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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Thermal Stability and Catalytic Properties of the Composite Amorphous Al_2O_3–Nanocrystals ZrO_2

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Abstract—Catalytic properties in relation to the hydrogen oxidation reaction and thermal stability of materials based on the nanocomposite amorphous Al_2O_3-nanocrystalline ZrO_2 were studied.

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Composites based on the system Al_2O_3–ZrO_2 are widely used as catalyst carriers and catalysts of various processes [1-5]. At the same time when the most active non-equilibrium forms of aluminum oxide (γ- and η-Al_2O_3) are used in catalytic processes a problem of their thermal stability arises. To stabilize non-equilibrium Al_2O_3 modifications, the versatile methods [6-12] are used, namely, the co-precipitation of aluminum and zirconium hydroxides with their subsequent dehydration [6, 7], the introduction of oxides of alkaline, alkaline-earth, and rare-earth metals in the carrying agent composition (aluminum oxide) [8–10], the coating of the surface of porous granules by a coke layer [11], and the coating of the γ-Al_2O_3 surface with SiO_2 using the layer-deposition method [12, 13].

Application of nanosized particles as catalysts, as a rule, considerably raises their activity [14–16]. It is fully applicable to nanoparticles of zirconium dioxide [17–19]. At the same time the use of nanoparticles in catalysis meets certain limitations with respect to the temperature and duration of effective catalyst operation owing to the tendency of nanocrystals to sintering and coarsening [16, 20, 21].

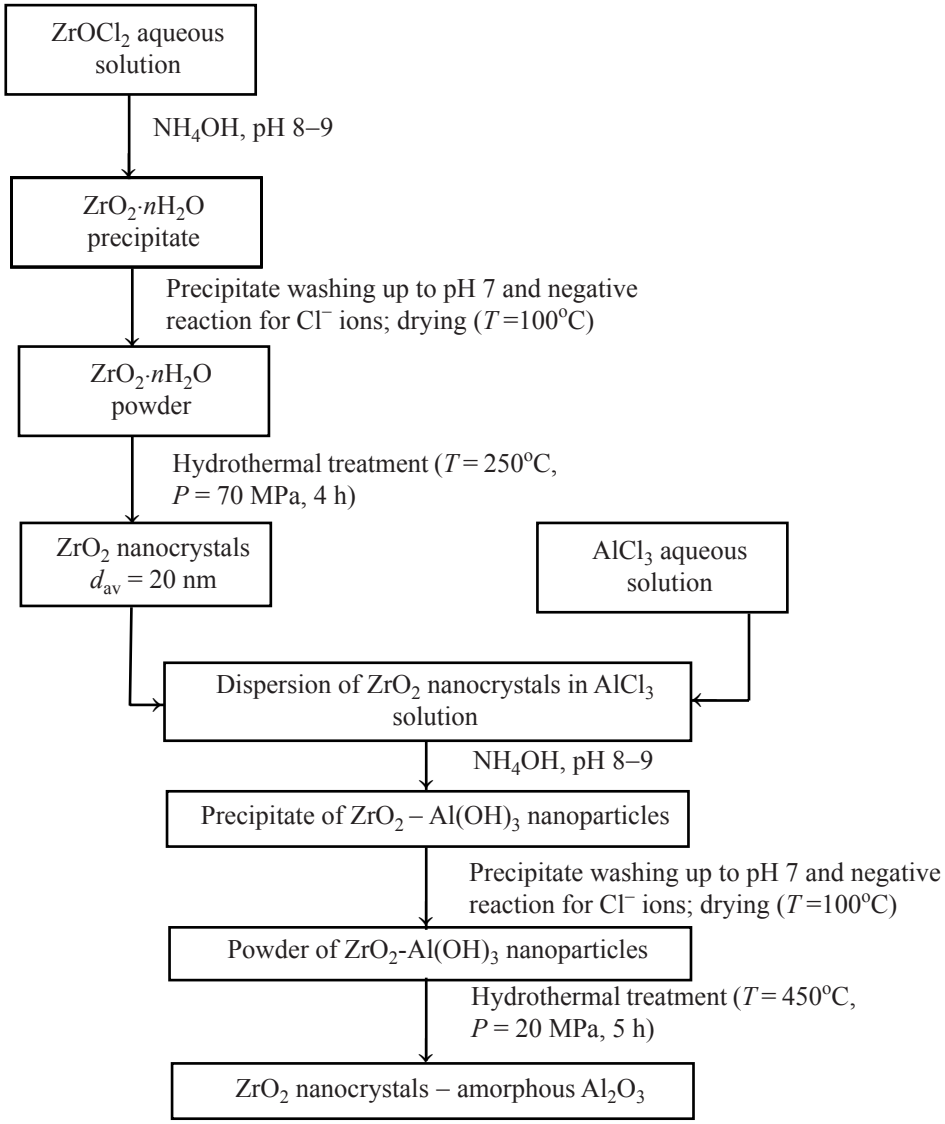
Thus, the efficiency of catalysts connected with the use of substances in structurally non-equilibrium and nanodispersed states conflicts with their resistance to degradation, especially at elevated temperatures. Therefore, a great number of works [22, 23] is devoted to the development of the catalysts capable of retaining a phase state, a microscopic structure, and especially a size of the most catalytically active nano-size components for a long time at elevated temperatures.

