500 and 27500 cm^{-1} in the spectra.

The influence of cobalt content on its electron state in n%Co(*6*)-ZSM-5(17) with *n* varied between 0.1 and 2 wt % is exemplified in Fig. 2. Inspection of the UV-Vis DR spectra shows the appearance of new electron states, which differ from those in the above discussed 1%Co(*6*)-ZSM-5(17), both at lower (0.1, 0.5 wt %) and at higher (2 wt %) contents of cobalt. In the UV-Vis DR spectra of air-dry samples of 0.1%Co(*6*)-ZSM-5(17) and 0.5%Co(*6*)-ZSM-5(17), there are bands at 27700 and 32500 cm^{-1} that are not observed in the spectrum of 1.0%Co(*6*)-ZSM-5(17). Absorption bands at 13200, 19000, 27700 and 36200 cm^{-1} are characteristics of the calcined low-loaded samples.

Apparently, polycondensation of hydrolyzed cobalt ions in pores of the catalyst with the low cobalt content and, respectively, low ammonia concentration results in predominant formation of $[Co(OH)]^+$ cations and CoOOH nanoclusters but not polynuclear species similar to the 1%Co(*6*)-ZSM-5(17) catalyst. Cations of $[Co(OH)]^+$ are transformed to $[Co\text{-}O\text{-}Co]^{2+}$ structures with CTB L-M 27700 and 32500 cm^{-1} during drying and to CoO during thermal treatment. However, there is a low proportion of CoO-like clusters in 0.5%Co(*a6*)-ZSM-5(17) in comparison to isolated $Co^{2+}{}_{Oh}$ (19000 cm^{-1}) ions in the exchange positions of the zeolite.

Along with the triplet at 14400-15000-15900 cm^{-1} and the slowly growing absorption at 20000 – 33000 cm^{-1}, a triplet at 15900-17700-18700 cm^{-1} appears in the spectrum of the air-dry sample 2%Co(*6*)-ZSM-5(17); the energy of this triplet is close to ammonia complexes of Co^{3+} in various ligand surroundings [30]. Upon calcining, 2%Co(*6*)-ZSM-5(17) comprises Co_3O_4-like clusters ($Co^{2+}{}_{Td}$ 13200, 14600 and 16100 cm^{-1}; $Co^{3+}{}_{Oh}$ 27700 cm^{-1}) and isolated Co^{2+} ions in exchange positions of the zeolite ($Co^{2+}{}_{Oh}$ 18500 cm^{-1}). It seems like a part of Co_3O_4-like clusters reside in the zeolite mesopores and not interact with the zeolite matrix.

Redox properties of catalysts n%Co(α)-Z(s)

Data on the electron state of cobalt cations in the n%Co(α)-ZSM-5 catalysts were clarified using the TPR-H_2 technique. In addition, this technique provides information on redox properties of the catalysts. Experimental TPR-H_2 profiles (Figs. 3 and 4) were obtained with the series of catalysts prepared by varying the NH_4OH/Co^{2+} ratio and cobalt content. Three regions of the reduction of Co^{n+} cations can be identified in the profiles: low temperature (below 450 °C), moderate temperature (550–700 °C) and high temperature (750–800 °C). According to literature data [44-48], these temperature regions in the profiles of reduction of Co-ZSM-5 relate to reduction of easily reducible CoO_x-like clusters and nanosize particles, bi- and polynuclear oxocomplexes of Co^{n+}, and hard reducible Co^{2+} cations in the cation-exchange positions of the zeolite, respectively. Inspection of the TPR-H_2 profiles of the n%Co(α)-ZSM-5 catalysts revealed that the temperature ranges of the catalyst reduction depend on the NH_4OH/Co^{2+} ratio during the catalyst preparation. First, temperature ranges of the reduction of isolated Co^{2+} ions in the impregnated sample 1%Co(*0*)-ZSM-5 are identical to the data on the reduction of ion-exchanges zeolites Co-ZSM-5 [43, 44], Co-MOR [43, 47] (ca. 750–780 °C). However, the high-temperature peak of hydrogen uptake shits towards lower temperature for the samples at the NH_4OH/Co^{2+} ratio between 3 to

