ISSN 1070-4272, Russian Journal of Applied Chemistry, 2008, Vol. 81, No. 4, pp. 609–613. © Pleiades Publishing, Ltd., 2008.
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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Thermochemical Analysis of Desorption and Adsorption of Water on the Surface of Zirconium Dioxide Nanoparticles

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Received July 26, 2007

Abstract—Desorption and adsorption of water on the surface of ZrO_2 particles obtained under hydrothermal conditions were considered. The heat effect of desorption was determined.

DOI: 10.1134/S1070427208040071

The large specific surface area of nanopowders and the active state of functional groups on the surface of nanoparticles [1–5] make promising their use in development of highly efficient sorbents, catalysts, and catalyst supports and in syntheses of substances with a developed and active surface. ZrO_2-containing materials are known as sorbents [6–8] and are widely used as catalysts [9–13]. Because ZrO_2 particles have a hydrophilic surface and actively adsorb water [14–17], data on the adsorption and desorption of water on the surface on ZrO_2-based nanocrystalline powders are necessary for development and use of these materials. It should be noted that data on these processes for ZrO_2 nanoparticles are also exceedingly important for development of a technology for production of ceramic materials from nanopowders, because adsorption and desorption of water on the surface of nanoparticles exert a decisive influence on the densification of materials in their compaction and, particularly, sintering [18–24].

This study is devoted to a thermochemical examination of the adsorption and desorption of water on the surface of nanocrystalline ZrO_2 particles by the method of comprehensive thermal analysis.

EXPERIMENTAL

Nanocrystalline zirconium dioxide was produced by hydrothermal treatment of zirconium hydroxide precipitated from a solution of $ZrOCl_2 \cdot 8H_2O$ (chemically pure grade) with a concentrated solution of NH_4OH. The hydrothermal treatment was carried out at a temperature of 250°C and pressure of 70 MPa in the course of 4 h. The parameters of synthesis of ZrO_2 nanocrystals were chosen in accordance with [25–27] and corresponded to complete dehydration of zirconium oxyhydroxide.

The structural state of ZrO_2 nanoparticles was determined by X-ray phase analysis (XPA). X-ray diffraction patterns of samples were measured on a DRON-3 diffractometer (Cu_{K_α} radiation).

The size of crystallites (coherent-scattering regions, CSR) was found from the line broadening in X-ray diffraction patterns by the Scherrer formula. In addition, the particle size was determined by transmission electron microscopy (TEM) on an EM-125 electron microscope with U_{acc} = 75 kV and from small-angle scattering data obtained on the installation described in [28].

The specific surface area of the nanopowder was found by analyzing isotherms of butanol adsorption.

The desorption and adsorption of water on the surface of nanoparticles was studied in a flow of air containing H_2O in an amount corresponding to a 70–80% relative humidity of air and to a saturated vapor pressure at atmospheric pressure and temperature of 25°C ($P_{H_2O\,(sat)}$ = 0.0312 atm [29]) by the method of comprehensive thermal analysis on a Netzsch STA-429 installation. The heat effects accompanying these processes were found from data furnished by differential scanning calorimetry. The composition of the gas phase over a sample was monitored by mass spectrometry [QMS 403C Aecolos (Netzsch)].

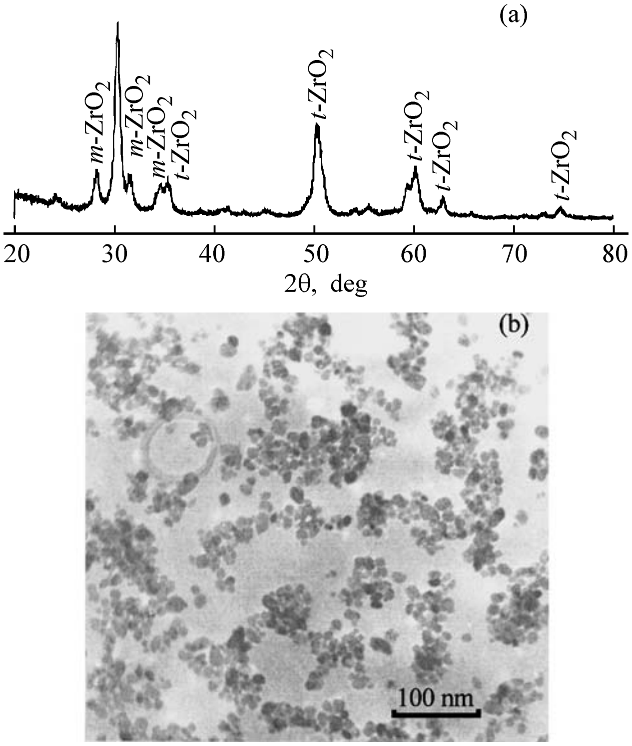

Fig. 1. (a) X-ray diffraction pattern and (b) TEM micrograph of zirconium dioxide nanocrystals produced by hydrothermal synthesis. (2θ) Bragg angle.

