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Heteronuclear hydroxo complexes of Al(III), REM and some 3d-metals

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Abstract

In a number of cases the activity of hydroxide and oxide catalysts received from coprecipitation method is not equal to the total activity of mixed hydroxides or oxides. Assumption that heteronuclear hydroxides could be formed by coprecipitation of metal hydroxides was stated. In the case of rare-earth and two charged 3d-metal ions it was shown that heteronuclear hydroxo complexes can be formed by interaction of these metal ions at initial stages of their cohydrolysis under certain conditions. In some cases these complexes are destroyed with time. Such heteronuclear hydroxo complexes are new compounds and can show high catalytic activity owing to features of their structure. Highly effective oxide catalysts can be produced by thermal decomposition on the basis of these heteronuclear hydroxides. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Heteronuclear hydroxo complexes; Heteronuclear hydroxides

1. Introduction

Catalysts produced on the basis of coprecipitated aluminum, 3d-metals and rare-earth metals (REM) are widely used in the various chemical processes, including petrochemical industry [1]. It has been well known that in a number of cases such catalysts display catalytic activity much higher than the mechanical mix of appropriate hydroxides or oxides. The structure of various hydroxides produced by coprecipitation methods was investigated in detail [2]. The assumptions have been repeatedly expressed that chemical interaction which occurred with coprecipitation between the components, is displayed in properties of hydroxides and appropriate oxides [3]. Research has shown that there is not much information about initial stages of coprecipitation process of metals ions in water solutions. Therefore we decided to study the initial stages of cohydrolysis of metal ions in water solutions, to show how chemical interaction between hydrolyzed metal ions occurs. Thus form a basis from which it is possible to predict the formation of heteronuclear hydroxo complexes. This complex being a new chemical compound can have new catalytic properties in a number of cases.

2. Experimental

The systems were investigated by a dialysis method [4]. Solutions were prepared as follows: 1 M solution of $NaNO_3$, necessary for maintenance of constant ionic force was added to a 0.1 M solution of metal nitrate in 0.1 M HNO_3. Then a 0.2 M NaOH with

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specific ratio of metal ion to quantity was added to the solution. The ratio [OH]/[M] is designated negative at partial neutralization of free acid. The pH-value of systems was measured in a balance condition after dialysis.

The process of polynuclear hydroxo complexation is related to changes of pH-value with time [5]. Therefore the pH=f(τ) dependence was carried out in investigated systems for the study of the hydrolysis of metal ions with the concentration of metal ions being 1×10^{-2} mol/l. Solutions were prepared as for dialysis method. The pH-value was measured in time after addition of NaOH solution.

Potentiometric titration by the 0.2 M NaOH solution was conducted on pH-meter manufacturer I-130 with glass electrode. Accuracy of measurement was made ±0.02 pH units. A chlorosilver electrode manufacturer EVL-1M3 was used as an electrode of comparison. Mainly precipitation of nitrates from aqueous solutions was performed. The salts $Al(NO_3)_3.9H_2O$, $Cu(NO_3)_2.3H_2O$, $Co(NO_3)_2.6H_2O$, $Cr(NO_3)_3.9H_2O$ etc. were used for research of the hydroxide receptions.

The solutions with 0.01 M of metal ions were prepared from these salts for study of formation of heteronuclear complexes in solution, and the solutions with 1 M concentration were prepared for production of precipitates. In this case 1 M NaOH solution was added. The precipitation was conducted with constant mixing and pH control of solution. Investigations of the solid phase by heat treatment were carried out by thermal analysis on the thermograph manufacturer Paulik, Paulik, Erdey, with speed of heating 5°C/min from 20°C up to 1000°C.

3. Results and discussion

It was shown earlier that heteronuclear hydroxo complexes of aluminum(III) and chrome(III) would be formed in solution [6]. The kinetic analysis was applied to study the interactions of metal ions in aqueous solutions at initial stages of hydrolysis (Fig. 1). Comparing the kinetic curves in Fig. 1 shows that pH-value in the Al^{3+}–Cr^{3+}–NO_3^-–H_2O system is less than that in individual solutions of Al(III) and Cr(III). It testifies that the hydrolysis process is deeper when heteronuclear hydroxo complex Al(III)–Cr(III) is formed. According to this experiment and other data received by the oxidizing potential method [7] it was shown that intermediate molecules with hydrogen bonds would be formed in solution [5]. These intermediates are destroyed with time forming heteronuclear hydroxo complexes:

