ISSN 0036-0244, Russian Journal of Physical Chemistry A, 2011, Vol. 85, No. 7, pp. 1155–1161. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © A.V. Mekhaev, A.V. Pestov, L.S. Molochnikov, E.G. Kovaleva, M.G. Pervova, Yu.G. Yaltuk, I.A. Grigor'ev, I.A. Kirilyuk, 2011, published in Zhurnal Fizicheskoi Khimii, 2011, Vol. 85, No. 7, pp. 1261–1267.

STRUCTURE OF MATTER
AND QUANTUM CHEMISTRY

Structure and Characteristics of Chitosan Cobalt-Containing Hybrid Systems, the Catalysts of Olefine Oxidation

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Received June 7, 2010

Abstract—Cobalt-containing hybrid organo–inorganic materials based on the chitosan–SiO_2, chitosan–Al_2O_3, and chitosan–cellulose systems were obtained. The surface structure and processes that occur during the formation of metal-containing materials, the catalytic properties of which were studied in the oxidation reactions of alkene, were investigated by EPR spectroscopy using a stable pH-sensitive nitroxyl radical, 4-dimethylamino-2-ethyl-5,5-dimethyl-2-(pyridin-4-yl)-2,5-dihydro-1H-imidazole-1-oxyl, as the adsorbed probe molecules.

Keywords: chitosan cobalt-containing hybrid systems, catalysis, olefine oxidation, probe molecules.

DOI: 10.1134/S0036024411070211

INTRODUCTION

The use of hybrid organo–inorganic materials as supports is a new area in the development of new metal-containing catalytic materials. It allows us to obtain supports with specific surfaces that are capable of retaining the metallic component of a catalytic system more strongly. Chitosan, poly-D-β-glucosamine, is a commercially available amino polymer that is a perfect complexing agent, due to the strong donor properties of both the amino and hydroxyl groups [1]. Chitosan is thus widely used in obtaining various catalytic materials, including those containing Au^0 that are used in the hydroamination of alkenes [2]; Pd^0, used for the reduction of ketones [3]; the Pd^0–Ni^0 bimetallic system, used for carbonylation [4]; Os(VIII), used for hydroxylation [5]; Co^{2+}, used for hydration [6]; and Cu^{2+}, used for the oxidation of catecholamines [7]. Metal-containing hybrid organo–inorganic materials can also be used as antibacterial composites [8], as sorbents of proteins [9], and as pervaporation membranes [10]. This work is devoted to investigating the surface of hybrid catalytic support (SiO_2, Al_2O_3, cellulose)–chitosan–Co^{2+} systems by means of EPR spectroscopy, and to assesing their catalytic properties in the reaction of alkene oxidation.

EXPERIMENTAL SECTION

Materials and Instruments

We used microcrystalline cellulose (MCC) with an ash content of 0.16% and a humidity of 1.1% produced by JSC Polyex; Basic aluminum oxide; BS-50 silicon oxide; and chitosan produced by JSC Sonat (Moscow), for which the degree of deacetylation (DD) as determined by ^1H NMR spectroscopy was 0.84, the molecular weight as determined by viscosimetry was 250 kDa [11], and the ash content was 0.19%. The hybrid chitosan–support (SiO_2, Al_2O_3, cellulose) systems were obtained by depositing chitosan on the support surface. To measure pH near the surface of the samples, we used an aqueous solution of stable pH-sensitive nitroxyl radical (NR), 4-dimethylamino-2-ethyl-5,5-dimethyl-2-(pyridin-4-yl)-2,5-dihydro-1H-imidazole-1-oxyl [12], with a concentration of 10^{-4} mol/l. The EPR spectra of the nitroxyl radical solutions were registered using an ADANI PS-110X EPR spectrometer (Belarus) in the 3 cm wavelength range at room temperature and under optimum conditions of microwave power and amplitude of the magnetic field modulation.