15 as compared to the data on the reference sample 1%Co(*0*)-ZSM-5, i.e. from 750–780 °C to 650–660 °C (Fig. 3). Lowering of the temperature of reduction of Co^{n+} ions indicates the presence of at least two Co^{2+} ions bound through bridging oxygen, e.g. oxocomplexes of Co^{2+}, in the structures formed at the stage of polycondensation of hydrolyzed Co^{2+} ions followed by calcination [43, 47]. We observed similar effects before in experimental TPR-H_2 studies of Cu-substituted ZSM-5 zeolites with high Cu contents obtained by inpregnation with ammonia complexes of copper [50]. Second, the medium temperature peak of hydrogen uptake decreases in intensity when high concentrations of ammonia are used for the catalyst preparation (for example, NH_4OH/Co^{2+} = 20 and 30), whereas a total of hydrogen consumption taken relative to the quantity of supported Co^{n+} (H_2/Co) tends to grow. At H_2/Co=0.30–0.33, the medium temperature signal in the profiles of n%Co(*α*)-ZSM-5 (at NH_4OH/Co^{2+} between 6 and 15) corresponds to the reduction of 55–65 % of all the cobalt ions reduced in the catalyst. The proportion of moderately reducible ions decreases down to 10–15 % in the catalysts prepared at NH_4OH/Co^{2+} equal to 20 and 30, while H_2/Co is practically doubled (up to 0.55) in 1%Co(*30*)-ZSM-5. The reason is a decrease in the proportion of oxoclusters of Co^{2+}, as well as a variation in their reducibility. The decrease in the reducibility can be accounted for by the interaction between a part of ammine complexes of Co^{2+}/Co^{3+} and terminal SiOH groups at the outer zeolite surface in strongly alkaline solutions to decrease in the cobalt quantity in the zeolite channels. On the other hand, Ulla et al. [43] suggest that isolated Co^{2+} ions in Co-ZSM-5 are reduced slowly, so that they have no time for complete reducing during the TPR-H_2 experiment. Third, the width and asymmetry of the low-temperature peak of hydrogen uptake (200–400 °C) indicates the non-uniform composition and localization of CoO_x-like species on the surface and pores of the n%Co(*α*)-ZSM-5. For example, catalyst 1%Co(*0*)-ZSM-5 consumes hydrogen at rather narrow temperature range (300–380 °C) but with two maxima at 310 (shoulder) and 340 °C. The mode of the catalyst reduction may indicates the presence of Co_3O_4 in its composition. There are usually two poorly resolved peaks at 325–330 and 360–430 °C in the profile of reduction of bulky Co_3O_4 particles, which relate to the two-stage reduction of Co_3O_4 to CoO and then to cobalt metal [51, 52]. Dispersion of the Co_3O_4 particles through the surface of inert supports is accompanied by drop of the reduction temperature down by 30–40 °C in the case of Co-ZSM-5 [43, 44]. In the profiles of 1%Co(*3*)-ZSM-5 and 1%Co(*30*)-ZSM-5 catalysts, the range of hydrogen uptake is broadened as 180–420 °C; the peaks with maxima at 250-265, 310, 340 °C and a shoulder at 430 °C can be identified there. The first three peaks may

indicate the reduction of Co_3O_4-like nanoparticles differing in size and/or the manner of interaction with the support. The peak at 430 °C may relate to the reduction of CoO-clusters decorated by the support [43, 48]. On the other hand, it is reported in literature [53, 54] that at low temperatures (215–230 °C) bulky CoOOH is reduced to Co_3O_4 to be then reduced to CoO (260–279 °C) and Co (350 °C) [53]. We cannot exclude the presence of CoOOH in 1%Co(*30*)-ZSM-5. However, 1%Co(*3*)-ZSM-5 seem to contain polydisperse Co_3O_4-like nanoparticles. The proportion of polynuclear clusters is maximal in 1%Co(*3*)-ZSM-5 and decorated particles in 1%Co(*20*)-ZSM-5 and 1%Co(*30*)-ZSM-5. Co_3O_4-like clusters and isolated Co^{2+} ions are in comparable quantities in 1%Co(*α*)-ZSM-5 catalysts prepared at NH_4OH/Co^{2+} equal to 6–15, their proportions being practically unchanged upon an increase in the cobalt content from 1 to 2 wt % (Fig. 4).

Note that the molar ratio of the quantity of absorbed hydrogen to the cobalt content (H_2/Co) in both series catalysts n%Co(*α*)-ZSM-5 was much lower of the stoichiometric quantity of hydrogen required for the reduction of CoO, Co_3O_4, and isolated Co^{2+} ions to the cobalt metal (H_2/Co=1, 1.33, 1; see Figs. 3b and 4b). This is an evidence of the incomplete reduction of cobalt cations in catalysts n%Co(*α*)-ZSM-5. The maximal H_2/Co ratio (0.55–0.6, Fig. 3b) was characteristic of the catalysts prepared at the ratio NH_4OH/Co^{2+} equal to 6–15. Co-containing species were most hardly reduced in 1%Co(*0*)-ZSM-5 during TPR-H_2 experiments due to modifying the catalyst surface and/or CoO_x-like species with chloride ions which usually inhibit the reduction of oxides and oxide clusters of transition and noble metals [22, 48].