The preparation of a nanocomposite amorphous aluminum – nanoparticles of zirconium dioxide is described in [6, 7, 24]. As the amorphous state of aluminum oxide seems to be its most non-equilibrium solid-phase state among its all known crystalline modifications, is was of interest to study catalytic properties of this composite material, taking into consideration a high catalytic activity of non-equilibrium forms of aluminum oxide.

EXPERIMENTAL

The nanocomposite of amorphous aluminum oxide–nanocrystalline zirconium dioxide was obtained in several stages including a hydrothermal treatment (see the scheme). To compare catalytic properties, we also have prepared the basic oxide Co-Mn catalyst widely used for the hydrogen catalytic oxidation [25–26]. This catalyst was obtained by the known procedure [26]: by mixing pseudo-boehmite peptizated by acetic acid of the concentration 0.06 mol of CH_3COOH/mol of Al_2O_3 with cobalt oxide (Co_3O_4, 18 wt %) and manganese oxide (MnO_2, 12 wt %) with particle sizes of 4-6 μm followed by a thermal treatment including drying at 110°C within 6 h and a calcination at 400°C within 4 h. To study the catalytic properties, the resulting powdered materials were grained by the procedure described in [27].

Scheme of the operating sequence for the preparation of the nanocomposite amorphous Al_2O_3–nanocrystalline ZrO_2



The phase state of materials was determined by X-ray phase analysis. The X-ray diffractograms of samples were taken on a DRON-3 diffractometer ($Cu_{K\alpha}$ radiation).

The size of the nanocrystals was calculated by Sherer's formula based on the data on broadening of X-ray diffraction lines. In addition the size and the shape of nanoparticles were determined by transmission electron microscopy (an EM-125 microscope with U_{acc}=75 kV).

To characterize the catalysts, we determined their density, specific surface area, compression strength of granules, and catalytic activity in the reaction of hydrogen oxidation. The density of samples relative to water was determined by pycnometry (GOST 2211-65). The specific surface area was determined by the thermal nitrogen desorption on a "Sorbtometr" installation. The compression strength of granules was determined by the procedure described in [28] on an IPG-1 extensometer from a sample size of 20 granules. The temperature dependence of the oxidation degree of hydrogen with the initial concentration of 0.98 vol % was determined on a flowing installation in an adiabatic reactor at a volume flow rate of feeding dry gas-air mixture (a relative humidity of no more than 3%) 0.76–3.61 s^{-1} with a chromatographic analysis of the products on a "Tsvet-500" instrument. The catalyst volume was 2.3 cm^3.

The changes in the phase composition of the material and in sizes of nanocrystals were determined from the

Properties of materials based on the system Al_2O_3–ZrO_2

Composition of material	Apparent density of granulated material, g cm^{-1}	Specific surface area, m^2 g^{-1}	Material phase composition		Size of ZrO_2 nanoparticles, nm		Comression strength of granulated material, MPa	Degree of H_2 oxidation at 150°C	Efficiency $Q \times 10^5$, m^3 m^{-2} s^{-1} at 150°C
			initial	after thermal treatment	initial	after thermal treatment			
$ZrO_2(Y_2O_3$ 4 mol%)	3.05	125	t-ZrO_2	–	12.5	>100	5.2	0.54	1.98
$Al_2O_3 : ZrO_2$: 50:50	–	–	t-ZrO_2	t-ZrO_2	12	–55	–	–	–
70:30	3.40	87	t-ZrO_2	–	12	–	4.8	0.2	1.19
90:10	2.95	70	t-ZrO_2	–	12.0	–	3.3	0.11	0.93
	traces γ-AlOOH								
$A1_2O_3 : Co_3O_4 : MnO_2$ = 70 : 18 : 12	3.23	175	–	–	–	–	6.1	0.03	0.09