Citrate-phosphate (pH 3.5–7.8) and citrate-salt (pH 1.6–4.8) buffer solutions were used to vary the pH within the NR sensitive range of 2.5–7.5; the ionic strength of the solutions, I, was maintained at 0.1 (KCl). Determination of pH in the pores and near

Table 1. Composition of cobalt-containing hybrid systems (the numerator corresponds to the obtained value; the denominator, to the calculated value. In %)

System	C	H	N	Cl	Co	Formula
MCC–chitosan–Co^{2+}(I)	43.12/43.12	6.15/6.04	0.59/0.40	1.30/1.28	1.38/1.33	$10C_6H_{10}O_5 \cdot 0.5C_6H_{11}NO_4 \cdot Co_{0.4}(OH)_{0.17}Cl_{0.63}$
Al_2O_3–chitosan–Co^{2+}(II)	3.64/3.82	0.79/0.58	0.47/0.74	2.69/2.63	2.18/2.19	$16Al_2O_3 \cdot C_6H_{11}NO_4 \cdot 0.7CoCl_2$
SiO_2–chitosan–Co^{2+} (III)	4.02/4.26	0.89/0.65	0.58/0.82	2.03/2.02	3.07/3.07	$24SiO_2 \cdot C_6H_{11}NO_4 \cdot Co_{0.88}Cl_{0.96}$

the sample surface was performed by means of spin pH-probes, following the method of multiple batches: 0.05 g of sample was kept in 5 ml of buffer aqueous solution containing nitroxyl radicals for two days (established experimentally). The solution was then decanted, and pH was determined using a Mettler Toledo (Switzerland) ionometer and a glass electrode; the surface moisture was removed from the sediment by blotting it with filter paper or by centrifugation. Measurements of the EPR spectra of the samples containing nitroxyl radicals were performed in unsealed quartz ampoules.

CHN analysis was performed using an automatic analyzer developed by PerkinElmer, Inc. The surface area of the samples was determined by nitrogen adsorption in accordance with the BET method using a TriStar 3000 V.6.03A instrument. The instrument error was 0.1 m^2/g. The elemental compositions of the hybrid system surfaces were determined using an analytical setup based on a VEGA II LMH scanning electron microscope and an INCA ENERGY energy dispersive microanalysis system.

Synthesis of Cobalt-Containing Chitosan–Support Systems

A mixture containing 0.24 g of $CoCl_2 \cdot 6H_2O$, 2 g of chitosan–support hybrid system and 20 ml of ethanol was stirred under reflux for 24 h. The obtained sediment was filtered off, rinsed with ethanol (15 ml × 3 times) and dried at room temperature until the weight became constant. The data are shown in Table 1.

Investigating the Catalytic Properties of Cobalt-Containing Hybrid Systems

We added 2 ml of water, 0.32 ml of octen-1 (2 mmol), and 0.2 g of catalyst to 10 ml of ethanol. The reaction mixture was kept under constant stirring at 75°C for 24 h. The catalyst was filtered out, the filtrate was extracted by methylene chloride, and the extract was analyzed by gas–liquid chromatography (GLC). This experiment was repeated for the same quantities of reagents, but acetonitrile or triglyme were used instead of ethanol. A 1 M solution of HCl was used for the reaction in the aqueous ethanol at various pH values; the amount added was determined by measuring the pH of an aqueous solution containing the same contents of the components.

Chromatographic measurements were performed using a GS-17A (Shimadzu, Japan) gas–liquid chromatograph with a flame ionization detector. The peaks were identified by relying on standard specimens. Our chromatography–mass spectrometric study was performed on a Fisons MD-800 chromatography–mass spectrometer (ionization by electron impact, 70 eV; capillary column, 30 m × 0.25 mm; HP-5 stationary phase).