The shift of the hydrogen consumption peak towards higher temperatures in TPR-H_2 experiments is usually caused by strong metal-support interactions [54, 55]. Obviously, the stronger interaction between Co_3O_4-like particles and zeolite support, the higher is~~are~~ activation energy~~ies~~ of its reduction. The observed activation energies for the reduction of Co_3O_4-like clusters or nanoparticles to CoO and the following reduction of CoO to Co are shown in Table 2 for some catalysts supported on H-ZSM-5(17). The minimal activation energy for the reduction of Co_3O_4-like clusters or nanoparticles wa~~i~~s observed in the case of catalyst 2% Co(*6*)ZSM-5(17) (E_a= 21 ± 3 kJ/mol). It indicates that the interaction between Co_3O_4-like clusters or nanoparticles and zeolite surface is weaker than that in catalysts 1% Co(*α*)ZSM-5(17) with *α=3-10*.

Thus, catalysts 1%Co(*α*)-ZSM-5 feature different reductability due to stabilization of different electron states of Co^{n+} constituents. Isolated Co^{2+} ions in cation-exchange positions of the zeolite are most stable to reduction and, most likely, do

not participate in redox stages of water decomposition. Polynuclear oxo-species of Co^{2+} were somewhat more reducible, and the highest reducibility was characteristic of Co_3O_4-like species involved in two-stage reduction: Co^{3+} - Co^{2+} - Co^0 that can be important for stabilization of intermediate oxidation state of cobalt during water decomposition.

The influence of the structure type of zeolite and silica ratio on the catalytic performance during water oxidation with complex $Ru(bpy)_3^{3+}$

A series of Co-containing catalysts 1%Co(*6*)-Z(s) based on zeolites with different structures (Mordenite - MOR, Beta - BEA, Faujasite - Y, ZSM-5 - MFI) were tested for the reaction (IV) of water oxidation using complex $Ru(bpy)_3^{3+}$:

$$4\ Ru(bpy)_3^{3+} + 2\ H_2O \xrightarrow{Catalyst} 4\ Ru(bpy)_3^{2+} + O_2\uparrow + 4\ H^+ \qquad \text{(IV)}.$$

Note that the characteristic time of the reaction of releasing molecular oxygen form water is less than 1 ms [56] but the response time of the Clark electrode used as an oxygen meter ca. 30 s. When so, the data on the catalytic activity can only be obtained based on the yield of oxygen. That the oxygen yields differ from 100 % of the reaction IV stoichiometry is accounted for by side reactions proceeding by non-catalytic (or autocatalytic) (V) and catalytic (VI) pathways of the oxidant consumption [**Ошибка! Закладка не определена.**~~12~~]:

$$Ru(bpy)_3^{3+} \rightarrow Ru(bpy)_2(bpy\text{-}ox)^{2+} \qquad \text{(V)},$$

$$Ru(bpy)_3^{3+} + bpy \xrightarrow{Catalyst} Ru(bpy)_3^{2+} + bpy\text{-}ox \qquad \text{(VI)};$$

where bpy-ox is the oxidized bipyridyl ligand. Stage (V) of autocatalytic destruction of the oxidant is responsible for a decrease in the oxygen yield at low concentrations of the catalyst [57], and catalytic stage (VI) for a decrease in the oxygen yield at the high concentrations of the catalyst.

The yields of oxygen obtained in the presence of catalysts 1%Co(*6*)-Z(s) are shown in Table 3 (samples Nos. 1–4). Under identical conditions, the maximal yield of oxygen (64 % of the stoichiometry of reaction (IV)) was observed with the catalyst supported on ZSM-5 zeolite. The catalysts based on Beta and Y zeolites were similarly

effective and provided 60 % of the oxygen yields. The minimal oxygen yield (52 %) was in the presence of 1%Co(*6*)-MOR(6).

