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NEW TECHNOLOGIES FOR DESIGN AND PROCESSING OF MATERIALS

Frame Catalysts of Al_2O_3–ZrO_2–CeO_2 System

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Abstract—Xerogels and powders of Al_2O_3–ZrO_2–CeO_2 systems with different pore structure and matrixes of ZrO_2 and Al_2O_3 are obtained. The specific surface area of xerogels with ZrO_2 matrix and Al_2O_3 matrix exceeds 200 and 90 m^2/g, respectively. After calcinations at 950°C, the powders retain nanoscale, with the size of individual particles ranging from 70 to 28 nm. The main crystalline phase in these powders is a solid solution of tetragonal zirconia. Total ethanol conversion of xerogels with ZrO_2 and Al_2O_3 matrixes has similar values. Selectivity to ethylene conversion is about 50% and does not depend on calcination temperature. For samples with an Al_2O_3 matrix, ethylene selectivity of 50% was reached after heating at 950°C. It is shown that the catalytic activity of ethanol conversion reaction is higher for samples with a more crystallized phase based on solid solution of tetragonal zirconia, namely, for samples with the ZrO_2 matrix calcined at 950°C.

Keywords: ceramics, zirconia, alumina, phase structure, ethanol, catalytic activity

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INTRODUCTION

Powders of oxide systems are very promising materials for catalysts, which is due to high chemical and structural stability, which provides resistance to high-temperature exposure of reaction products, as well as the possibility of their regeneration. Powders of aluminum, zirconium and cerium oxides are used in modern heterogeneous catalysis as catalysts for low-temperature oxidation of carbon monoxide, methanol and ethanol reforming, and hydrogenation of carbon dioxide to methane [1–8]. It is shown in [6, 7] that these oxides are most effective in the processes of obtaining dimethyl ether, a new more environmentally friendly fuel, than catalysts based on previously used calcium or zinc oxides.

The efficiency of the catalytic function of frame catalysts is related to their dispersity, since the developed catalyst surface provides a high level of contacts between the reagents. Sol-gel synthesis is one of the methods allowing one to obtain powders with high specific surface and nanoscale individual particles in complex oxide systems.

The purpose of this work is to study the effect of phase composition and dispersity of the powders synthesized in the Al_2O_3–ZrO_2–CeO_2 system with alumina and zirconia matrices on the catalytic activity in the ethanol conversion reaction.

EXPERIMENTAL TECHNIQUE AND METHODS OF STUDY

For the study, the following compositions in the system were chosen (here and further in mol %): Al_2O_3–[88% ZrO_2–12% GeO_2], respectively, containing 5 and 50% Al_2O_3.

The precursors of powders were synthesized by simultaneous precipitation of all components with 6 N ammonia solution according to the procedure described in [9, 10]. In the synthesis, 1 M solutions of salts were used: $Ce(NO_3)_3$, $ZrOCl_2$, $Al(NO_3)_3$. Gel-like precipitates (hydrogels) were dried at 180°C, and then xerogels were heat treated at temperatures of 450 and 950°C. Powders were designated by the content of Al_2O_3: 5 Al_2O_3–95 (Ce–TZP)–5 Al; 50 Al_2O_3–50 (Ce–TZP)–50 Al.

The phase composition of the samples was determined on an XRD-6000 diffractometer in CuK_α radiation ($\lambda = 1.54$ Å) in the angular interval of $2\theta = 22°$–55°. Phase identification is carried out according to the International Bank of Standards (JCPDS).

The low-temperature adsorption–desorption method—the Browner–Emmett–Teller method (BET) (adsorption-structural analyzer TriStar-3000 by Micromeritics, USA)—was used to measure the specific surface of the powders. According to the results of analysis, the dependences of the distribution