RESULTS AND DISCUSSION

The presence on the support surface of a polymer that is capable of acquiring metal ions of high coordination numbers is needed to fix these ions more firmly on metal-containing composites. This role was played by chitosan on the surfaces of the inorganic (SiO_2, Al_2O_3) and organic (MCC) supports. Cobalt(II) ions were sorbed from an aqueous ethanol solution (Fig. 1). The composition of the catalysts was characterized by elemental analysis. According to the data, the sorption capacity of the hybrid systems relative to cobalt(II) ions is different and declines in the following order: $SiO_2 > Al_2O_3 >$ MCC. We must note that in this case, there is a difference between the mechanisms of binding ions for different supports, since their surfaces have the same coating influencing the process.

As follows from the data on the elemental analysis, chitosan plays the role of a complexing agent; in this case, all of the amino groups are involved in the coordination by cobalt ions (ratio, Co : NH_2 = 1 : 1–1.5). In the case of the Al_2O_3–chitosan system, some of the amino groups do not participate in the complexation, but the Co : Cl ratio corresponds to the composition of the initial salt that provides the coordination mechanism for binding cobalt ions (Fig. 2). In the case of the SiO_2–chitosan system, the Co : Cl ratio is ~1. The need to obey the law of electroneutrality for the obtained composites requires assuming that the support, in addition to being a weak acid, also plays a coordinating role with respect to cobalt ions, which accords with the covalent mechanism of binding

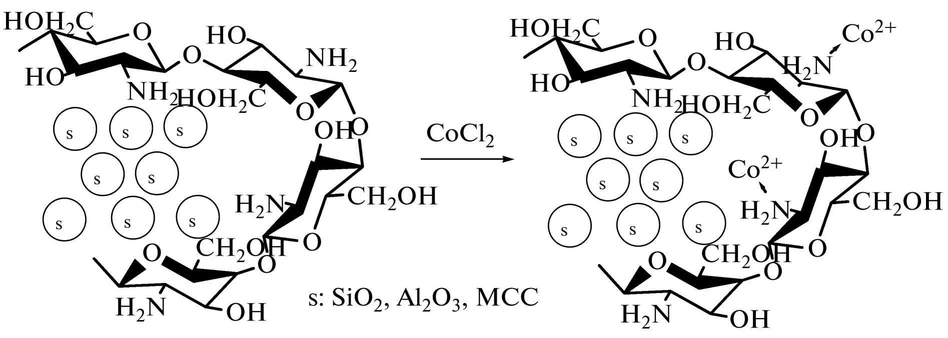


Fig. 1. Scheme for obtaining cobalt-containing hybrid systems (where s is the support).

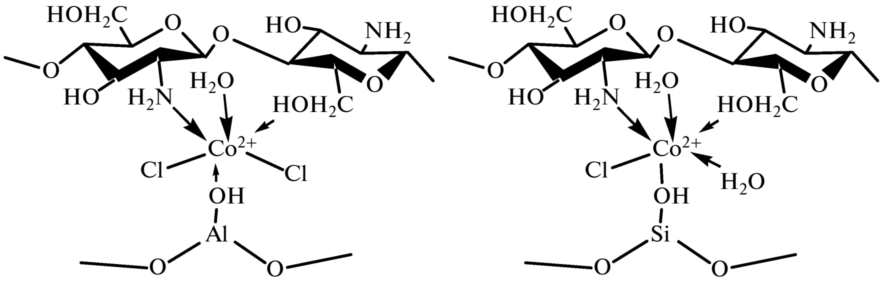


Fig. 2. Scheme for the mechanism of binding cobalt by hybrid systems.

cobalt ions (Fig. 2). In the case of the MCC–chitosan system, metal ions are sorbed in the form of a basic salt, and hydroxyl groups on the surface provide weaker coordination binding than Al_2O_3.

The elemental composition of the surface shows that chitosan does not cover it completely and some part of the functional groups remains on the support surface in free form. The more complex structure of the composite surface was characterized by investigating its acid–base properties via EPR spectroscopy of the nitroxyl radicals (NR) used as pH probes. The NR titration curves on the surface of the cobalt-containing system are shown in Figs. 3–5. The shift in these curves relative to the calibration curve left or right allows us to determine whether the surface has a positive or negative charge, respectively [13, 14].