Apparently, the different activities of 1%Co(*6*)-Z(s) catalysts are caused by specific textures and microstructures of the zeolite, as well as by the composition of catalytically active cobalt species. It was discussed above that the active components of all the 1%Co(*6*)-Z(s) catalysts comprise (in different proportions) Co_3O_4-like clusters/nanoparticles, polynuclear oxocomplexes of Co^{2+}_{Oh} and isolated Co^{2+}_{Oh} cations in the exchange positions of the zeolite. However, the oxygen yields observed with these catalysts correlated only slightly with the H_2/Co ratio in low- and high-temperature regions (310–340 and >700 °C, respectively) during TPR-H_2 studies. These are the regions where Co_3O_4-like clusters/nanoparticles and isolated Co^{2+}_{Oh} cations, respectively, are reduced. While the participation of isolated Co^{2+}_{Oh} ions in water oxidation is low probable due to their high stability to reduction, the catalytic behavior of nanosize Co_3O_4 constituents of supported [6, 7, 11, 12, 18, 61] and colloidal [53] catalysts is the subject of active discussions in literature. With our catalysts, an increase in the oxygen yield in reaction IV was only observed with an increase in the proportion of polynuclear oxocomplexes of Co^{2+} that were reduced at 640–660 °C during TPR-H_2 studies.

On the other hand, the observed oxygen yields depended nonlinearly on the zeolite texture and on exposure of zeolite channels for stabilization of CoO_x-like clusters and polynuclear particles, as well as on the chemical composition of the zeolite matrix. A trend to an increase in the oxygen yield (reaction IV) was observed with an increase in silica ratio in the series: ZSM-5 > Beta, Y > MOR. The increase in the silicate module results in a decrease in the number of proton centers in the zeolite and, correspondingly, in minimization of the site appropriate for stabilization of isolated Co^{2+} ions which are inactive to the reaction under study.

Inspection of the correlations between zeolite channel structures and the oxygen yields leads to conclude about close (64 %) or identical (60 %) selectivities of zeolite catalysts with close sizes of three-dimensional channels: 5.3 × 5.6 Å and 5.1 × 5.5 Å in ZSM-5; 7.6 × 6.6 Å in Beta; 7.4 × 7.4 Å in Y [59]. At the same time, complex oxidant $Ru(bpy)_3^{3+}$ is too large in size to penetrate inside these zeolite channels [7, 60]. Therefore, the reaction of one-electron transfer from the oxidant to the catalyst is thought to occur at the channel inlet; as a result, the size and interaction of Co_3O_4-like clusters with the zeolite surface and of polynuclear oxocomplexes of Co^{2+}_{Oh} with functional groups of the zeolite becomes of importance. Apparently, when the Co

content is less than 1 wt %, Co_3O_4-like clusters are formed in the zeolite channels, and the channel size limits the cluster size. This assumption is supported by the similarity of textural parameters such as micropore volume and external surface of the crystallites in pure zeolites (ZSM-5(17) [21, 22]) and catalysts with the supported active Co-component (Table 1). A topic for earlier discussions in literature was the activity of 1–2 nm $Co(OH)_2$ particles supported on nanosize SiO_2 [61] and 3–7 nm Co_3O_4 particles on silica [7]. However, these were the cases when active Co species were much larger in size than the zeolite channels (no more than 0.75 nm). A decrease in the size of CoO_x particles results in strengthening of their interaction with the support surface and, correspondingly, in a decrease in their redox potential [62]. At the same time, a decrease of the CoO_x particles in size produces more defects that is accompanied by narrowing of the band gap [63] and, as a consequence, by lowering of the energy of electron transfer to/from the valence band and by the trend to stabilization of higher valent Co^{n+} cations. It is evident that these two factors have opposite effects on the behavior of the catalytic system. Therefore, in choosing the size of CoO_x particles, one should find balance between the positive influence on the catalytic activity caused by the higher defectness of the particles and the negative effect resulted from the lowering of the redox potential of CoO_x [64].

On the other hand, the external surfaces of the crystallites in 1%Co(*6*)-beta and 1%Co(*6*)-Y were 4–6 times as large as those in 1%Co(*6*)-ZSM-5 (Table 1). As a result, they sorb more $Ru(bpy)_3^{3+}$ to accelerate side reactions V and VI and to decrease the oxygen yield by reaction IV. Previously, the difference in the catalytic behavior during photoinitiated water decomposition in the presence of $Ru(bpy)_3^{3+}$ and persulfate was accounted for by adsorption of the ruthenium complex on the larger surface of Co-catalysts with nanosize Co_3O_4 particles (4 nm) supported on SBA-15 and MCM-41 [7].

