Stabilizing effect of the carbon shell on phase transformation of the nanocrystalline alumina particles

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ABSTRACT

Intensive phase transformations of alumina are known to occur at temperatures above 1000 °C. In the present work, high temperature behaviour of pure Al_2O_3 and the carbon coated $Al_2O_3@C$ sample with core-shell structure was comparatively studied using low-temperature nitrogen adsorption, transmission electron microscopy, powder X-ray diffraction (XRD) analysis and solid-state nuclear magnetic resonance (NMR). The solid-state NMR ^{27}Al method has allowed us to identify and estimate the concentration of all phases appeared during the transformation of pseudoboehmite γ-Al_2O_3 into corundum α-Al_2O_3. The data obtained correlate well with the results of XRD analysis and low-temperature nitrogen adsorption. It is shown that the deposition of carbon coating with formation of core-shell $Al_2O_3@C$ system stabilizes the size of oxide core and prevents the formation of corundum phase until the temperatures of 1350–1400 °C, which are close to the temperature of carbothermal reduction of alumina. The stabilization of the size of the oxide core nanoparticles was considered as a main factor preventing the formation of corundum phase at high temperatures. At the same time, the carbon coating does not affect the phase transformation of γ-Al_2O_3 to δ-Al_2O_3.

1. Introduction

Nowadays, the oxide materials with developed surface area are widely applied in different areas of modern science and technology. One of their most important fields of application is catalysis, where both the specific surface area and surface functional groups play an important role defining the properties of these oxides used as a catalyst or a catalyst's support [1–3]. On the other hand, stability of the materials during the high temperature treatment, which is usually applied in the catalytic processes, is of great importance. For instance, phase transformations of alumina as well as agglomeration of its particles diminish the value of specific surface area due to the structural collapse and decrease the amount of the surface electron-donor or electron-acceptor sites, thus causing the irreversible deactivation of the catalyst [1,3]. Thereby, stabilizing of the nanocrystalline oxides in a disperse state and preventing their phase transformation is a big challenge.

The size effects are known to play a defining role in the phase transformations taking place in oxide systems, as well as during the chemical reactions with participation of solids. Thus, in numerous works, the impact of the size of TiO_2 and Al_2O_3 nanoparticles and the

environment on the stability of different phases of these oxides was studied in detail [4–10]. It was demonstrated that for the TiO_2 nanoparticles below 20 nm, the anatase phase is thermodynamically favourable, while the formation of rutile phase, which takes place at higher temperatures, is facilitated by the particles enlargement caused by their sintering [4–6]. A quite similar situation was observed for alumina. In the case of the samples with high specific surface area, which corresponds to the smallest particle size, the γ-Al_2O_3 phase is the most stable. Formation of the corundum phase, as a rule, occurs only after an increase of particle size [7–10].

Thereby, the key factor leading to an enlargement of the oxide particles at elevated temperatures is their sintering. This process is stipulated by the presence of a direct contact between the nanoparticles. An elimination of such contact via isolation of the pristine nanoparticles with an inert shell can give rise to a possibility to stabilize their sizes at a higher temperature. In this case, the existing domain of such core-shell structured system will be limited by the temperature when the shell starts to react with the core.

In our recent works, the possibility of stabilization of the oxide core sizes at high temperature treatment for TiO_2, Al_2O_3, and calcium

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aluminate C12A7 was reported [11–15]. In all these cases, the carbon coatings were deposited on the surface of nanoparticles, and the core-shell structure Oxide@C was formed. This approach has allowed us to study the features of solid phase transformations of the oxide nano-particles at high temperatures without any significant changes in their size. It should be mentioned that the high enough dispersity of C12A7 system inside the carbon shell was maintained even at temperatures exceeded the melting point of calcium aluminate [14,15]. For the TiO_2@C system, it was possible to stabilize the initial size of TiO_2 na-noparticles and, correspondingly, the anatase phase up to the maximal temperature of 800 °C, while at higher temperatures, the reactions of carbothermal reduction of the oxide core as a result of its interaction with carbon shell occurs [11,12]. It should also be emphasized that the carbon shell in the systems of the Oxide@C type plays a role of 'na-noreactor', inside which the phase and chemical transformations of the oxide core can take place. The results of preliminary studies showed that the 'carbon nanoreactor' concept can be efficiently applied for the stabilization of alumina core inside the Al_2O_3@C system [12].

On the other hand, solid-state nuclear magnetic resonance (NMR) method is well known to be an efficient tool for obtaining the in-formation about the local coordination of the ^{27}Al nuclei in the alu-minium-containing oxide systems. The method provides the trusted determination of the coordination of the aluminium ions presented in the samples, identification of their phase composition, and investiga-tion of their transformations at the temperature increase [13,16–19].

The aim of the present study was to compare the high temperature behaviour of the pristine and carbon-coated aluminium oxides. The nanocrystalline alumina used was prepared by means of an aerogel technology [20,21]. The most attention was paid to the analysis of the phase transformations taking place in these systems using the data of solid-state NMR method about the local coordination of the ^{27}Al nuclei.