The technique for introducing cobalt(II) ions into the hybrid materials from the ethanol solutions could lead to the formation of sediments of basic cobalt chloride or chloride–alcoxide micelles on the surface of these materials. In the case of the MCC–chitosan (Fig. 3) and Al_2O_3–chitosan (Fig. 4) systems, the titration curves of the cobalt-containing materials at pH > 5 are shifted slightly to the left relative to the titration curves of the initial samples. Consequently, the occurrence of basic cobalt chloride on the surface of these materials does not lead to a change in the surface charge, but changes its value slightly. This is due to the effective neutralization of a positive charge of cobalt ions by negative chloride and hydroxide ions. In order to confirm our hypothesis, we present the published data on studying the sorption of Co^{2+} ions from aqueous solutions and on the nature of the interaction between the metal center and amino groups of chitosan. According to [15], maximum adsorption starts to decrease with increasing pH due to the formation of

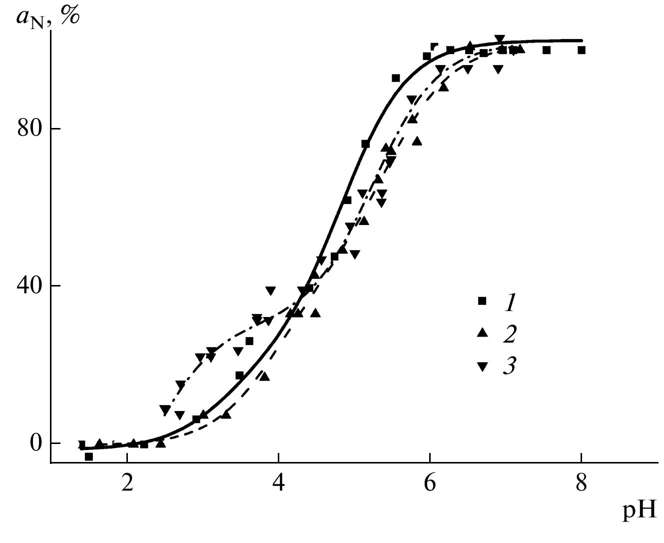


Fig. 3. Dependence of the change in the a_N parameter on the pH of the solution: *1* corresponds to the calibration curve; *2*, to the titration of the MCC–chitosan system; *3*, to the titration of the MCC–chitosan–Co^{2+} system.

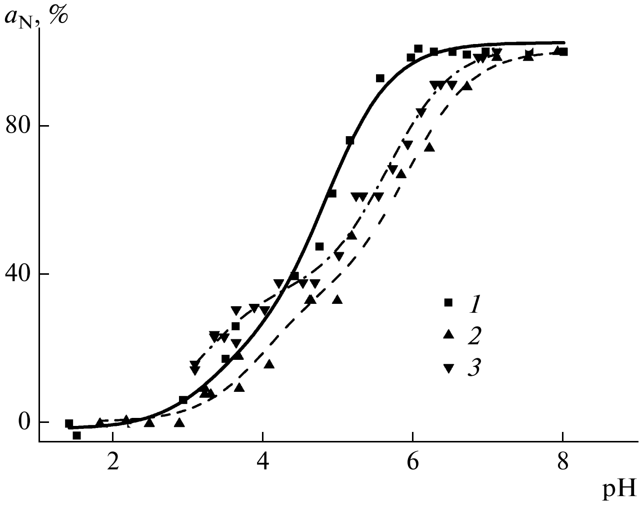


Fig. 4. Dependence of the change in the a_N parameter on the pH of the solution: *1* corresponds to the calibration curve; *2* corresponds to the titration of the Al_2O_3—chitosan system; *3*, to the titration of the Al_2O_3—chitosan—Co^{2+} system.