A series of catalysts 1%Co(*6*)-ZSM-5(s) prepared by polycondensation on H-ZSM-5 zeolite with silica ratios 17, 30 and 45 were used for studying the influence of silica ratio on the catalytic activity. The oxygen yields by the reaction of water oxidation over 1%Co(*6*)-ZSM-5(s) are shown in Table 1, Nos. 4–6. Close oxygen yields (ca. 63–64 % of the reaction stoichiometry) were observed with the zeolite with silica ratio 17 and 30 but decreased down to 59 % as the Si/Al ratio was increased up to 45. Apparently, an increase in the proportion of lattice Al^{3+} cations leads to an increase in the concentration of proton centers in the zeolite. However, these centers reside in the zeolite channels and cannot participate in the ion-exchange adsorption of the oxidant but only affect indirectly the equilibrium of the ion exchange reaction with the functional

groups of the zeolite catalyst. The points of zero charge (pH) of H-ZSM-5(45) and H-ZSM-5(17) zeolites in water are 3.4 and 3.1, respectively. Therefore, at pH 9.2 used for studying the reaction of water oxidation, terminal SiOH groups of the zeolite are deprotonated and can take part in the adsorption of $Ru(bpy)_3^{3+}$ (VIII) the way similar to the suggested stage of ion-exchange adsorption of the oxidant on the active site of the Co-catalyst (VII) [2]:

$$\cdots Co^{III}\text{–}OH + Ru(bpy)_3^{3+} \longrightarrow \cdots Co^{III}\text{–}O^{-} \cdots Ru(bpy)_{3,\,ads}^{3+} + H^{+} \quad \text{(VII)},$$

$$\cdots Si^{IV}\text{–}OH + Ru(bpy)_3^{3+} \longrightarrow \cdots Si^{IV}\text{–}O^{-} \cdots Ru(bpy)_{3,\,ads}^{3+} + H^{+} \quad \text{(VIII)}.$$

The sorbability with respect to Ru(bpy)33+ increased with a decrease in the silica ratio of H-ZSM-5(s) zeolites even at close external surfaces of the crystallites. The sorbabilities of H-ZSM-5(17) and H-ZSM-5(45) zeolites were only 15 % different; they were 8.3 and 7 mg/g, respectively (Table 3). The difference may cause acceleration of reaction IV of water oxidation but, at the same time, acceleration of side reaction VI, too.

Of course, the proportion of Co_3O_4-like clusters and Co^{2+} oxocomplexes is higher in the zeolites with higher silica ratio (30, 45) than in the zeolites with lower Si/Al (17). But apparently, the influence of the electron state of Co-constituent of catalysts 1%Co(*6*)-ZSM-5(s) on the process efficiency was less critical under the chosen reaction conditions than the influence of acid properties of the zeolite.

The influence of the Co supporting procedure on the catalytic efficiency

The role of the method for catalyst preparation in the formation of electron states of cobalt and their catalytic activities was studied using two procedures for supporting the active component on H-ZSM-5(17) zeolite: polycondensation and incipient wetness impregnation. The impregnating solutions were prepared using aqueous (α=0) and water-ammonia (α=24) solutions of cobalt chloride, the composition of the solutions being identical or close to two boundary compositions used for polycondensation. The first stage of the catalyst preparation via polycondensation is introduction of cobalt cations into zeolite channels by impregnating the zeolite with an aqueous solution of cobalt chloride. The second stage is addition of an ammonia solution of Co^{2+} cations to achieve polycondensation in the zeolite channels. During the second stage, the polycondensation proceeds concurrently with the complex formation to form ammonia

complexes of Co^{2+}/Co^{3+} at the probability increasing with high α. The results of the catalyst testing for water oxidation are summarized in Table 4. The tabulated data demonstrate that both impregnated samples are less effective catalysts than the sample prepared by polycondensation which provided the oxygen yield as high as 64 %. The oxygen yields over the impregnated samples prepared with the aqueous and water-ammonia solutions were 49 and 28 %, respectively. In catalyst 1%Co(*6*)-ZSM-5(17), the active component resides in the zeolite channels in the forms of α-Co_3O_4-like clusters, oxocomplexes of Co^{2+}_{Oh} and isolated Co^{2+}_{Oh} ions. After calcination, the impregnated sample 0.5%Co(*24*)-ZSM-5(17)-IWI prepared with the water-ammonia solution contained 0.5 wt % Co as isolated Co^{2+}_{Oh} in the cation-exchange positions. The predomination of electron state Co^{2+} in 0.5%Co(*24*)-ZSM-5(17)-IWI indicates unambiguously the low activity catalyst activity of the isolated Co^{2+}_{Oh} ions to water oxidation and may bear responsibility for the low efficiency of this catalyst.

