Composite materials on the base of the SiO_2 - TiO_2, TiO_2 - Al_2O_3 systems modified by macrocyclic endorreceptors

A. N. Murashkevich, O. V. Fedorova, I. M. Zharsky, O. A. Alisienok
Belarusian State Technological University, Minsk, Belarus,
Institute of Organic Synthesis A.Y. Postovsky Ural Devision of RAS, Ekaterinburg, Russia
e-mail: man@belstu.by

Composite materials based on heterocyclic endoreceptors functionalized by benzo-crown ethers, fixed on the surface or incorporated into the polymer matrix, belong to relatively new class of sorbents and catalysts that permits to resolve a number of problems in the phase transfer catalysis, organic synthesis, analytical chemistry, biology and medicine [1]. The consumption of endoreceptors can be reduced by directional change of the effective surface and other properties of the sorbent. Binary SiO_2–TiO_2, TiO_2–Al_2O_3 oxides nanoparticles. Dual Si-Ti, Ti-Al nanooxides used as macrocycle substrate are of particular interest, because they combine the positive properties of individual oxides and have certain specific characteristics, due to components interference or interaction effects [2].

Preparation of composite materials was carried out by sol-gel and co-precipitation methods using as precursors inorganic titanium, silicon and aluminum components. Introduction of dibenzo-18-crown-6, dibenzo-21-crown-7, dibenzo-24-crown-8 crown ethers was performed by two methods: 1) by stair-step sol-gel transition from dimethylformamide solution into oxide sols without side-holding components; 2) by injection into hybrid xerogels or coprecipitated powders with high specific surface area. The final step was a drying to a constant weight at 120–150°C. Method of chemical grafting of aminosubstituted dibenzo-ester as a mixture of isomers to the surface of the nanocomposites SiO_2–TiO_2 was used.

Targeted modification of the properties of composites was carried out by variation of the components ratio, processing temperatures, introduction of templates, structure modifiers and macrocyclic endoreceptors into sols of the oxides under mixing. For the first time using IR spectroscopy method it was shown that three benzo-crown-ethers, asymmetric dibenzo-21-crown-7 provided the strongest interaction with the surface of mixed SiO_2-TiO_2 nanoparticles, resulting in a distortion in the structure of the macrocycle that can affect the material sorption properties.

The results of differential-thermal analysis of the organic–mineral composite revealed that physically adsorbed water was removed at the temperatures up to 100 ^oC. The amount of this water rose with an increase in the titanium-containing component and a reduction of an amount of the crown ether. Noticeable weight loss of the samples (10–45 %) in the temperature range 100–200 °C was caused by the removal of residual solvent (DMF). It was especially typical for composites based on titanium and aluminum oxides that characterized surface properties of these composites. In the temperature range 300–500 °C crown ethers and products of their thermal destruction were removed. Common weight loss amounted to 27–40 % for SiO_2–TiO_2 composites and to 70–75 % for TiO_2–Al_2O_3 composites depending on a content of crown ethers which increased from 3 to 50% in dibenzo-18-crown-6, dibenzo-21-crown-7, dibenzo-24-crown-8 crown ethers row.

References:

1. Y.A Zolotov. JHChS D.I. Mendeleev. (1985) 30 (5): 584.
2. A.N. Murashkevich , A.S. Lavitskaya, O.A. Alisienok, I.M. Zharsky. Inorg. Mater. (2009) 45 (10): 1146