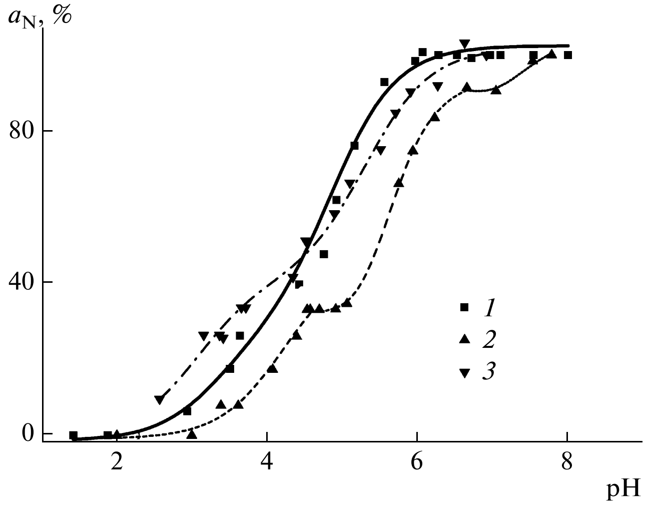


Fig. 5. Dependence of the change in the a_N parameter on the pH of the solution: *1* corresponds to the calibration curve; *2* corresponds to the titration of the SiO_2—chitosan system; *3*, to the titration of the SiO_2—chitosan—Co^{2+} system.

cobalt hydroxocomplexes. The maximum sorption of cobalt ions by chitosan found at pH 6–8 in [16] is in good agreement with the data from [15] and is determined by the formation of $Co(OH)_2$ phase or poorly soluble basic salts. No chemical interaction with amino groups of chitosan occurs in this case [17].

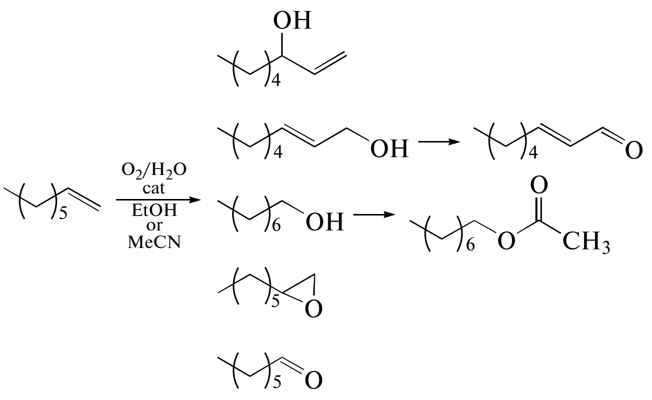
The SiO_2—chitosan system behaves differently. Even at the highest pH values, the titration curve of the sample modified with cobalt (Fig. 5) was appreciably shifted to the left relative to the NR calibration curve of the initial sample, although it remains to the right of the calibration curve. Accordingly, the formation of the chloride hydroxyl cobalt micelles immediately leads to a considerable reduction in the negative surface charge of the SiO_2—chitosan system. The different behavior of the titration curve for system III is most likely associated with the initially lower content of Cl^- ions in the cobalt micelles (Co : Cl = 1 : 1), i.e., to its higher content of OH^- ions. Acid sites on the SiO_2 surface (silanol groups) also likely interact with the basic cobalt chloride particles precipitating on the surface, thereby replacing the Cl^- ions. In both cases, the titration curve must shift left due to the neutralization of the negative surface charge. In investigating the samples in the aqueous medium at high pH values, the transformation of systems I–III thus occurs; hydration of the surface, followed by hydrolysis leading to the formation of colloidal particles based on chlorohydroxo complexes of cobalt(II), is observed.