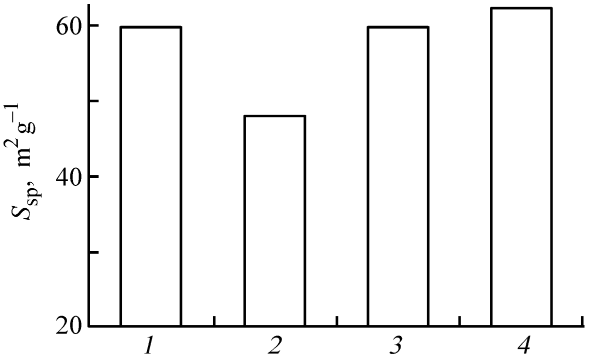

Fig. 2. Specific surface area of nanocrystalline ZrO_2, found by analyzing (*1*) small-angle X-ray scattering data, (*2*) widths of X-ray diffraction lines, (*3*) TEM data, and (*4*) data on butanol adsorption. (S_{sp}) Specific surface area of nanoparticles.

Comparison of the values obtained for the specific surface area of nanoparticles by the adsorption–desorption method and from the nanoparticle sizes found from X-ray diffraction line broadening (Fig. 1a) and by TEM (Fig. 1b) shows that these values coincide within the experimental error (Fig. 2). This coincidence is only possible if the following conditions are satisfied: nanoparticles have an isometric shape, are single crystals, the amorphous phase is virtually absent, and the nanoparticle size distribution is narrow. These characteristics of the zirconium dioxide nanoparticles under study, produced in hydrothermal conditions, is confirmed both by published data [25–27, 30] and by the results of separate experimental methods used in the study. For example, TEM data (Fig. 1b) show that the nanocrystals have an isometric shape and only slightly vary in size. It should be noted that the most pronounced, even though only falling within the experimental error, discrepancy between the specific surface areas is observed for the method in which S_{sp} is calculated from the SCR size. This, presumably, occurs because the procedure used to calculate the SCR size by the Scherrer formula for the most part takes into account coarser crystals, which results in that S_{sp} values are underestimated.

The results of a comprehensive thermal analysis of ZrO_2 nanocrystals (Fig. 3) indicate that two endothermic effects associated with the desorption of water from the surface of zirconium dioxide nanoparticles and with the transition of the monoclinic modification of ZrO_2 to t-ZrO_2, the equilibrium modification at the given temperature. Four exothermic effects, accompanied by a noticeable loss of mass, are presumably due to a structural rearrangement of ZrO_2 nanoparticles. A mass-spectrometric analysis of the gas phase over a sample demonstrated that mainly water is desorbed (Fig. 3b). The loss of mass by the sample, attributed to the desorption process, is virtually independent of the rate at which temperature is raised, but depends on the partial pressure of water of the sample in its isothermal keeping at 25°C. The data obtained demonstrate that the loss of mass by a nanopowder kept under saturated-vapor conditions at 25°C is about 3.7 wt %, and that by samples kept at room temperature in an atmosphere with a humidity of 70–80% is 2.2–2.7 wt %. It is noteworthy that the latter data are also confirmed by the results of other studies of ZrO_2 nanopowders obtained under similar conditions [13, 14, 30].