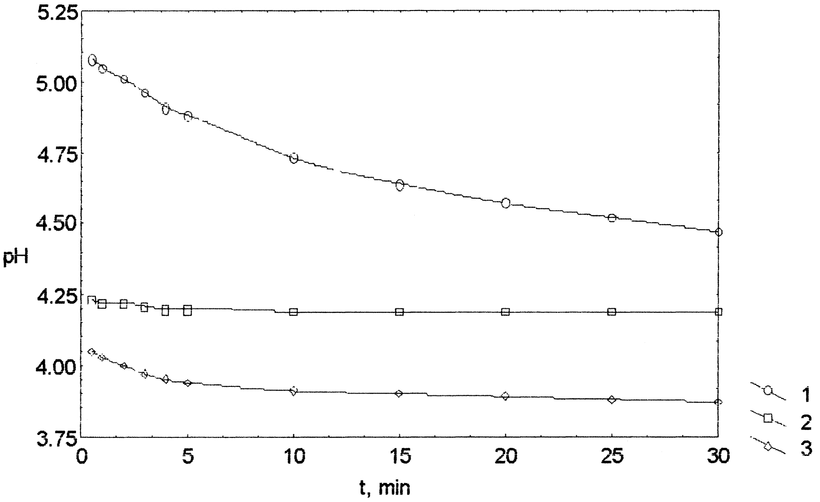
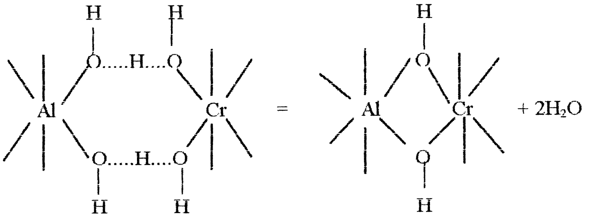


Fig. 1. pH-value depending on time in the water system of Cr(III) – (1), Al(III) – (2), and in Al(III)–Cr(III)–NO_3^-–H_2O system – (3). ([OH]/[M]=1).



The rate of destruction of heteronuclear hydroxo complexes is more than that of the homopolynuclear hydroxo complexes because of the non-symmetry of the heteronuclear structure. However the ratio of the rate constants of direct and reverse reactions of heteronuclear hydroxo complex formation in this case is some times more than it is at formation of homopolynuclear hydroxo complexes. This results in the existence of the heteronuclear complexes in solutions, and explains new properties of the hydroxides produced.

The study of Al(III)–iron(III) and Al(III)–scandium(III) systems has also allowed us to make the conclusion that the interaction of mononuclear hydroxo complexes of metal ions results in formation of intermediates with hydrogen bonds in solution [8]. This intermediate can be destroyed or transformed into heteronuclear hydroxo complexes with various ratios of rate constants of the direct and reverse reaction. This ratio depends on such properties of cooperating metal ions as acidity–alkalinity and stability–liability.

The Al(III)–Cu(II)–NO_3^-–H_2O system was investigated by potentiometry and dialysis methods. It is possible to conclude the method of precipitation and to establish a nature of formed compounds by comparing pH titration curves. Titration curves in individual components of the Al(III), Cu(II) and in double component system, Al(III)–Cu(II), are shown in Fig. 2. Nitric acid was titrated up to pH=3.8 ([OH]/[M]=0) at first, then formation of the polynuclear forms of the aluminum and $Al(OH)_3$ precipitate begins. It finishes at pH=6.7 (curve 1) at the titration of 0.01 M solution of $Al(NO_3)_3$ with the 0.2 M NaOH solution. The curve of potentiometric titration of copper(II) with the same concentration has two jumps at pH=4.2 and pH=8.3. The beginning of $[CuOH]_n$ formation is observed at pH=4.4. The termination of this process occurs at pH=7.8 (curve 2). The point of equivalence corresponds to formation of individual hydroxo complex Al(III)–Cu(II), and is observed in titration curve with the titration of mixed Al(III) and Cu(II) salts taken in the ratio of 1:1 (curve 3). There are two points of equivalence that correspond to precipitation of hydroxo complex Al(III)–Cu(II), then comes the hydroxide of a Cu(II) on titration curve if the ions of Cu(II) are in excess in system. The aluminum hydroxide and then hydroxo complex Al(III)–Cu(II) are precipitated in the beginning when Al(III) ions are in excess in system.