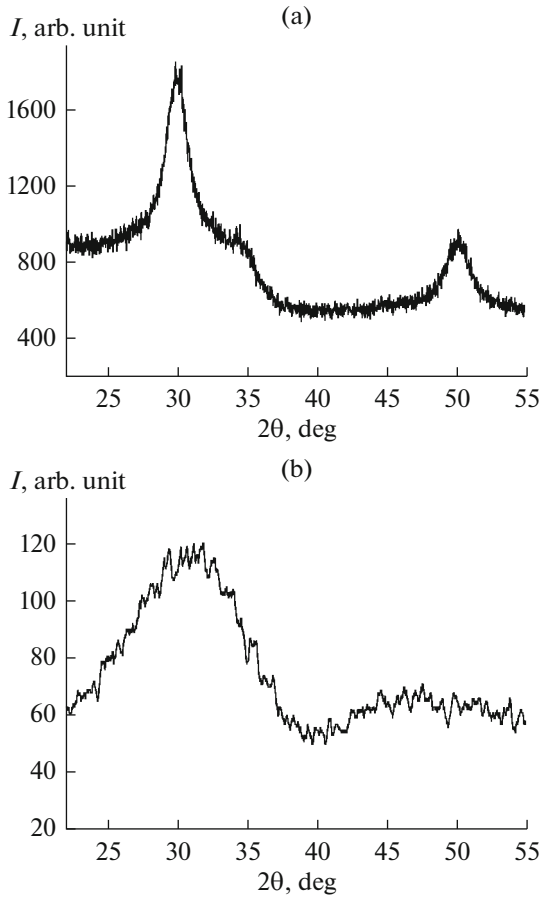

Fig. 1. XRD patterns of samples calcined at 450°C: (a) 5 Al, (b) 50 Al.

of the volume of pores on their diameter in the regions of nano- and mesopores were determined.

The average sizes (D) of individual particles were calculated by the estimated formula derived for ideal powder systems consisting of globular monodisperse particles:

$$D = \frac{6000}{S_{sp}\rho},$$

where S_{sp} is the specific surface area of the powder, m^2/g, and ρ is the density, g/m^3.

Using an Annalizette-22 laser analyzer, the distribution of agglomerates in the synthesized powders was obtained.

Visualization of powder systems was carried out by scanning electron microscopy using a Tescan Vega II scanning electron microscope.

The catalytic activity of the samples was studied in the reaction of ethanol conversion in the temperature range of 250–400°C in a Chromatec-Crystal 5000 flow-through catalytic unit with gas chromatographic analysis of the products (carrier gas—helium, ionization-flame detector (IFD)).

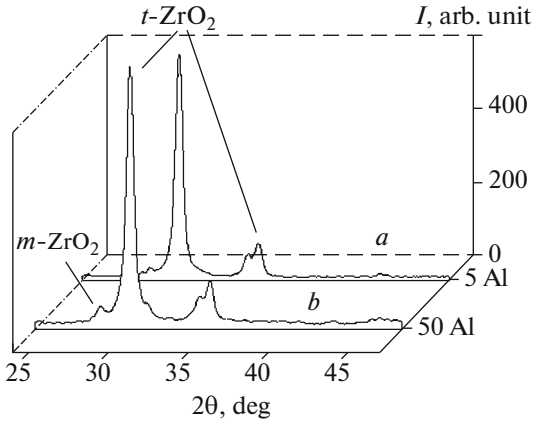

Fig. 2. XRD patterns of samples calcined at 950°C: (*a*) 5 Al, (*b*) 50 Al.

The total acidity of the surface of the samples was tested by the spectrokinetic method on the adsorption of pyridine.

RESULTS AND DISCUSSION

Samples of xerogels of the compositions of 5 Al and 50 Al are X-ray amorphous; even after heat treatment of xerogels at 450°C, the main phase remains X-ray amorphous, and weakly formed diffuse reflexes are fixed in the regions corresponding to the phases of zirconium dioxide and transition forms of aluminum oxide, as illustrated by the fragments of diffraction patterns in Fig. 1.

Increasing the heat treatment temperature to 950°C promotes formation of the main crystalline zirconium-containing phase in the samples with ZrO_2 matrix and Al_2O_3, represented by the solid solution based on tetragonal zirconia (Fig. 2).

In the diffraction patterns of the samples obtained after heat treatment at 950°C (Fig. 2), traces of zirconium dioxide of the monoclinic modification are noted. In the powders of 5 Al and 50 Al, the crystalline forms of Al_2O_3 are not identified, which is due to the low intensity of the corresponding reflexes, determined by the nanoscale dimensionality of the objects, as well as low mass absorption coefficient of aluminum oxide [11].

Heat treatment of the synthesis products causes a different dispersion value of the powders of 5 Al and 50 Al, which is explained by their different degree of crystallizing.

The dimensional characteristics of the powders on which the catalytic properties were determined are presented in Table 1.