The predominant formation of α-Co_3O_4-like clusters/nanoparticles on the support mesopore surface and isolated Co^{2+}_{Oh} in the cation positions of the zeolite was observed during calcination of the impregnated sample 1%Co(*0*)-ZSM-5(17)-IWI prepared from the aqueous solution of cobalt chloride. The suggested composition of the active component of 1%Co(*0*)-ZSM-5(17)-IWI indicates the less efficiency of Co_3O_4-like clusters/nanoparticles for water oxidation. Again, it is not improbable that the catalyst efficiency decreases due to modifying the zeolite surface and/or Co_3O_4-like clusters by chloride ions that deteriorates the reducibility of the catalyst. This assumption agrees with the TPR-H_2 data on the minimal H_2/Co ratio in 1%Co(*0*)-ZSM-5(17)-IWI among the catalysts under study.

The influence of the conditions of Co-catalyst preparation on the catalytic efficiency

As shown above, the electron state and localization of the active component in the zeolite can be intentionally changed by varying some conditions (quantity of supported Co, NH_4OH/Co^{2+} ratio, calcination temperature) of polycondensation of Co^{2+} ions in zeolite pores.

A series of n%Co(*6*)-ZSM-5(17) catalysts prepared of H-ZSM-5(17) zeolite at identical NH_4OH/Co^{2+}=6 were used for studying the influence of Co content (varied between 0.1 and 2 wt %) on the efficiency of water decomposition. The oxygen yields over these catalysts are shown in Table 5 (samples Nos. 1–4).

Note that the initial zeolite H-ZSM-5(17) was not effective, it provided less than 3 % yield of the stoichiometric quantity (Table 5, No. 13). Even minor quantity of cobalt (0.1 wt %) supported on zeolite resulted in acceleration of the oxygen formation and an increase in the oxygen yield up to 33 %. An increase in the cobalt content (up to 0.5 and 1.0 wt %) in n%Co(*6*)-ZSM-5(17) favored progressive increase in its catalytic efficiency to give 55 and 64 % oxygen yields, respectively. When the cobalt content reached 2 wt %, the oxygen yield decreased down to 57 %. Thus, the maximal catalyst selectivity to water oxidation was observed when the Co content was no more than 1.0 wt %.

It is though that the inefficiency of catalysts with low cobalt content (0.1 wt %) results from the formation of isolated Co^{2+} ions in cation-exchange positions of the zeolite. They reside preferably in the zeolite channels that make them hardly accessible for $Ru(bpy)_3^{3+}$, and the low efficiency is characteristics of the one-electron transfer from $Ru(bpy)_3^{3+}$ to the isolated Co^{2+} ions. Even though the formation of α-$Co(OH)_2$-like clusters and Co_3O_4-like nanoparticles is detected in UV-Vis DR spectra of 2%Co(*6*)-ZSM-5(17) before and after calcination, respectively, they all are localized in the zeolite mesopores that results in a small decrease in the catalyst efficiency. This catalyst is inferior to 1%Co(*6*)-ZSM-5(17) in efficiency of oxygen evolution from water. The formed Co_3O_4-like clusters degrade upon acidifying of the reaction medium during the reaction, probably, because these clusters are weakly bound with the mesopore surface, as TPR-H_2 data showed (Table 2). The textural characteristics of the 2%Co(*6*)-ZSM-5(17) catalyst indicates on localization of Co_3O_4-like clusters on the surface of the mesopores, in particular the increase in outer sphere of the crystallites and the volume of the mesopores (Table 1) compared to 1%Co(*6*)-ZSM-5(17) and pure zeolite.

The studies of catalytic properties of a series of 1%Co(*α*)-ZSM-5(17) catalysts with identical contents of cobalt supported at varying the NH_4OH concentration revealed that the catalyst efficiency to water decomposition depends on the NH_4OH/Co^{2+} ratio. The maximal yields of oxygen (63–64 %) were observed at α ranging from 3 to 10. From UV-Vis DR and TPR-H_2 data, the active components of these catalysts comprise predominantly Co_3O_4-like clusters and oxocomplexes of Co^{2+}. The lowest oxygen yield (50 %) was observed over the 1%Co(*0*)-ZSM-5(17) catalyst (Table 4, No. 3) prepared similarly to the impregnated 1%Co(*0*)-ZSM-5(17)-IWI catalyst and bearing the active component of similar composition. It is reasonable to suppose that the active cobalt states are formed during polycondensation in the zeolite channels through transformation of isolated and associated aquacomplexes of $Co^{2+}{}_{Oh}$

and Co^{2+}_{Td} to [α-Co^{2+}(Co^{3+})$(OH)_x$]-like clusters and hydroxocomplexes of Co^{2+}. As α increases up to 15, 20 and 30, the catalytic efficiency of oxygen evolution decreases. The oxygen yields over the said catalysts were 60, 58 and 54 %, respectively. A possible reason is the decrease of [α-Co^{2+}(Co^{3+})$(OH)_x$]-like clusters in size and an increase in the proportion of ammonia complexes $[Co(NH_3)_n]^{2+}$ in the course of polycondensation.