After that the Al(III)–NO_3^-–H_2O, Cu(III)–NO_3^-–H_2O, Al(III)–Cu(II)–NO_3^-–H_2O systems were investigated by dialysis. It is possible to find out the

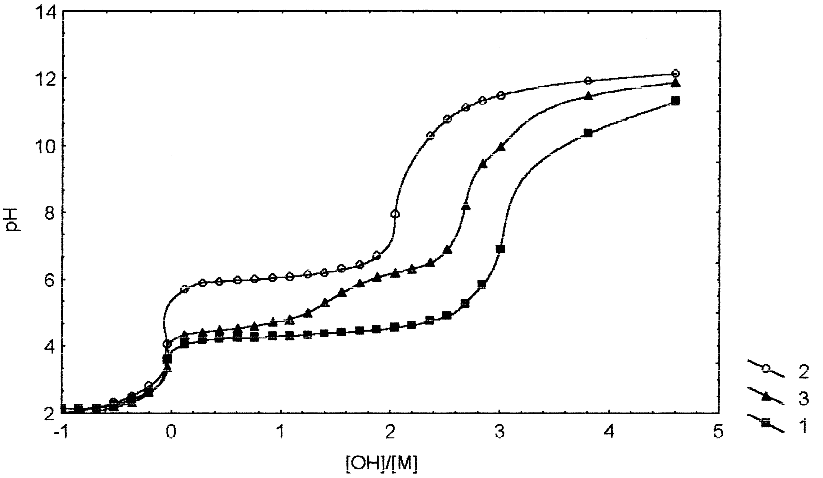


Fig. 2. Integrated curves of potentiometic titration: Al(III) – (1); Cu(II) – (2); Al(III)–Cu(II) – (3).

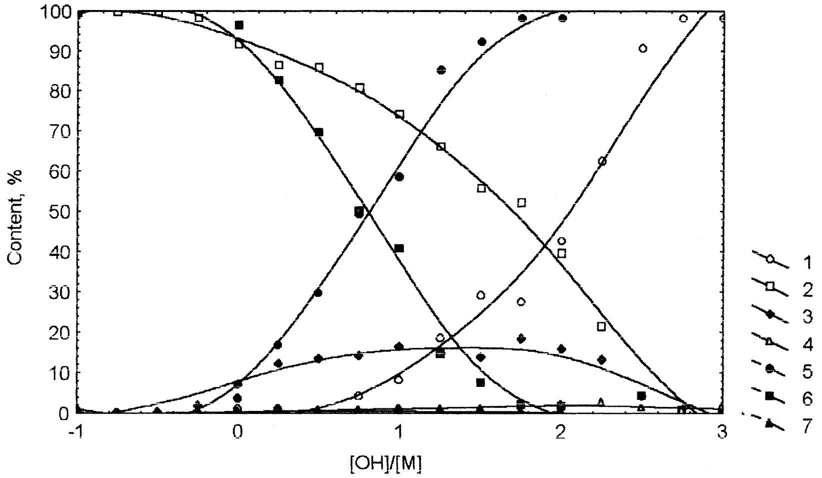


Fig. 3. Distribution of the various forms of the Al(III) and Cu(II) in individual solutions depending on [OH]/[M]: polynuclear forms of Al(III) – (1); Al^{3+} – (2); $AlOH^{2+}$ – (3); $Al(OH)^{2+}$ – (4); polynuclear forms of Cu(II) - (5); Cu^{2+} – (6); $Cu(OH)^{+}$ – (7).

quantity of the polynuclear and mononuclear forms in solution using this method. Quantities of each form were dependent on [OH]/[M] and equilibrium pH significance were produced using constants of the mononuclear forms hydrolysis. The diagram of distribution of the various forms of the Al(III) and Cu(II) in individual solutions was constructed (Fig. 3). The distribution diagram in a double system Al(III)–Cu(II) is shown in Fig. 4.