These micelles of cobalt(II)chloro-hydroxocomplexes begin to dissolve at pH ≤ 5 for all investigated systems I–III. The dependence of sorption of cobalt ions on pH [15] shows that the maximum adsorption starts to decline at pH < 5, and Co^{2+} ions in the solution are in the form of aqua complexes [17]. The latter are sorbed by the chitosan primary amino groups, thereby charging the surface positively; in this case, the titration curves of systems I–III (Figs. 3–5) are shifted left relative to the corresponding curves for the initial samples and to the calibration curve. A further reduction in pH leads to the neutralization of OH^- groups, and no further changes in pH near the particle surface are observed upon a change in external pH. This indicates the presence of a horizontal section (step) on the titration curve. The value of the horizontal section is lower for system III than for systems I and II, since some of the OH^- groups are replaced by residues of silicic acid. At high pH values, Co^{2+} ions initially cause a substantial decrease in the negative surface charge for the case of system III; their transformation into the form coordinated by the chitosan NH_2 groups thus influences the surface charge to a lesser degree upon declining pH. Our results indicate the participation of chitosan amino groups in the complexation with Co^{2+} ions. During the interaction of the hybrid materials with the cobalt-containing solution, at least a part of glucosamine rings are consequently turned outward and are capable of becoming ligands.

Our data thus completely describe the structure of the surface of cobalt-containing hybrid systems, including features of the structure related to the support used and the pH of the medium. This allows us to investigate the influence of different factors upon using synthesized hybrid systems as heterogenic catalysts in the transformation reaction of terminal alkenes by the example of octen-1.

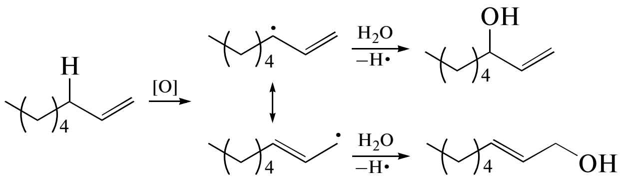
Catalytic Properties of Hybrid Systems

The reactions occurred in aqueous ethanol without the creation of an inert atmosphere in the presence of cobalt-containing hybrid systems, thereby providing data on a mixture of different functional derivatives during the oxidation of olefin; these products were identified by gas–liquid chromatographic and mass-spectrometric analysis.

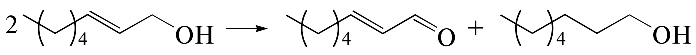


The ratio between the reaction products in dependence on the catalyst used is shown in Table 2. The system based on MCC has the most activity in the oxidation of octen-1, while the Al_2O_3-based system is less active by a factor of 100. The ratio between the reaction products is almost the same for all cobalt-containing systems, indicating that the mechanism of the process is defined only by cobalt. Additional study of the catalytic activity of hybrid systems containing no metal showed there was no conversion of octen-1. As was shown earlier, the chemical surroundings of a metal ion depend on the hybrid system, which is why the catalysts have different activities. It should thus be noted that the chemical surroundings of the metal are least favorable for the oxidation of olefins only in the case of Al_2O_3–chitosan, where the metal ion is sorbed in the form of $CoCl_2$.

As we can see from Table 2, the main products are alcohols. Products of further oxidation are also observed, indicating the presence of successive reactions catalyzed by cobalt. The structure of the obtained compounds most likely indicates a radical mechanism for the oxidation reaction of octen-1. Oxidation of the double bond leads to the production of heptanal and hexyloxirane, while the allylic oxidation of octen-1 causes the formation of 1-octen-3-ol and 2-octen-1-ol:



Octen-2-al, in turn, can be a product of the further oxidation of 2-octen-1-ol, and octanol-1 appears due to the disproportionation of 2-octen-1-ol.



In addition, *n*-octyl acetate is found in the reaction medium, indicating the participation of the solvent in the successive reactions:

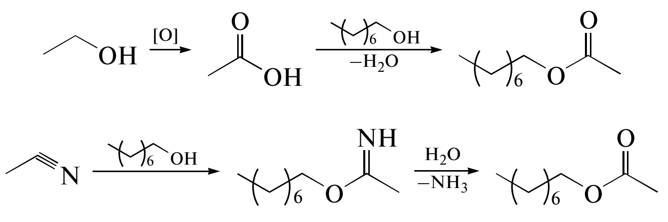


Table 2. Results from the transformation of octene-1 into ethanol for systems I–III