X-ray diffraction patterns of samples before and after thermal treatment, which was carried out at a constant heating rate of 10 deg min^{-1} up to a temperature of 1200°C.

Properties of materials under study of various composition are shown in the table. An examination of the results obtained shows that the catalysts based on nanoparticles of zirconium dioxide and on the nanocomposite amorphous aluminum oxide – nanocrystalline zirconium dioxide are several times more active than the basic oxide catalyst in the reaction of hydrogen oxidation at 150°C. Unfortunately, the maximal efficiency of the reactor with respect to oxidized hydrogen calculated per a unit catalyst surface for nanoparticles of zirconium dioxide (see the table) is leveled by its low stability at high temperatures first of all manifested as a decrease in the specific surface area due to increasing particle size with increasing temperature (Fig. 1).

An examination of the degree of hydrogen oxidation on the catalyst based on nanocrystalline zirconium dioxide as a function of the hydrogen-air mixture input (Fig. 2) shows that the process proceeds in the outer-diffusion region, which is proved by the increase in the

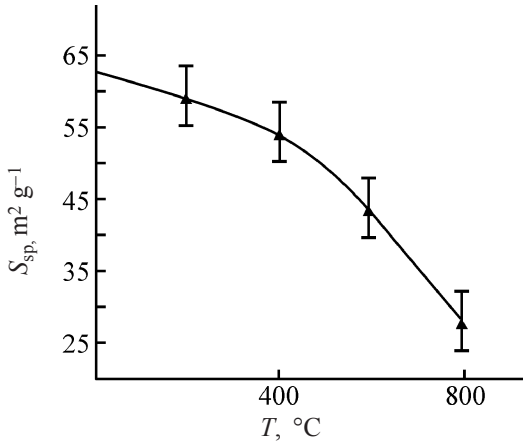


Fig. 1. Dependence of the specific surface area S_{sp} of the ZrO_2-based material on the treatment temperature T.

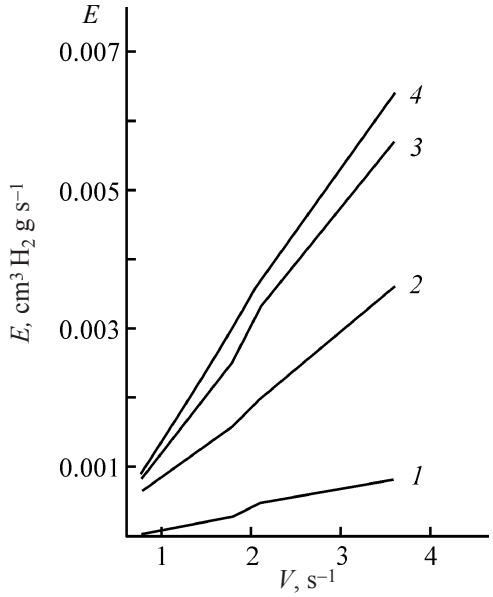


Fig. 2. Dependence of the reactor efficiency (degree of hydrogen oxidation) E on the discharge of hydrogen-air mixture V at various temperatures. T (°C): (*1*) 100, (*2*) 300, (*3*) 150, (*4*) 200.