Another important parameter of the catalyst preparation affecting the catalytic efficiency is the temperature of sample calcination. Table 5 shows oxygen yields over 1%Co(*3*)-ZSM-5(17) and 1%Co(*6*)-ZSM-5(17) dried at 298 K (Nos. 11 and 12). Comparison of the catalyst efficiency of the samples calcined at different temperatures reveals that the calcination temperature equal to 298 and 723 K had practically no influence on the catalytic properties of 1%Co(*3*)-ZSM-5(17). The oxygen yields were 63 and 64 %, respectively. However, the oxygen yields over 1%Co(*6*)-ZSM-5(17) decreased (from 67 to 64 %) upon thermal treatment of the catalyst. Apparently, the transformation of α-$Co(OH)_2$-like clusters to oxide-like clusters with the structure close to Co_3O_4 resulted in lowering the activity.

The data on the influence of parameters of preparation of n%Co(*α*)-Z(s) catalysts on the composition of the active component and activity to water oxidation lead to conclude that the factors determining the catalytic efficiency are both state of Co^{n+} cations and the size of the formed structures/complexes, as well as textural, microstructural and acid properties of the zeolite. However, the textural and microstructural features do not always promote catalytic properties of the n%Co(*α*)-Z(s) system. The optimal composition was characteristic of the 1%Co(*6*)-ZSM-5(17) catalyst. Apparently, its functional groups on the zeolite surface localized on comparatively small external surface of the crystallites bear responsibility for adsorption of $Ru(bpy)_3^{3+}$, while Co_3O_4-like clusters and nanoparticles and oxocomplexes of Co^{2+} localized in the zeolite channels close to the surface are involved in electron and proton transfer.

The influence of the conditions of water oxidation by $Ru(bpy)_3^{3+}$ on the oxygen yield

The most effective catalyst 1%Co(*6*)-ZSM-5(17) prepared by polycondensation was used as an example for studying the influence of pH (7.0; 9.2; 10.0), buffer nature (0.06 M borate and phosphate buffers) and catalyst concentration (10^{-4}–10^{-3} M expressed as the quantity of the active components) on the yield of oxygen (Fig. 5). The

curves of oxygen yield *vs* catalyst concentration pass through maxima that indicate occurrence of processes (V) and (VI) at low and high catalyst concentrations, respectively. We observed the similar behavior with colloidal Co, Fe, Mn- hydroxides stabilized with starch [65]. However, in the case of colloid catalysts, the dependence of the oxygen yields on the concentration of the active component was significantly lower – even tenfold deviation from the optimum catalyst concentration did not significantly change the oxygen yields in contrast with zeolite supported catalysts. Nevertheless, we assume that the observed similarities indicate identical mechanism of the process in both cases. The suggested mechanism discussed in details elsewhere [**Ошибка! Закладка не определена.**~~2~~, **Ошибка! Закладка не определена.**~~12~~]. With the catalyst containing 1.1×10^{-3} M of cobalt, the maximal oxygen yields were 56, 73 and 78 % at pH 8.0, 9.2 and 10.0, respectively. These data are comparable to the maximal oxygen yields observed in the presence of polyoxometallate complex $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ (64% at pH 8) [66], colloidal starch stabilized cobalt hydroxide (54, 73, 82% and pH 7.9, 9.2 and 11.0, respectively) [12] but inferior to the yields over Co(II) hydroxide stabilized on silica nanoparticles (88–100% at pH 7) [59]. Emphasize that we observed the maximal yields at the active components concentrations higher by two orders of magnitude that those reported in cited literature. This is an evidence of the participation of a minor part cobalt particles (which are close to the surface) due to steric hindrance for the oxidant to enter the zeolite channels. Hence, the application of fine crystalline zeolites such as ZSM-5 with the large surface area, and mesoporous and hierarchical zeolites ZSM-5 as supports for the water oxidation catalysts seems more promising.