Figure 3 shows SEM images of 5 Al and 50 Al powders obtained after heat treatment at 950°C. Nanoscale powders have high surface energy; in this regard, they really represent hierarchical structures.

Table 1. Structural characteristics of samples

Samples	Heat treatment temperature, T, °C	Specific surface, S_{sp}, m^2/g	Diameter of individual particles, nm	Total porosity, cm^3/g
5 Al	180	230	4	0.17
	950	13	70	0.105
50 Al	180	90	13	0.11
	950	43	28	0.27

Table 2. Catalytic activity and selectivity of ethanol conversion for samples with 5 Al and 50 Al

Sample	Treatment temperature, T, °C	Selectivity, %			Total conversion of ethanol, %
		on acetaldehyde	on ethylene	on diethyl ether	
5 Al	180	21	58	21	23
	950	8	57	35	47
50 Al	180	71	22	7	27
	950	32	54	15	14

Nanoscale xerogels and powders have a complex porous structuring depending on the heat treatment temperature. Xerogels are dominated by pores with dimensions not exceeding 5 nm. An increase in the heat treatment temperature determines formation in the powders of pores with a particle size from 10 to 50 nm (Fig. 4).

Since performance properties of catalysts are determined not only by chemical and phase compositions but also by porous structuring (volume of the pore space and pore geometry), it is of interest to compare catalytic activity not only of the samples with a variable matrix but also of xerogels and powders of the same composition.

Ethanol conversions proceeded in three directions: dehydrogenation with the formation of acetaldehyde; dehydration with the formation of ethylene and diethyl ether. The main reaction products (acetaldehyde, ethylene, and diethyl ether) were fixed as chromatographic peaks. Owing to the low concentrations (trace amounts), other reaction products were not taken into account. The results of tests of catalytic activity are presented in Table 2.

For the sample with a zirconia matrix (5 Al), an increase in the heat treatment temperature leads to an increase in the total conversion of ethanol, mainly because of an increase in the yield of diethyl ether. For the sample with an alumina matrix (50 Al) heat-treated at the temperature of 950°C, the catalytic activity decreases by a factor of two in comparison with the activity of xerogels of the same chemical composition. Probably, this fact is associated with a sharp decrease in nanosized pores in these powders.

The selectivity for ethylene yield for the samples with ZrO_2 matrix is independent of the heat treatment temperature and exceeds 50%, and for the samples with Al_2O_3 matrix, the selectivity of 50% is achieved after heat treatment at the temperature of 950°C.

The heat treatment temperature of the samples and, correspondingly, the phase composition, disper-

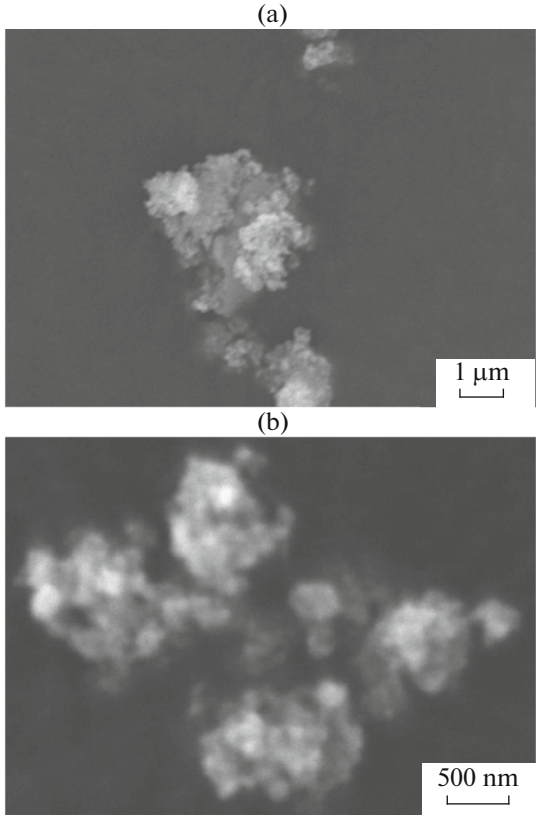

Fig. 3. Morphology of powders obtained at 950°C: (a) 5 Al, (b) 50 Al.