Parameter	I	II	III		
s_{sp}, m^2/g	3.2	96.4	28.6		
pH	6.1	6.1	6.1	3.7	2.9
η	96	27	52	18	8
η_{sp}	30	0.3	1.8	0.6	0.3
Products, wt %					
heptanal	3.4	4.5	4.7	0.0	0.0
1-octen-3-ol	32.5	31.7	30.0	44.0	44.0
hexyloxirane	2.9	1.4	4.8	0.0	0.0
2-octenal	14.9	20.8	17.5	31.0	31.0
2-octen-1-ol + octanol-1	46.3	34.8	38.1	25.0	25.0
octylacetate	0.0	6.8	4.9	0.0	0.0

Note: η is the conversion of octene-1, %; η_{sp} is the specific conversion of octene-1, %/m^2; and pH of the reaction corresponds to the pH of the aqueous solution.

Table 3. Results from the transformation of octene-1 into acetonitrile for systems I–III

Parameter	I	II	III
s_{sp}, m^2/g	3.2	96.4	28.6
η	69	67	90
η_{sp}	21.5	0.7	3.1
Products, wt %			
heptanal-1	5.1	5.5	3.8
1-octen-3-ol	29.2	24.8	26.2
hexyloxirane	9.1	7.4	6.9
2-octenal	27.7	31.4	26.8
2-octen-1-ol + octanol-1	24.1	25.4	31.4
octyl acetate	4.8	5.6	4.9

Note: η is the conversion of octene-1, %; η_{sp} is the specific conversion of octene-1, %/m^2; and pH of the reaction corresponds to the pH of the aqueous solution.

Note that, in the case of system I, no formation of ester is observed. This could be due to the basic form of the cobalt and the absence of a Lewis etherification catalyst; Al_2O_3 and SiO_2 correspond to this type of catalyst.

We estimated the influence of pH on the structure and ratio of the products obtained via oxidation of octen-1 using the example of system III, which exhibits medium catalytic activity. It should be noted that direct measurement of the activity of hydrogen ions in organic solvent–water mixtures is impossible using an ionometer. The estimated pH values for these solutions were recalculated with allowance for the dilution factor. The effect of the media on the activity coefficient of hydrogen atoms was negligible [18] and was therefore not taken into account. It was found that at an aqua pH value of 6.3–6.5, the pH value of the aqueous ethanol solution would be expected to be 7.1–7.3. To study the influence of cobalt transformation on the catalytic activity upon a change in pH value, we selected pH values that correspond to the 3.4 < pH > 5.6 step on the titration curve (Fig. 3) to the range before and after the step. According to the data in Table 2, a decline in the pH value reduces the conversion of octen-1; this occurs due to a reduction in the catalytic activity of system III to the value that corresponds to system II. This confirms our previous conclusions on dissolving micelles of chloro-hydroxo cobalt(II) complexes and the formation of Co^{2+} ions in the form of $CoCl_2$, as this salt is responsible for the least activity in the oxidation reaction of octen-1. Additional analysis of the systems after the reaction showed that the content of cobalt falls by 13% at pH 6.1 and by 88% at pH 3.7. A decrease in the activity, however, leads to a certain increase in the selectivity of the process of alcohol production.

No changes in the structure of the reaction products are observed with declining polarity of the medium by replacing ethanol for acetonitrile during the oxidation of octen-1 (Table 3). The sequence of the system activities remains the same, I > III > II, and the main products of oxidation are still alcohols. A further drop in the polarity of the solvent via the use of triglyme leads to the absence of any conversion in octen-1.

CONCLUSIONS

The investigated cobalt-containing hybrid systems demonstrated the possibility of catalyzing the oxidation of terminal alkenes by the example of octen-1; the main product of this process is a mixture of alcohols. The MCC-based system is the one most active and most likely to provide the best coordination surroundings of the metal center. The practical value of the catalytic properties established in this work is the possibility of transforming the products of oil cracking (terminal olefins) into primary alcohols using these catalytic systems with the subsequent reduction of a mixture of incomplete oxidation products. Our estimate of the conversion of alkenes into saturated alcohols by the example of octen-1 indicates a total yield of ~60%.

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