

CATALYTIC REACTION MECHANISMS

Effect of Indium Oxide Modification on the Phase Composition, the Structure of a Hydroxyl Cover, and the Electron-Acceptor Properties of Zirconium Dioxide

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Abstract—The effect of modification with indium oxide on the crystal structure, hydroxyl cover, and electron-acceptor properties of zirconium dioxide was studied. It was found that complex binary systems with a highly thermally stable tetragonal ZrO_2 phase can be prepared by the modification. The concentration of In^{3+} in the lattice of ZrO_2 depends only slightly on the total concentration of In_2O_3 in the system. The major portion of the indium oxide added is localized as an individual X-ray amorphous phase in intercrystallite voids. The In_2O_3 phase formed in these systems does not cover the surface of ZrO_2 but is mainly localized in the intercrystallite space. The presence of the modifier component affects the predominant crystallographic direction and the defect structure of the surface formed. The modification was found to affect the structure of a hydroxyl cover and the electron-acceptor properties of zirconium dioxide.

INTRODUCTION

The preparation of finely dispersed ZrO_2 with a developed surface and specified adsorption properties is a topical problem for the use of zirconia as a catalyst or effective support. The heterogeneous doping of zirconium dioxide with rare earth oxides is favorable for the stabilization of a tetragonal or cubic crystal modification of ZrO_2 . These systems are solid solutions with highly mobile lattice oxygen. Along with rare earth elements, Group III nontransition metals, such as indium oxide, can serve as modifier components. According to published data [1, 2], heterogeneous compositions with ionic or mixed ion–electron conduction can be obtained depending on the concentration of In_2O_3 in the system.

The high electron conduction of indium oxide and solid solutions on its basis (in particular, with the addition of ZrO_2 [1, 3, 4]) is responsible for its use as a material for reducing gas sensors (for CO and H_2) [5]. Presently, In_2O_3 supported on a substrate of stabilized tetragonal ZrO_2 is under active study as a promising sensor for oxidizing gases. Interest in complex indium-containing binary systems, in particular, In_2O_3 – ZrO_2 , has quickened in the past few years in the context of their applicability as promising heterogeneous catalysts. Thus, according to Madou and Morrison [6], the catalytic oxidation of reducing gases with chemisorbed oxygen can occur on the surfaces of In_2O_3 and solid solutions on its basis.

In this work, we report the results of a study of the effect of indium oxide modification on the phase composition, hydroxyl cover, and electron-acceptor properties of zirconium dioxide.

EXPERIMENTAL

Samples of complex binary indium–zirconium oxide systems were prepared by the coprecipitation of zirconium and indium hydroxides from nitrate solutions (0.6 M) with an aqueous ammonia solution (5%) at a constant pH 9. The resulting precipitate was dried in air at 120°C for 6 h and then calcined in air at a given temperature for 4 h. The table summarizes the characteristics and designations of the samples prepared (the concentration of the modifier oxide, the specific surface area, the temperature of calcination, and the crystal modification of ZrO_2).

The diffuse-reflectance spectra were measured on an Equinox 55/S spectrometer equipped with a FRA 106/S Raman module (YAG laser; $\lambda = 1064$ nm) (Bruker) at room temperature with a spectral resolution of 2 cm^{-1} in accordance with a procedure described elsewhere [7]. The Raman spectra were measured at room temperature in air.

The specific surface areas of samples were determined by chromatography from the low-temperature adsorption of nitrogen. X-ray diffraction analysis was performed on a Dron-3 diffractometer.

RESULTS AND DISCUSSION

Crystal Structure and Thermal Transformations of ZrO_2 Modified with Indium Oxide

The phase composition of the test systems was studied by X-ray diffraction analysis and Raman spectroscopy.