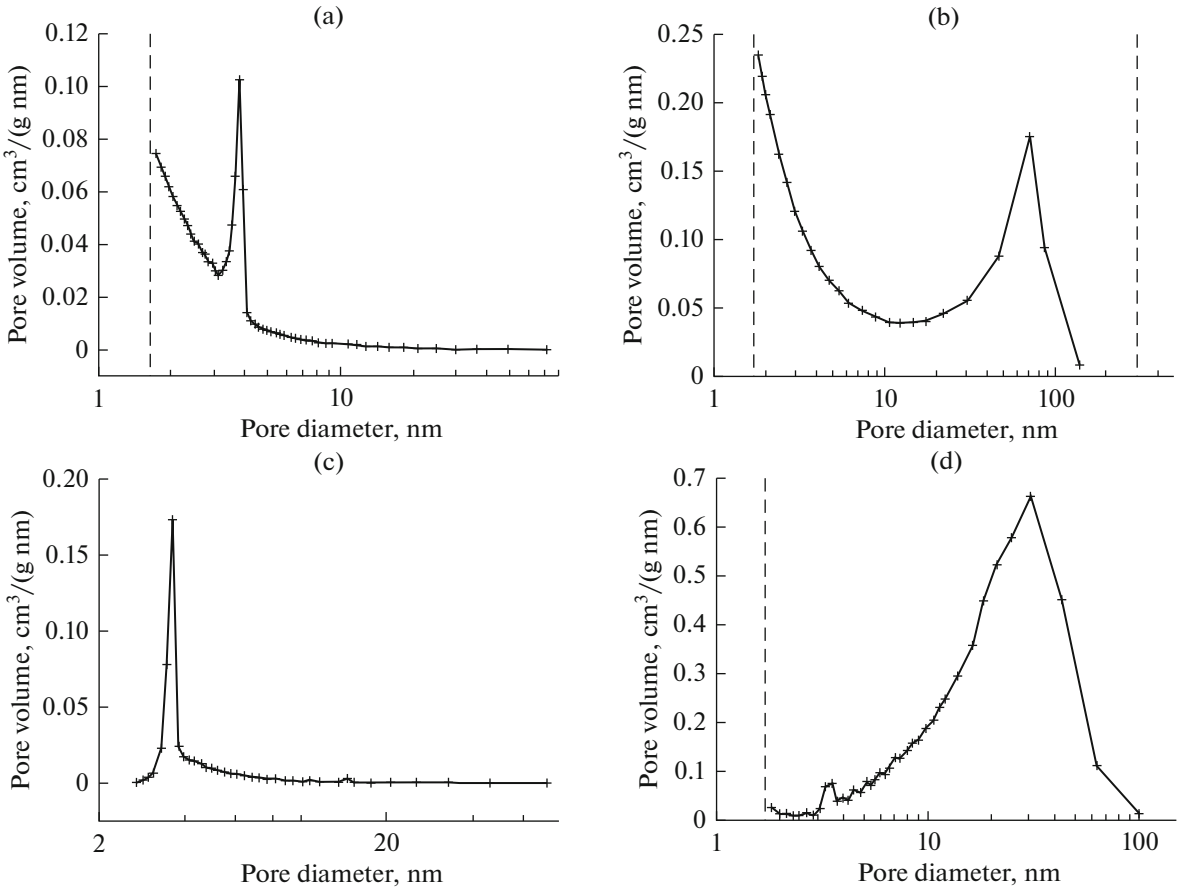

Fig. 4. Pore distribution in samples with (a, b) 5 Al and (c, d) 50 Al; (a, c) xerogels, (b, d) powders.

sity, and porous structuring do not unambiguously affect either the total alcohol conversion or the selectivity of the process.

CONCLUSIONS

The used technique of synthesis of the powders of the Al_2O_3–ZrO_2–CeO_2 system made it possible to obtain nanoscale xerogels and nanoscale powders with different porous structuring.

The xerogels with both ZrO_2 and Al_2O_3 matrices are X-ray amorphous; in the powders, the main crystalline phase is represented by the solid solution based on tetragonal zirconia.

The total conversion values of ethanol for xerogels with ZrO_2 and Al_2O_3 matrices are close, and an increase in the heat treatment temperature leads to an increase in the total conversion in the powders with ZrO_2 matrix and a decrease in the activity in the powders with Al_2O_3 matrix.

The catalytic activity in the reaction of ethanol conversions is higher for the samples with a predominant and more crystallized phase of the solid solution based on tetragonal zirconia—in the samples with ZrO_2 matrix.

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