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Synthesis of co-hydrolysates from metals and alkoxides

Yury M. Rodionov,[a] **Eugeny M. Slyusarenko,***[b] **Eugeny A. Chernyshev**[a] **and Valery V. Lunin**[b]

[a] *State Scientific and Research Institute of Chemistry and Technology of Organoelement Compounds, 111123 Moscow, Russian Federation. Fax: +7 095 273 1323*

[b] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119899 Moscow, Russian Federation. Fax: +7 095 939 0171*

The synthesis of co-hydrolysates from metals and alkoxides at high temperatures (120–200 °C) affords a number of scientific and practical advantages.

Glasses and ceramics obtained by the alkoxide sol-gel process possess a number of advantages (purity, lower sintering temperatures, homogeneity in multicomponent systems, *etc*.). However, such materials are expensive. This results from the high cost of the alkoxides, more complicated technology and greater quantity of organic solvents required. These problems are solved to some extent when alkoxides are synthesized from group II and III metals in the presence of alcohols with I_2 as the initiator.[1] One more problem with the alkoxide sol-gel process is in providing molecular homogeneity during co-hydrolysis of several alkoxides of different reactivity. Preliminary partial hydrolysis of the less reactive alkoxide has been proposed for solving this problem.[2,3] However, this approach has several drawbacks, such as the use of inorganic acids, the considerable duration of the process and the large volumes of organic solvents required.

We carried out the synthesis of partial co-hydrolysates from mixtures of E(OR) (E = Si, Ti, Zr; R = alkyl) and group II and III metals. The process was performed at high temperatures (120–200 °C) without initiators and with low alcohol consumption, and involved joint stages of hydrolysis and alkoxide preparation.

The preparation of mullite-forming co-hydrolysates (molar ratio Al/Si = 3) was carried out as follows: 8.1 g (0.3 mol) aluminium chips and 20.8 g (0.1 mol) tetraethyl orthosilicate (TEOS) were warmed in an N_2 atmosphere at 150 °C and 5 ml Cellosolve® was added dropwise. The activation of aluminium chips and their reaction with Cellosolve® and butanol formed during the exchange reaction between TEOS and Cellosolve® were completed in 5 min. A mixture of 7.2 g (0.4 mol) water and 45 ml Cellosolve® was added dropwise with vigorous stirring to the reaction mixture; the aluminium dissolved in 1 h. The temperature of the reaction mixture was decreased to 120 °C. The resulting transparent solution of mullite-forming co-hydrolysate was used to obtain mullite coatings and as a binder for ceramics and composites. Gel-monolites and powders were obtained by complete hydrolysis of the co-hydrolysate with excess water in the presence of HCl or NH_3 as catalysts, respectively.

The syntheses in the mixtures aluminium (chips)–magnesium (chips)–TEOS, aluminium (chips)–$Ti(OBu)_4$ and yttrium (chips)–$Zr(OBu)_4$ were also carried out by this method.

Promotion of the activation of metals is the important feature of our method. Mercury salts, I_2 and other activators are not used and do not contaminate the co-hydrolysate solution. Even inactive isopropyl alcohol activates aluminium in a few minutes. It seems that alcohols possess higher reactivity at high temperatures, and the added alkoxide reacts with an oxide coating on the metal.

It is known[4] that the degree of generation of the Al–O–Si bonds due to the addition of water to mixtures of aluminium and silicon alkoxides is insignificant because the reactivities of these alkoxides with respect to the hydrolysis of RO groups and condensation of RO and HO groups differ by several orders of magnitude. The hydrolysis rate of silicon alkoxides is determined by kinetic factors, whereas that of aluminium alkoxides is determined by water diffusion.

Our approach makes it possible to create such reaction conditions that in the first stage the concentration of TEOS is significantly higher than that of an aluminium alkoxide. This concentration factor provides favourable conditions for generating Al–O–Si bonds and attaining high homogeneity.

There are also other factors: i, the rates of condensation and hydrolysis become closer; ii, associates of alkoxides are decomposed; iii, free alcohols are absent; and iv, the rearrangement of [element]oxane bonds is facilitated.

The following elementary reactions occur in the first stage of the synthesis of mullite-forming co-hydrolysate:

$$\mathrm{Al + ROH \rightarrow Al(OR)_3 + H_2} \quad (1)$$

$$\mathrm{Al(OR)_3 + H_2O \rightarrow Al(OR)_2OH + ROH} \quad (2)$$

$$\mathrm{Si(OR)_4 + H_2O \rightarrow Si(OR)_3OH + ROH} \quad (3)$$

$$\mathrm{Al(OR)_2OH + Si(OR)_4 \rightarrow (RO)_2AlOSi(OR)_3 + ROH} \quad (4)$$

$$\mathrm{Al(OR)_3 + Si(OR)_3OH \rightarrow (RO)_2AlOSi(OR)_3 + ROH} \quad (5)$$

$$\mathrm{R = Et,\ EtOC_2H_4}$$

The hydrolysis of $Al(OR)_3$ [reaction (2)] generated in the activation stage takes place immediately after the addition of the first portion of water. Simultaneously, hydrolysis of the less reactive $Si(OR)_4$ occurs [reaction (3)] because its concentration is significantly higher then that of $Al(OR)_3$ and due to a high temperature. The $Al(OR)_2OH$ formed due to hydrolysis of $Al(OR)_3$ predominantly undergoes reaction (4). The probability of reactions between two molecules of $Al(OR)_2OH$ or between $Al(OR)_2OH$ and $Al(OR)_3$ is negligible due to concentration factors. The less reactive $Si(OR)_3OH$ reacts with $Al(OR)_3$, which is generated from Al chips and ROH formed in reactions (2)–(4).

A subsequent portion of water leads to similar reactions with formation of partial co-hydrolysates. This is a simplified reaction scheme for the first step. In the next stages the mechanism is more complicated.

The thermal analysis of the mullite-forming co-hydrolysate confirmed the high homogeneity attained by our method. An exothermic process is observed at 980 °C. This phenomenon is related to mullite formation and is considered to be the main evidence of homogeneity in co-hydrolysates.[3]

References

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