According to Morozova and coauthors [8, 9], a homogeneous Zr – In – O solid solution can be formed

Characteristics of the samples

Sample	Concentration of In_2O_3 , mol %	T_{calcd} , °C	Phase composition	D , nm	S_{sp} , m^2/g	Sample color
3InZr	3	600	t	21	35	White
		930*	t	25		"
		1470	t	76		"
5InZr	5	600	t	20	44	"
		870*	t	19		"
		1100	t	28	50	Yellow
		1470	t	41		White
8InZr	8	600	t	—	75	"
		1470	t	—		"
10InZr	10	600	c + t	14	75	"
		740*	c + t	13		"
		1110	c + t	25	50	Yellow
		1470	c	69		White

Note: t and c refer to the tetragonal and cubic modifications of crystalline ZrO_2 , respectively.

* This temperature corresponds to the onset of a process accompanied by an exothermic effect (Fig. 2).

over the concentration region 6–25 mol % In_2O_3 . An analysis of X-ray diffraction data obtained with our samples allowed us to recognize only reflections that correspond to zirconium dioxide. Lines that correspond to other phases, in particular, an In_2O_3 oxide phase, were not observed. The shape analysis of high-angle lines ($2\theta = 60^\circ$ and 76°) allowed us to identify components that correspond to both tetragonal and cubic ZrO_2 phases. The table summarizes the results of this analysis.

According to X-ray diffraction data, the presence of a cubic ZrO_2 modification was detected in the system 10InZr. A band in the Raman spectrum should correspond to this ZrO_2 phase; however, we experimentally observed the presence of six bands characteristic of a tetragonal phase in the Raman spectra of all the test samples (Fig. 1). This difference between data obtained by X-ray diffraction analysis and Raman spectroscopy can be explained by a tetragonal distortion of the cubic phase. As the concentration of In_2O_3 was increased from 3 to 10 mol %, no significant changes in the positions of high-angle reflections in the diffraction patterns and in the positions of band maximums in the Raman spectra were observed.

Note that the phase composition of the resulting systems exhibited a high thermal stability over the tested temperature region. Even at a low concentration (3 mol %) of indium oxide, a monoclinic ZrO_2 phase was not formed and the system did not decompose into a monoclinic phase of ZrO_2 and a phase of In_2O_3 , which are detectable by X-ray diffraction analysis.

It is well known [10] that the crystallization temperature of a solid solution based on ZrO_2 is highly sensitive to the concentration of a modifier component, and

an increase in the crystallization temperature with modifier concentration is indicative of the formation of a complex binary system. In our experiments with systems containing 3 and 10 mol % In_2O_3 , the crystallization temperature insignificantly increased from 430 to 445°C, respectively (Fig. 2). In the temperature region 750–1100°C, all the test samples exhibited an extended exothermic effect, which occurred without a weight loss. The temperature of the onset of this process monotonically decreased from 930 to ~750°C as the concentration of In_2O_3 was increased from 3 to 10 mol %, respectively. On completion of this process, the samples changed to a yellow color (see the table), and the color saturation increased with increasing concentration of In_2O_3 . In our opinion, this exothermic effect corresponds to the segregation of In_2O_3 and the formation of an individual X-ray amorphous phase of indium

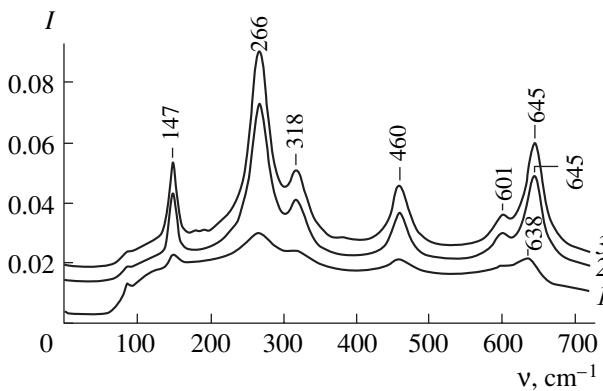


Fig. 1. Raman spectra of the samples (1) 3InZr, (2) 5InZr, and (3) 10InZr calcined at a temperature of 1470°C in air.