The area of the landing site for a water molecule is $\delta = 0.102$ nm^2 [31]. With account of the values obtained for the specific surface area of ZrO_2 nanocrystals [$S_{sp} = 61 \pm 1$ m^2 g^{-1} (Fig. 2)] and for the amount of water adsorbed on their surface [$\Delta m = (2.2–2.7) \times 10^{-2}$ or 3.7×10^{-2} g H_2O per gram of a sample], it can be concluded that, to within the error in the available data, a water layer that approaches a bimolecular layer as the air humidity increases to saturation is present in both cases on the surface of zirconium dioxide nanoparticles. This conclusion is based on the fact that the surface area that would be oc-

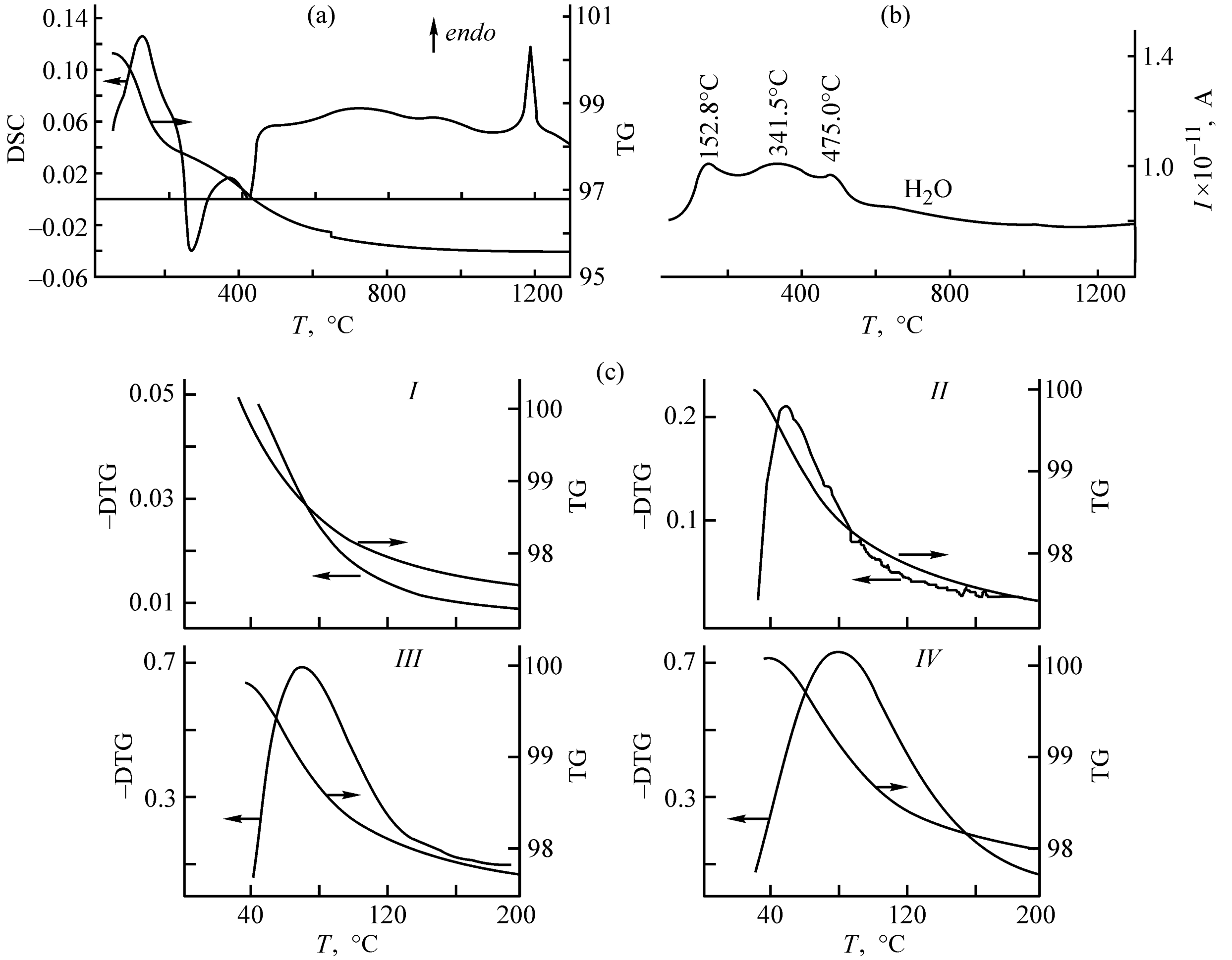

Fig. 3. Results of (a) differential-thermal, (b) mass-spectrometric, and (c) thermogravimetric analyses of nanocrystalline ZrO_2. (*T*) Temperature and (*I*) ionic current. Heating rate (deg min^{-1}): (*I*) 1, (*II*) 5, (*III*) 10, and (*IV*) 20.

cupied by a monomolecular layer of water released in desorption is $S_{\text{sp. mono}}$ = 75–92 or 126 m^2 (saturated vapor), which exceeds by a factor of 1.2–1.5 or nearly 2 (for the saturated vapor) the real specific surface area of ZrO_2 nanoparticles.