2. Experimental

The pristine nanocrystalline alumina used in the present work was obtained via an aerogel technique as described elsewhere [20,21]. Pseudoboehmite (AlOOH, Pural SB1 from Condea) was used as an alumina precursor. Before the experiments or carbon coating proce-dure, the alumina samples were calcined in a muffle at 650 °C for 6 h. In order to obtain the carbon shell, the pristine alumina sample was mixed with polyvinyl alcohol (PVA 16/1, Reakhim, Russia) in a weight ratio of 7:3. Then, the mixture was heated in a quartz reactor in an argon flow up to 750 °C with a ramping rate of 1.5 °C/min and kept at this tem-perature for 6 h. For the treatment at higher temperatures, the sample was placed into a graphite crucible that was installed into a corundum tube assembled inside a tubular Starbar TSR heater. Then, the sample was heated up to the desired temperature (varied in a range of 960–1450 °C) with a ramping rate of 3 °C/min in an argon flow and kept at this temperature for 6 h. The samples with carbon coating were labelled as Al_2O_3@C. A similar approach for carbon coating formation was described in our recently published papers [11–15]. In order to remove the carbon coating, the Al_2O_3@C samples treated at desired temperature in argon were additionally calcined at 650 °C in air. These samples were labelled as Al_2O_3@C-650. The reference Al_2O_3 samples of the pure alumina were also subjected to the similar thermal treatment procedures.

The values of specific surface area were calculated by the Brunauer-Emmet-Teller method. The low-temperature argon adsorption was performed using an ASAP-2400 instrument.

The solid-state NMR experiments were carried out using a pulse Fourier-spectrometer Bruker Avance 400 with a magnetic field of 9.4 T. ^{27}Al NMR spectra were recorded using the resonance frequency of ^{27}Al nucleus of 104.31 MHz by the MAS method. The sample was placed into a zirconium oxide rotor and rotated with frequency of 14 kHz. A single pulse sequence with short ($\pi/8$) pulse of 0.6 µs length was used. The delay between the experiments was 1 s; and a spectral width was

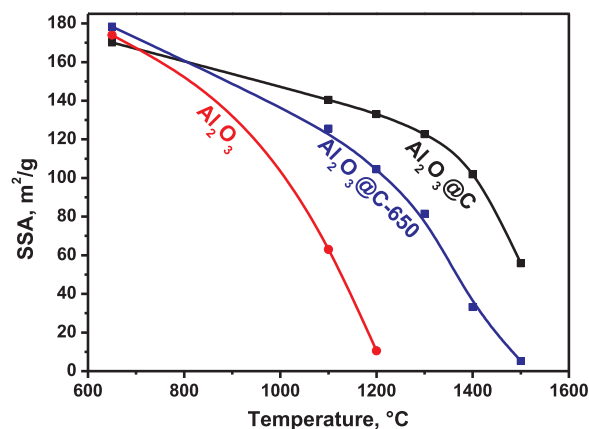**Fig. 1.** SSA for the pristine alumina sample, the carbon-coated Al_2O_3@C sample, and the Al_2O_3@C sample after calcination at 650 °C in air to remove the carbon coating as a function of the calcination temperature.

1 MHz. For each sample, 1024 scans were recorded. The spectra were recorded at the room temperature. A solution of $[Al(H_2O)_6]^{3+}$ was used as a standard, in which chemical shift was set to 0 ppm.

High resolution transmission electron microscopic (HR TEM) studies were performed using a JEM-2010CX microscope with a line resolution of 1.4 Å. Powder X-ray diffraction (XRD) analysis of the samples was carried out using a Brucker D8 diffractometer working on Co K_α irra-diation.

3. Results and discussions

The carbon-coated Al_2O_3@C samples of core-shell structure, as well as the reference samples of pristine alumina were calcined in argon within the temperature range of 1100 – 1450 °C. Fig. 1 shows the effect of the calcination temperature on the values of specific surface area (SSA) for these samples. It is clearly seen that in the case of pristine alumina, high temperature treatment results in a sharp decrease of the SSA. Thus, after the calcination at 1200 °C, the SSA value drops down to 3–5 m^2/g which is characteristic for the α-phase of alumina. At the same time, the carbon-coated Al_2O_3@C sample retains high enough values of SSA even after 1450 °C. It is quite possible that the significant contribution to these values can be made by the carbon shell. The exact information concerning the SSA values of the alumina core can only be obtained after the elimination of the carbon coating. Fig. 1 also shows the corresponding results for the Al_2O_3@C sample after its calcination in air at 650 °C. It is evident that the carbon coating used has stabilized the size of the alumina nanoparticles inside the 'carbon nanoreactor' and prevented the sintering of the latter. The relatively high values of SSA for the Al_2O_3@C samples (after removal of carbon) testifies the efficiency of the carbon shell in terms of its protective function even near the temperature of 1450 °C, when the processes of carbothermal reduction of alumina might take place.

The results of high resolution TEM studies of the as-prepared and calcined at 1200 °C Al_2O_3 and Al_2O_3@C samples are presented in Fig. 2. The effect of the carbon shell on the morphological changes of the samples at high temperature treatment is well seen. Thus, it is evident that the morphology of the pristine alumina and the carbon-coated Al_2O_3@C samples in their initial state is quite similar (Fig. 2A and C). When the samples were calcined at 1200 °C in argon, their morpholo-gies became noticeably different. The pure alumina sample has com-pletely transformed into corundum (Fig. 2B), while the alumina core inside Al_2O_3@C sample still corresponds to the δ-phase (Fig. 2D) with typical value of SSA above 100 m^2/g.

Fig. 3 shows the ^{27}Al 14 kHz MAS NMR spectra for the pure alumina samples calcined in a temperature range of 650–1400 °C. The spectra contain the bands corresponding to aluminium with octahedral ($\delta \sim$