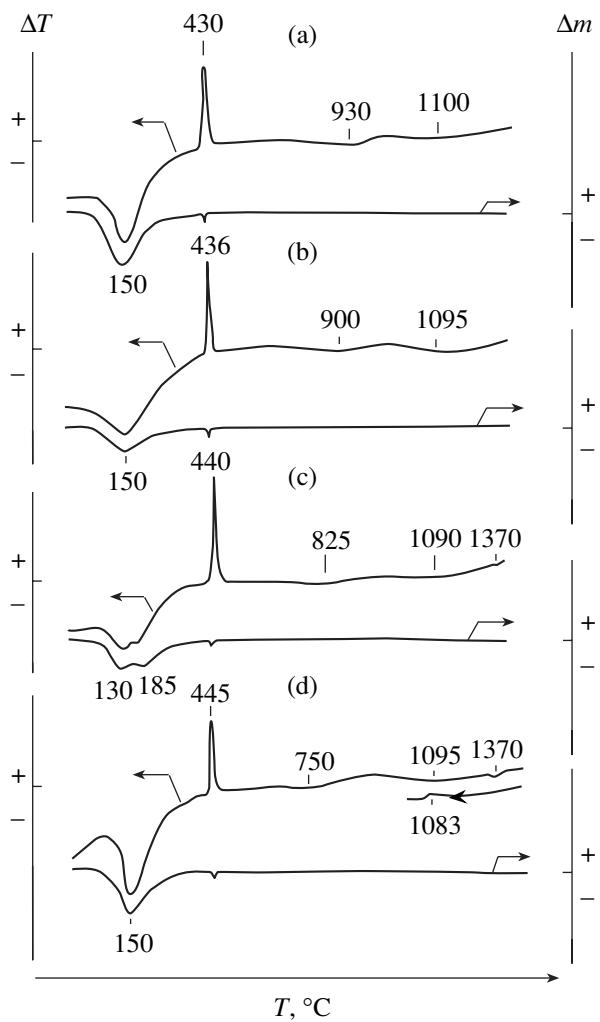


Fig. 2. Differential thermal analysis and thermogravimetric analysis data for the samples (a) 3InZr, (b) 5InZr, (c) 8InZr, and (d) 10InZr.

oxide in the intercrystallite voids of ZrO_2 . The possibility of the release of In_2O_3 from an $\text{In}_2\text{O}_3\text{--ZrO}_2$ solid solution and of the formation of an individual phase was first demonstrated by Morozova *et al.* [9, 11].

Thus, the set of the above data allowed us to assume that a portion of In^{3+} cations is embedded in the lattice of ZrO_2 in the course of the synthesis of the system. However, the weak dependence of the crystallization temperature on the concentration of In_2O_3 and similar arrangements of reflections in the diffraction patterns and bands in the Raman spectra of all the samples suggest that the lattice concentration of In^{3+} depends only slightly on the total In_2O_3 content of the system. The major portion of the indium oxide added is localized as an individual X-ray amorphous phase in intercrystallite voids, and the formation of an In_2O_3 phase is responsible for the occurrence of an exothermic process and for the colorization of the samples.

Data on the average size of the coherent-scattering region (D) are given in the table. From these data, it follows that after thermal treatment at 1470°C the average crystallite size was much higher than the critical size of 20–30 nm for the stabilization of a metastable tetragonal or cubic ZrO_2 phase due to the size factor. This supports the conclusion on the partial intercalation of In^{3+} cations in the lattice of ZrO_2 in the course of synthesis and on the stabilization of a tetragonal/cubic ZrO_2 phase due to both the inhibition of agglomeration processes in ZrO_2 and the introduction of cations with a lower valence and a greater ionic radius into the lattice of ZrO_2 .