The following scheme of the cohydrolysis process is based on the analysis of the distribution diagrams produced and the kinetic curves. Monohydroxoform of the Al(III) is formed in pH range 3.0–4.2. When content of this form reaches about 15%, the formation of dimers begins. The Al(III) dihydroxoforms occurs in the pH range 4.2–6.5. These forms interact with Cu(II) aquaions forming heteronuclear hydroxo complexes:

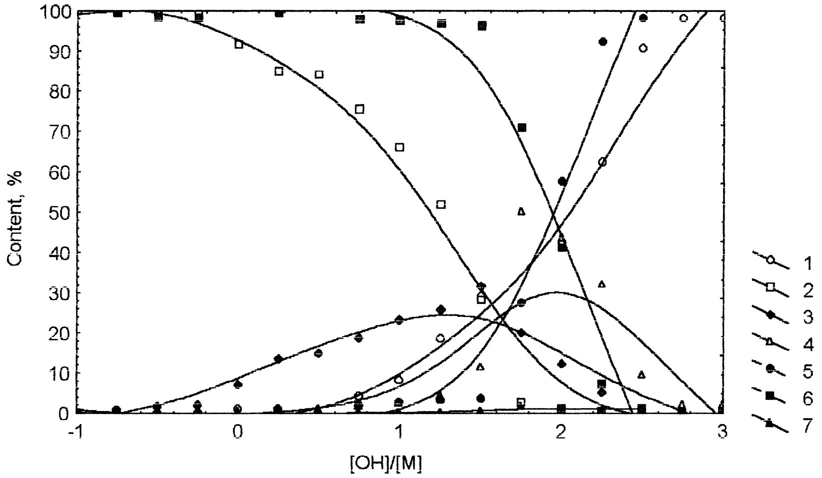


Fig. 4. Distribution of the various forms of the Al(III) and Cu(II) in a Al(III)–Cu(II)–NO_3^{-}–H_2O system depending on [OH]/[M]: polynuclear forms of aluminum (III) – (1); Al^{3+} – (2); $AlOH^{2+}$ – (3); $Al(OH)_2^{+}$ – (4); polynuclear forms of Cu(II) – (5); Cu^{2+} – (6); $Cu(OH)^{+}$ – (7).

$$[Al(OH)_2(H_2O)_4]^+ + [Cu(H_2O)_6]^{2+} \rightarrow [(H_2O)_4Al(OH)_2Cu(H_2O)_4]^{3+} + 2H_2O$$

Hydrolysis of the Al(III) polynuclear forms with formation of terminal OH-groups occurs simultaneously. The growth of the chain continues, up to formation of colloidal particles.

A solid phase produced in pH range 4.5–9.8 was filtrated, washed and dried at temperature 30–40°C to constant weight. This phase was analyzed; its structure is $Al_2Cu_3O_6.10H_2O$. Endoeffects reflecting step character of dehydration are observed on thermal curves (Fig. 5). The loss of weight corresponds to 4 and 6 M H_2O in the temperature range of 40–170°C and

