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Zirconium and aluminum oxyhydroxides particles formation during sol–gel process

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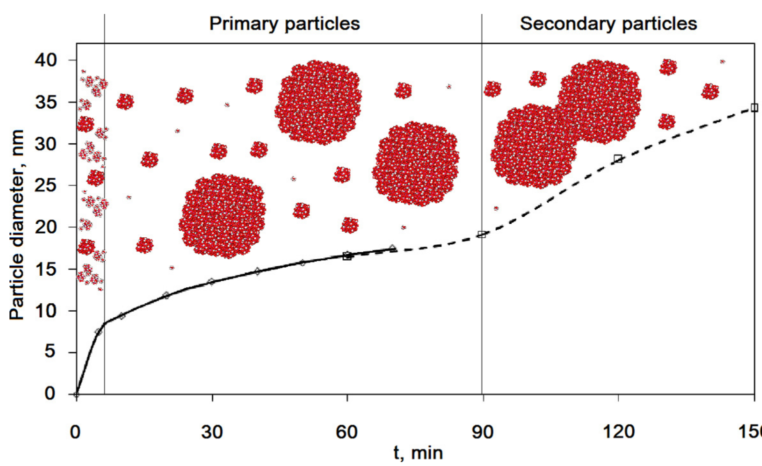
HIGHLIGHTS

- Zirconium and aluminum oxyhydroxides 25–44 nm particles were obtained during sol–gel synthesis.
- Growth rate of primary particles in mixed Zr–Al solution is twice higher than in pure.
- Reduction of carbamide concentration from M:carbamide = 1:3 to 1:1.75 leads to increasing of particles growth rate by 1.7 times.
- Nanoparticles form highly porous structures due to aggregation of 50–60 nm particles in 1–10 μm clusters.

GRAPHICAL ABSTRACT



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ABSTRACT

The hydrolysis kinetics of aluminum and zirconium oxychloride salts in the presence of carbamide was investigated. The determined rate constant varies in the range of 0.0027–0.0038 min^{-1} and is independent on initial mixture composition. The effect of initial components molar ratio and concentration on formation of sol particles was established. As a result, zirconium and aluminum oxyhydroxide 25–44 nm particles were obtained during sol–gel synthesis. It was found that particle size strongly depends on synthesis conditions. In addition, synthesis conditions determine porosity of final sample and allow to obtain highly porous material at certain conditions. The formation of porous oxyhydroxides structure via particles aggregation with formation of aggregates 60 nm ÷ 1–10 μm was confirmed. The specific surface area of samples varies from 85 to 540 m^2/g depending on composition and synthesis conditions The carbamide effect on zirconium oxyhydroxide gelation process was studied.

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1. Introduction

Preparation and application of nanostructured materials recently attracts a great attention due to their unique properties The usage of polyvalent metals oxyhydroxides as precursors for

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nanomaterials synthesis (Zr, Ti, V, Fe, etc.) is very well-known, as they possess high thermal and mechanical stability, resistant ability to oxidants, organic solvents and radioactive emissions and enhanced sorption properties [1]. Prepared nanostructured materials are used in a variety of applications: catalysts, coatings, ceramics, sensors and adsorbents [2].

Zirconium oxyhydroxide (ZOH) is one of the most effective adsorbents in a water treatment technology. It has significant absorption capacity toward polyvalent anions, such as phosphates [3], borates, carbonates, chromates [4], arsenates and arsenites, molybdates, heavy metal cations [5], as lead [6,7], copper, nickel [8] and strontium [9]. Sorption properties can be explained by the presence of hydroxyl-hydrate layer, surface positive charge and its amphoteric properties. Mentioned properties favorably distinguishes ZOH from other adsorption materials [10]. At the same time, the aluminum oxyhydroxide (AOH) has large amounts of surface active sites and a high surface area that makes it more active than other metal oxides [11].

The study reported here is an investigation of kinetic peculiarities of zirconium oxyhydroxide (ZOH) and aluminum oxyhydroxide (AOH) sol formation during zirconium and aluminum chloride solutions hydrolysis in the presence of carbamide via sol–gel route. Previous studies described strong advantages of mentioned sol–gel method [12–14]. Besides it also allows to control particles size and their morphology inside sol at early gelation stages, and, as a result, to obtain highly homogeneous multicomponent mixture used as a basis for final product preparation (ceramics, sorbents, coatings, etc.).

Mentioned process is based on hydrolysis reaction of carbamide in aqueous zirconium and aluminum solutions according to Eqs. (1) and (2):

$$ZrOCl_2 + CO(NH_2)_2 + 3H_2O = ZrO(OH)_2 + CO_2 + 2NH_4Cl \quad (1)$$

$$AlCl_3 + 3CO(NH_2)_2 + 9H_2O = Al(OH)_3 + 3CO_2 + 6NH_4Cl \quad (2)$$

During hydrolysis, carbamide decomposes and generates molecules CO_2 and NH_4OH, the last one is acting as hydrolysis agent [25]. Urea hydrolysis in aqua solution can be summarized as Eq. (3):

$$CO(NH_2)_2 + H_2O = CO_2 + NH_4^+ + OH^- \quad (3)$$

These reactions are simplified and do not reflect directly the mechanism of sol–gel process, consisting of two stages: hydrolysis of aqua-complexes and polymerization of formed aqua-hydroxo-complexes with further olation and oxolation.