An increase in pH of the reaction medium leads expectedly to an increase in the oxygen yield because reaction (IV) of water decomposition is pH-dependent. Inhibiting of the oxygen evolution in the phosphate buffer can be accounted for by the formation of insoluble cobalt phosphates that are catalytically inactive to water oxidation. To check this assumption, we conducted the reaction in the presence of the Co-catalyst at pH 0.8 in the borate and phosphate buffers to reveal that the oxygen yield was no more than 13 % in the phosphate buffer but 56 % in the borate buffer (Fig. 5).

The catalyst was tested during five successive cycles under the following conditions: pH 10.0, $[Ru(bpy)_3^{3+}] = 5\times10^{-4}$ M, $[Co] = 8.13\times10^{-4}$ (Fig. 6a). The oxygen yields decreased slightly in every next cycle (64, 63, 61, 60, 60 %) that was caused by the catalyst mechanical losses during its filtering and washing. For example, the catalyst samples weighed initially 120 mg but 102 mg after the fifth cycle. It is important that

complex $Ru(bpy)_3^{2+}$ is strongly sorbed of the surface of 1%Co(*6*)-ZSM-5(17) that is seen from changes in the catalyst color to light orange, the complex being not washed away with water. To understand the influence of adsorbed $Ru(bpy)_3^{2+}$ on the catalytic efficiency we tested the same amounts of weighed catalyst samples, both freshly prepared and after reaction with $Ru(bpy)_3^{3+}$. We conducted two reaction cycles with 120 mg of 1%Co(6)-ZSM-5(17) (O_2 yield was 64 %) and merged two portions of the catalyst after filtering and drying. Then we tested once again 120 mg of catalyst with absorbed Ru-complex collected after the reaction (O_2 yield was 63 %). After washing and drying procedure, the weight of the catalyst decreased to 118 mg; therefore we added the catalyst with adsorbed Ru-complex again to reach 120 mg. We repeated this procedure four times (Fig. 6b) and did not observe any decrease in the O_2 yields. Thus, we can conclude that adsorbed $Ru(bpy)_3^{2+}$ complexes on the catalyst surface reduces only slightly the O_2 yield only in first cycle that can be accounted for by the competitive adsorption of Ru $(bpy)_3^{3+}$ (see reaction VII) and Ru $(bpy)_3^{2+}$ (IX) on the same catalyst sites [**Ошибка! Закладка не определена.**~~2~~]:

$$\cdots Co^{III}\text{–}OH + Ru(bpy)_3^{2+} \rightleftarrows \cdots Co^{III}\text{–}O^{-} \cdots Ru(bpy)_{3,\,ads}^{2+} + H^{+} \qquad \text{(IX)},$$

These facts demonstrate the high stability of the catalysts with respect to the reaction medium and the possibility of its long application for the photocatalytic reaction when the oxidant is generated directly in the reaction medium under the action of light.

4. Conclusions

Oxo/hydroxo complexes of cobalt (II, III) and nanosize Co_3O_4 particles stabilized in zeolite channels were demonstrated to be effective catalysts for water oxidation by one electron oxidant $Ru(bpy)_3^{3+}$. The studies of the formation of electron state of cobalt in the zeolite-based catalysts under varied conditions (zeolite structure and silica ratio, procedure for cobalt supporting, cobalt loading, NH_4OH/Co^{2+} ratio, calcination temperature) revealed that polynuclear α-$Co(OH)_2$-like clusters and complexes stabilized in zeolite channels are most active to catalytic oxidation of water in the presence of $Ru(bpy)_3^{2+}$. The transformation of these species to Co_3O_4-like clusters/nanoparticles and oxocomplexes of Co^{2+}, respectively, during thermal treatment causes some decrease in the catalyst efficiency. The growth of Co_3O_4-like clusters/nanoparticles in size leads to the further decrease in the system efficiency. The minimal activity is characteristic of the catalysts comprising predominantly isolated Co^{2+}_{Oh} ions that indicates a kind of at least polynuclear structure of the catalytically active center Co_nO_x, where $n > 2$.

Among the prepared catalysts, 1%Co-ZSM-5(17) prepared by polycondensation at NH_4OH/Co^{2+} ratio equal to 6 was the most effective. In a weak-alkaline medium (pH 8.0, 9.2, 10.0) the catalyst provided the yield of oxygen as high as 56, 73 and 78 % of the stoichiometric quantity, respectively. This catalyst was demonstrated in consecutive cycle experiments to be very robust water oxidation catalyst. This makes it promising for photocatalytic oxidation and decomposition of water under the action of light.

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