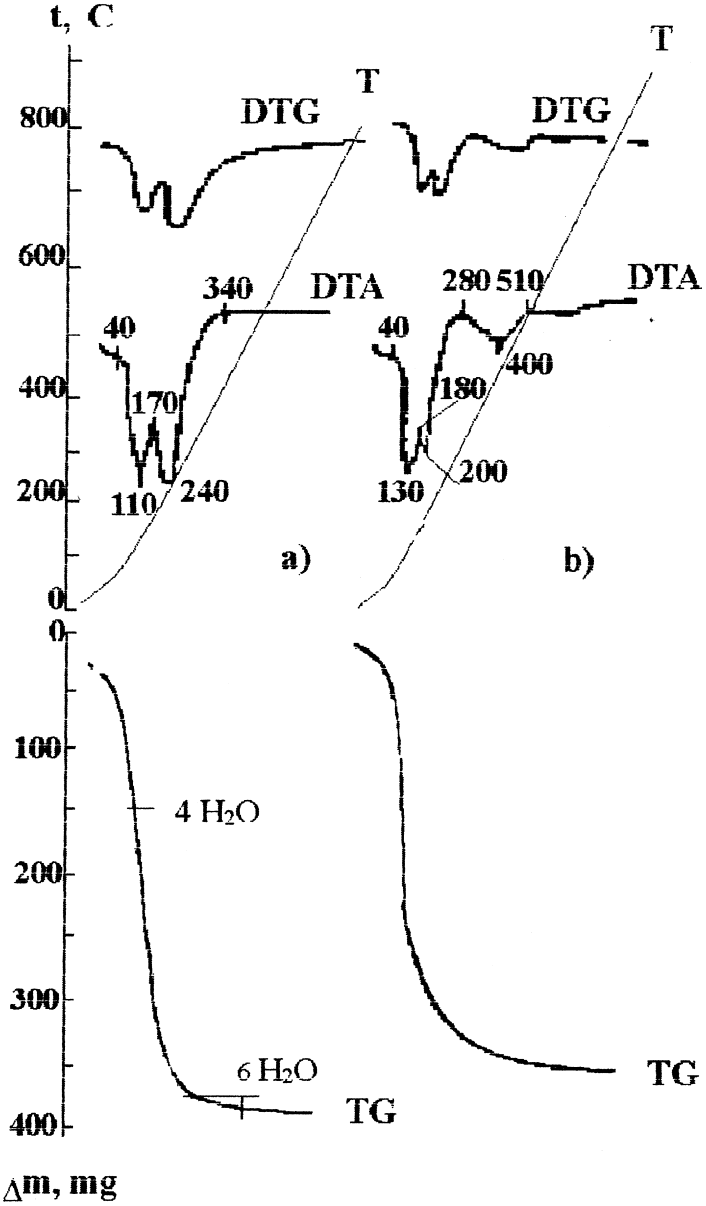


Fig. 5. Thermograms of solid phases: (a) hydroxo complex Al(III)–Cu(II); (b) the mixture of Al(III) and Cu(III) hydroxides.

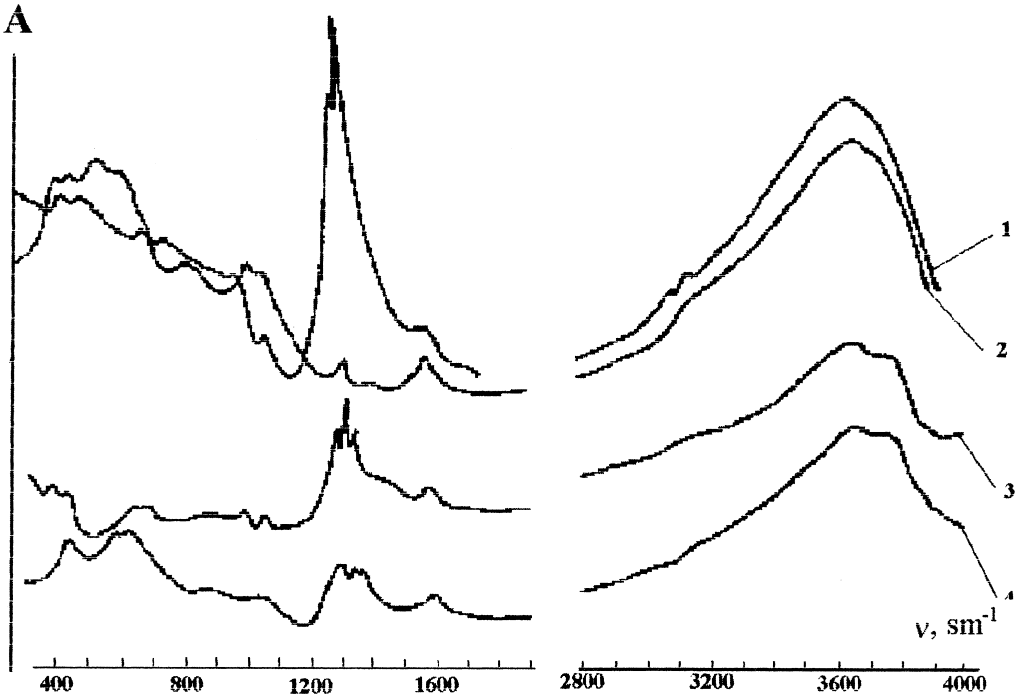


Fig. 6. IV spectrum of solid phases: (1) – the synthesized compound $Al_2Cu_3O_6.10H_2O$; (2) – Al(III); (3) – Cu(II) hydroxide; (4) – the mixture of Al(III) and Cu(II) hydroxides.