According to published data [4], the diffusion of In^{3+} cations from an In_2O_3 phase to the lattice of ZrO_2 is hindered even at high temperatures, whereas the diffusion of Zr^{4+} cations into an In_2O_3 phase can occur. Therefore, it is likely that a solid solution based on In_2O_3 is gradually formed in intercrystallite voids. It is our opinion that the formation of a solid solution based on indium oxide is responsible for a color change from yellow to white as the temperature of thermal treatment was increased (table) to 1470°C. The endothermic effect observed at 1370°C with a linear increase in the temperature and the exothermic effect observed at 1083°C with a linear decrease in the temperature (Figs. 2c, 2d) can be interpreted as those that correspond to the reversible $t \rightarrow c$ transition in a $\text{ZrO}_2\text{--In}_2\text{O}_3$ solid solution with a high concentration of In_2O_3 in accordance with the phase diagram [8].

Hydroxyl Cover

Figure 3 demonstrates the IR spectra of the hydroxyl covers of $\text{In}_2\text{O}_3\text{--ZrO}_2$ samples calcined in air at 600°C after a thermal vacuum treatment at 400–500°C. For reference, Fig. 3d demonstrates the spectrum of indium oxide treated under oxidizing conditions at 450°C.

The absorption spectra of the hydroxyl covers of $\text{In}_2\text{O}_3\text{--ZrO}_2$ samples are the superposition of three groups of absorption bands due to hydroxyl groups with different coordination numbers of the oxygen atom. The spectra of the samples 3InZr and 5InZr are similar over the entire range of temperatures, and they exhibited absorption bands with maximums at 3772, 3762–3765, 3742, 3678–3680, 3654–3656, and 3593 cm^{-1} after a thermal vacuum treatment at 400°C (Figs. 3a and 3b, curves 1). The absorption bands at 3772 and 3762 cm^{-1} can be attributed to the terminal hydroxyl groups of zirconium dioxide localized at the faces of tetragonal ZrO_2 with different crystallographic orientations. The bands at 3742 and 3768–3780 cm^{-1} can be attributed to two-coordinated bridging and three-coordinated bridging OH groups, respectively.

After the calcination of the samples 3InZr and 5InZr at 500°C, their reflectance decreased, probably because of the partial reduction of the present In_2O_3 phase to InO under the conditions of thermal vacuum treatment.

The IR spectrum of a hydroxyl cover was also changed (Figs. 3a and 3b, curves 2). A broad absorption band due to terminal OH groups decomposed into three components: absorption bands with frequencies of 3780–3785 and 3765 cm^{-1} and a weak band at 3770 cm^{-1} , which appeared as a shoulder on the background of the band at 3765 cm^{-1} . Simultaneously, an absorption band with a maximum at 3727 cm^{-1} can be distinguished. This band coincides with the absorption band of the terminal hydroxyl groups of In_2O_3 in terms of frequency, and it can be attributed to terminal hydroxyl groups at In^{3+} cations.

As the temperature of hydroxylation was increased from 400 to 500°C, the band with a maximum at 3656 cm^{-1} became predominant in the spectrum. The frequency of this absorption band is close to the frequency of a type of the hydroxyls in the phase of In_2O_3 . However, its high intensity with reference to the intensity of an absorption band at 3727 cm^{-1} allowed us to ascribe it to the three-coordinated bridging OH groups of zirconium dioxide; Zr^{4+} cations enter into the coordination sphere of these groups in a defect position. Such a considerable contribution from this absorption band to the spectrum suggests the occurrence of a high concentration of structural defects on the surface of binary systems.

The IR spectrum of the hydroxyl cover of the sample 10InZr exhibits differences from the spectra of the samples 3InZr and 5InZr, and it is formed by two broad absorption bands due to the hydroxyl groups of ZrO_2 (Fig. 3c). Components with frequencies of 3780, 3772, and 3765 cm^{-1} , which correspond to terminal hydroxyls, and 3674, 3662, and 3652 cm^{-1} , which correspond to bridging three-coordinated hydroxyl groups, can be distinguished after thermal vacuum treatment at 500°C. The set of these absorption bands suggests the occurrence of surface regions with different crystallographic orientations of tetragonal ZrO_2 : 101 and 110, absorption bands at 3780 and 3772 cm^{-1} and 111, absorption bands at 3765 and 3662 cm^{-1} . The band intensity at 3652 cm^{-1} is much lower than that in the samples containing 3 and 5 mol % In_2O_3 ; in our opinion, this absorption band corresponds to bridging OH groups the coordination sphere of which includes cations in a defect position. This suggests the formation of a less defective surface structure. Note that the intensity of the band with a maximum at 3738–3740 cm^{-1} , which corresponds to bridging two-coordinated hydroxyls at regions with the 002 orientation, is extremely low. This fact is indicative of the effect of In_2O_3 concentration on the predominant crystallographic orientation of the surface and on the surface concentration of defects. The intensity of the absorption band at 3725 cm^{-1} is comparable with the intensity of this band in the spectra of samples with indium oxide concentrations of 3 and 5 mol %. This suggests that the concentrations of In^{3+} cations on the surfaces of these two samples are close although the concentration of In_2O_3 in the system increased from 3 to 10 mol %.