It is well-known that metal ions in aqueous solutions occurs in aqua-complexes: $[Zr(H_2O)_8]^{4+}$; $[Al(H_2O)_6]^{3+}$, which can hydrolyze under specified conditions and transfer hydrogen ion from the $M{-}OH_2$ group to water solution ((4) and (5)):

$$[Zr(H_2O)_8]^{4+} + H_2O \rightarrow [Zr(OH)(H_2O)_7]^{3+} + H_3O, \text{ etc.} \quad (4)$$

$$[Al(H_2O)_6]^{3+} + H_2O \rightarrow [Al(OH)(H_2O)_5]^{2+} + H_3O, \text{ etc.} \quad (5)$$

Complexes formed during hydrolysis and in the presence of appropriate charge and composition can polymerize via bond formation between OH groups of two metal ions (6):

$$4[Zr(OH)_2(H_2O)_6]^{2+} \rightarrow [Zr_4(OH)_8(H_2O)_{16}]^{8+} + 8H_2O \quad (6)$$

Because hydrolysis and polymerization rates mostly determine gel structure and morphology, assessment of kinetic regularities of these processes is very important and requires attention.

It is well-known, that final properties of synthetic inorganic adsorbents significantly depend on many factors, including reagents and solutions nature, colloidal and chemical properties of initial substances and intermediate sols and a way of their transformation into gel. Hydrolysis and polymerization conditions, size of formed primary particles, their charge, and ability to form aggregates play an important role during adsorbents synthesis. For example, authors [15] indicate strong correlation between coagulation time and molar ratio of initial reagents. Components variation gives an opportunity to prepare sols with different particle sizes resulting in formation of gels with different structural and mechanical properties.

Nowadays, different methods are used to study liquid nanosystems. There are spectroscopy of scattered light, acoustic spectroscopy and electro-acoustic spectroscopy [16]; ultrasonic method to measure the viscoelastic parameters based on multiple scattering from dense suspensions [17]; nucleation study with fluorescent substances, acting as microprobes into the spectrographic studies [18]; small-angle X-ray scattering [19–21], etc.

However, described techniques have a number of strong disadvantages. They are quite expensive and time consumed, which significantly reduces their applicability in laboratory conditions. Despite mentioned drawbacks and the fact that turbidity, small-angle X-ray scattering [22] and dynamic light scattering [23] require sample dilutions of optically active sol, they are successfully used for particle size measurement during nucleation process and are suitable for aggregation rate determination [24], which significantly extends area of their application.

Described state-of-art caused the aim of present research. The work was devoted to studies of kinetic and chemical regulations of ZOH and AOH particle formation during homogeneous hydrolysis of metals chlorides in the presence of carbamide. It was also important to investigate the effect of molar ratio and concentration of initial reagents on sol–gel process.

2. Experimental

2.1. Materials

Zirconium oxychloride ($ZrOCl_2{\cdot}8H_2O$) (98%, SRPE "Zirconium", Ukraine), aluminum chloride ($AlCl_3{\cdot}6H_2O$) (99%, "Reagent", Ukraine) and carbamide ($CO(NH_2)_2$) (95% "Reagent", Ukraine) were used as raw materials. Xylenol orange (95%, "Reagent", Ukraine) and n-dimethylaminobenzaldehyde (95%, "Reagent", Ukraine) were used as indicators.

2.2. Samples preparation

ZOH and AOH sols and gels were synthesized using sol–gel method by hydrolysis of aqueous solutions of zirconium oxychloride and aluminum chloride in the presence of carbamide at $T \approx 100\,^{\circ}C$ [26]. Compositions of sols are presented in Table 1.

Based on previous studies [27] metal composition of sol 4 (Zr:Al = 1:3 and M:$CO(NH_2)_2$ = 1:1.75) was selected to determine effect of initial metal concentration (C_M) on final materials properties. Total initial concentrations of metal ions are: C_M = 1 (sol 4.1), 0.75 (sol 4.2), 0.5 (sol 4.3) and 0.25 mol L^{-1} (sol 4.4).

Table 1
Composition of tested Zr/Al sols.

No. sol	Molar ratio Zr:Al	Molar ratio M:carbamide 1:3
1	1:0	
2	2:1	
3	1:1	1:1.75
4	1:3	
5	0:1	
1′	1:0	
2′	2:1	
3′	1:1	1:3
4′	1:3	
5′	0:1	

M – metal ion of Zr(IV) and Al(III).

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