Analysis of the thermogravimetric data shows that, at a heating rate of 1 deg min^{-1}, the curves that describe the loss of mass (TG and –DTG) and characterize the evaporation intensity monotonically decrease as temperature becomes higher (Fig. 3c). At the same time, at heating rates of 5, 10, and 20 deg min^{-1}, the TG curves remain monotonically decreasing, whereas the –DTG curves show a maximum that is shifted, depending on the heating rate, from 60 to 80°C (Fig. 3c). The peak in the –DTG curves is presumably due, on the one hand, to a kinetic hindrance to the desorption process at low temperatures, which becomes less pronounced as temperature is raised, in accordance with the known kinetic equations [32]. On the other hand, the fall of the desorption rate, observed as temperature is raised above a certain value may be due, in accordance with the desorption equation [32], both to a decrease in the amount of the adsorbed substance in the course of desorption and to a stronger binding of water molecules, desorbed at higher temperatures, to the surface of ZrO_2 nanoparticles.

It should be noted, when analyzing the case in which a virtually bimolecular layer of adsorbed waster is present on the surface of ZrO_2 nanoparticles (Fig. 4), that the desorption rate decreases if a predominantly monomolecular layer of H_2O, known to be more strongly bound to the hydrophilic surface [33], remains on the nanoparticle surface. According to [34], a virtually monomolecular layer remains on hydrophilic surfaces when temperature is raised 65–70°C, in good agreement with the results obtained in the present study (Fig. 3). The absence of a maximum

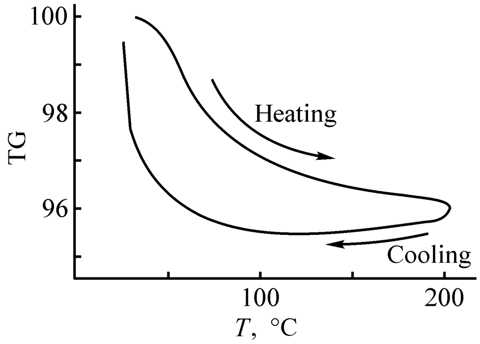

Fig. 4. Results of a thermogravimetric analysis (heating–cooling) of zirconium dioxide nanocrystals at P_{H_2O} = 0.0312 atm. (T) Temperature.

in the desorption rate at a heating rate of 1 deg min^{-1} presumably indicates that the kinetic factor is unimportant, i.e., this mode is close to the equilibrium desorption of water from the surface of ZrO_2 nanoparticles.

As follows from the results of the thermal analysis, the process of water adsorption on the surface of ZrO_2 nanoparticles is substantially slower than the desorption process and starts to occur with high intensity only at comparatively low temperatures (Fig. 4).

The DSC and DTG data were used to determine how the heat effect of desorption of 1 mol of H_2O from the surface of ZrO_2 nanoparticles depends on temperature. The results obtained indicate that, within the experimental error mostly associated with plotting of the differential curve describing the loss of mass, the heat effect can be considered constant in the whole range of desorption temperatures studied and equal to $\Delta H_{des} = 35 \pm 7$ kJ mol^{-1}. It is noteworthy that ΔH_{des} coincides within the experimental error with the enthalpy of water evaporation $\Delta H_{ev} = 40$ kJ mol^{-1} [35].

CONCLUSIONS

(1) It was shown that, upon an increase in the air humidity from 70% to a saturated vapor at room temperature, 1.2 to 2 molecular layers of water are adsorbed on the surface of nanoparticles.

(2) The heat effect of water desorption from the surface of zirconium hydroxide nanoparticles was determined ($\Delta H_{des} = 35 \pm 7$ kJ mol^{-1}) and it was demonstrated that ΔH_{des} coincides within the experimental error with the heat effect of water evaporation.

(3) It was found that, in the range of air humidities under consideration, the desorption of the monomolecular layer from the surface of zirconium dioxide nanoparticles begins at a temperature of about 74°C.

ACKNOWLEDGMENTS

The study was financially supported by the Russian Foundation for Basic Research (grant no. 07-03-00750).

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