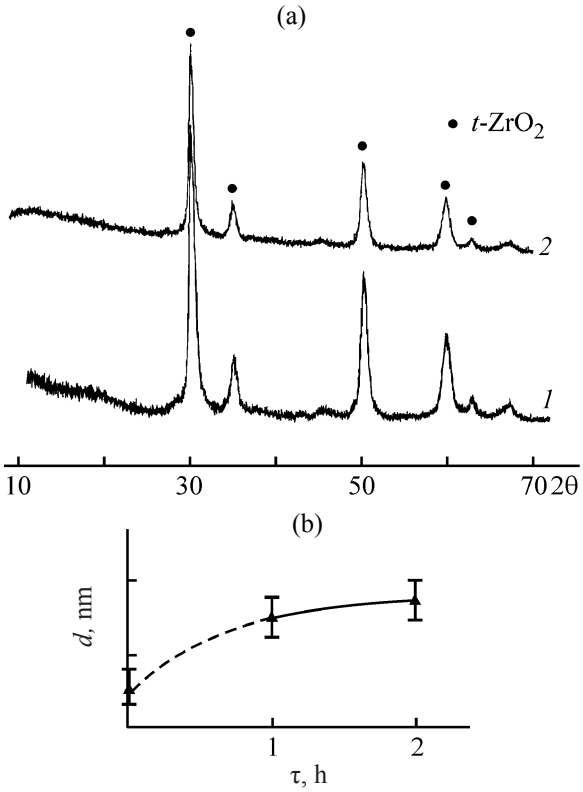


Fig. 3. (a) Diffractograms of samples of the composition ZrO_2: Al_2O_3 = 50 : 50 mol % and (b) dependence of ZrO_2 particle size d in the nanocomposite on the thermal treatment duration τ at T = 1100°C. θ is Bragg angle (deg). Sample: (*1*) initial, (*2*) after thermal treatment in air at 1100°C.

oxidation degree (reactor efficiency) with increasing the gas flow rate. It is supported by the fact that in this case an increase in the catalyst volume results in an increase in the oxidation degree. A similar dependence of the degree of hydrogen oxidation on the gas flow rate is observed also for catalysts based on the ZrO_2–Al_2O_3 nanocomposite.

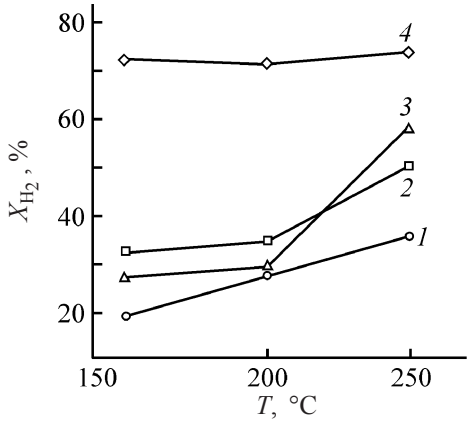


Fig. 4. Dependence of specific (referred to the catalyst with a specific surface area of 100 $m^2\ g^{-1}$) activity of the catalyst X_{H_2} on temperature T. (*1*) Industrial catalyst; ZrO_2 content (mol %): (*2*) 10, (*3*) 30, (*4*) 50.

At the same time, unlike the catalyst based on ZrO_2 nanoparticles, Al_2O_3 amorphous state and the size of ZrO_2 nanocrystals in the ZrO_2–Al_2O_3 nanocomposite are highly temperature-resistant (Fig. 3).

The study of the temperature dependence of the catalytic activity of materials in the hydrogen oxidation reaction (Fig. 4) has shown that the catalysts based on the system zirconium dioxide - aluminum oxide are low-temperature catalysts as the active hydrogen oxidation begins even since 50°C, unlike the H_2 oxidation on the basic oxide catalyst, on which the oxidation becomes noticeable only at 150°C. In this case catalysts based on ZrO_2 nanoparticles or amorphous Al_2O_3–nanocrystalline ZrO_2 nanocomposites show a higher specific activity than the basic oxide catalyst in the entire temperature range under consideration.

It is necessary to note that the considered catalysts based on the composition Al_2O_3–ZrO_2 are not optimized from the viewpoint of a microscopic structure necessary for catalysts and first of all of the porous structure, for the catalytic process, as is shown in the work, proceeds in the outer-diffusion region. The results obtained show that the optimization of the technology of the catalysts based on Al_2O_3–ZrO_2 will make it possible to raise considerably their functional characteristics on retention of a high thermal stability necessary, for example, when the materials are used in the safety system of atomic power stations [29, 30].

CONCLUSION

New thermoresistant nanocomposite based on amorphous Al_2O_3–nanocrystalline ZrO_2 were obtained. As compared with the oxide catalyst based on Al_2O_3–Co_3O_4–MnO_2 system they have a higher specific catalytic activity and a lower ignition temperature in the hydrogen oxidation reaction.

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