170–340°C respectively. Three intensive endoeffects (130°C, 200°C and 400°C) are observed due to the thermal decomposition of mix of the aluminum and copper hydroxides produced at pH=9.8. Loss of 1 mol of water occurs up to temperature 180°C. Dehydration of the copper hydroxide occurs at 180–200°C. Dehydration of the aluminum hydroxide occurs at 280–510°C. Such distinction in thermal analysis curves testifies that the individual compound $Al_2Cu_3O_6.10H_2O$ was formed in Al(III)–Cu(II)–NO_3^-–H_2O system at pH=9.8 and room temperature. The IR-spectra of absorption (Fig. 6) specify presence of a hydroxo complex from molecular water (3455 and 1620 sm^{-1} band), OH-groups (1385, 1355 sm^{-1} band). The bands of absorption 1050, 776, 509, 690 sm^{-1} may belong to fluctuations of bridge connection. The X-ray phase analysis has shown that the main phase after heat treatment at 1000°C is spinel $CuAl_2O_3$. Similarly the Al(III)–Co(II)–NO_3^-–H_2O system was investigated. It was shown on the thermal analysis curves of oxides in these systems that the existence of exo- and endoeffects indicates on the possible processes of dehydration of precipitates and their decomposition including heteronuclear complex (430–660°C). The formation of $CoAl_2O_4$ spinel is obviously occurs at the temperature of 980°C with diffraction maxima of 2.44; 2.86; 2.43 as well as CoO_4, distribution of ions in which can be shown as $Co_2^{+2}[Co^{+4}O_4]$.

A lot of new interesting facts were produced in the study of formation of hydroxide precipitates in systems containing the ions of Fe(III), Al(III) and a number of REM. Research shows that the process of complexation in the Fe(III)–REM, Al(III)–REM systems at concentrations of metal ions less than 0.01 moles/l consists of two stages: (a) formation of heteropolynuclear hydroxo complexes in a solution; (b) complexation in a solid phase, the precipitation of which is observed at pH >7. With reduction of concentration of metal ions the pH value of precipitates formation displaces in more alkalic area.

The polynuclear Fe(III)–REM, Al(III)–REM hydroxo complexes produced at pH appropriate to the first equivalent point or end of jump on titration curve are unstable in time. It is connected with phenomena that the electrostatic field of Al(III) and

Fe(III) which is greater than in ions of relative rare-earth metals. Therefore when hydroxides of the Al(III) and Fe(III) are precipitated, there are ions of considered rare-earth metals in solutions. The formation of heteronuclear Al(III)–Sm(III), Fe(III)–Sm(III) hydroxo complexes was determined in equilibrium conditions with concentration of metal ions of 1×10^{-2} mol/l using the dialysis method on the basis of potentiometric data. Conditions for the production of hardly soluble individual hydroxo compounds – heteronuclear hydroxides – are determined. A structure of produced compounds is determined relative to the to chemical formulas $AlSm(OH)_6.2H_2O$, $FeSm(OH)_6.2H_2O$. The recommendations for study of formation of heteronuclear hydroxides in mixed solutions in equilibrium conditions are given. If to compare points of probable existence of heteronuclear particles in investigated systems, it is possible to note that in bimolecular solutions with the Al(III) they are close and make on the average 4.50–5.50, and in bimolecular solutions with an Fe(III) are 3.00–4.50.

In the study of interaction of a number of two-charge ions of 3d-metals it was shown that heteronuclear hydroxo complexes can be formed with the interaction of these metal ions at initial stages of cohydrolysis process under certain conditions. These complexes are destroyed with time. In particular it was shown by a number of methods that heteronuclear Cu(II)–nickel(II) hydroxides had been formed in water solution containing ions of Cu(II) and Ni(II) at initial moment of joint hydrolysis. These unstable complexes are destroyed after a few hours owing to non-symmetry of their structure and the mix of homopolynuclear hydroxides was formed [9]. Hence it is necessary to insolate the hydroxide precipitate during the first minutes after its production to subject it further heat treatment for the production of oxide and hydroxide catalysts on basis of the specified hydrolysed metals. The specific critical time of the precipitate separation can be determined by the help of kinetic experiments for each particular system. It is possible to adjust a structure of the precipitate and hence its catalytic property by increasing or reducing the settling time of the precipitate.

4. Conclusions

In the case of Al^{3+}–Cr^{3+}–NO_3^-–H_2O, Al(III)–Cu(II)–NO_3^-–H_2O and Al^{3+}–Sc^{3+}–NO_3^-–H_2O systems it was shown that heteronuclear hydroxo complexes would be formed in solutions. It was shown that such properties as acidity–alkalinity and stability–liability had influenced the result of cohydrolysis process of metal ions in water solutions. In particular the combination of hydrolyzed metal ion having more acidic properties with metal ion having greater liability of its complexes as in case of Al(III)–Cr(III) system results in formation of steady heteronuclear hydroxo complexes in a wide interval of pH-value. These hydroxo complexes pass from solution into the structure of solid phase at the formation of a precipitate and then can be used for reception of new hydroxide and oxide catalysts.

Acknowledgements

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