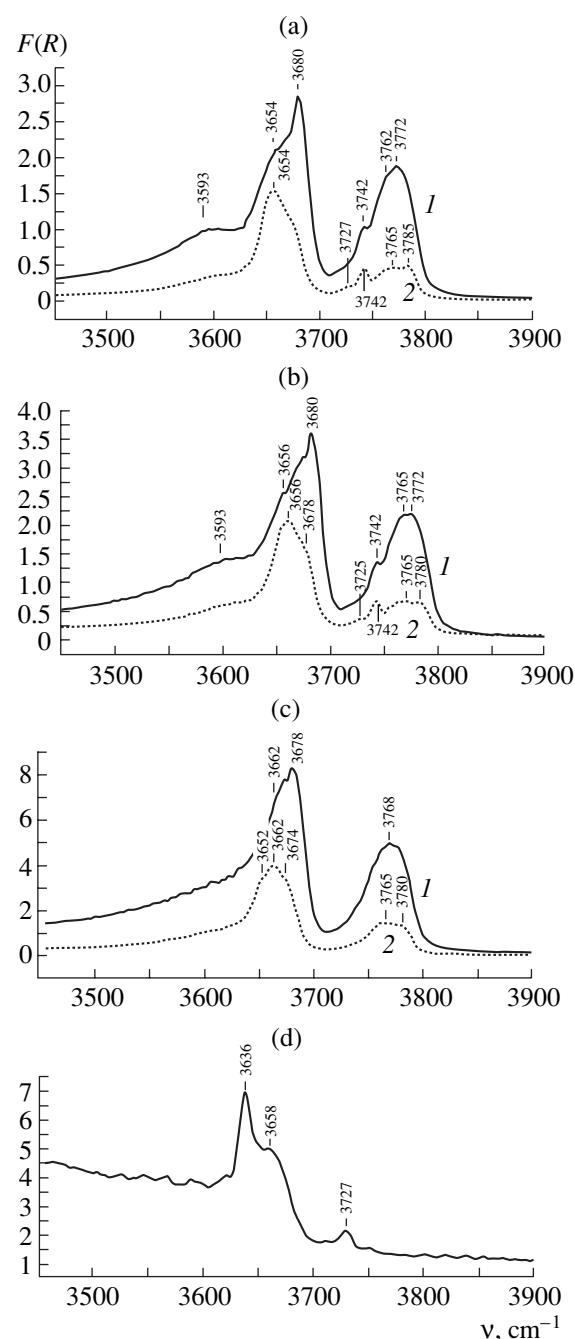


Fig. 3. IR spectra of hydroxyl groups in the samples (a) 3InZr, (b) 5InZr, and (c) 10InZr evacuated at (1) 400 and (2) 500°C and (d) in indium oxide evacuated at 450°C for 1 h and oxidized in oxygen (50 torr) at the specified temperature for 0.5 h.

The above results indicate that hydroxyls characteristic of zirconium dioxide were mainly present on the surface of the indium–zirconium oxide systems obtained. The contribution of hydroxyl groups characteristic of an In_2O_3 phase was insignificant. This fact suggests that the In_2O_3 phase formed in these systems does not cover the surface of ZrO_2 but is mainly local-

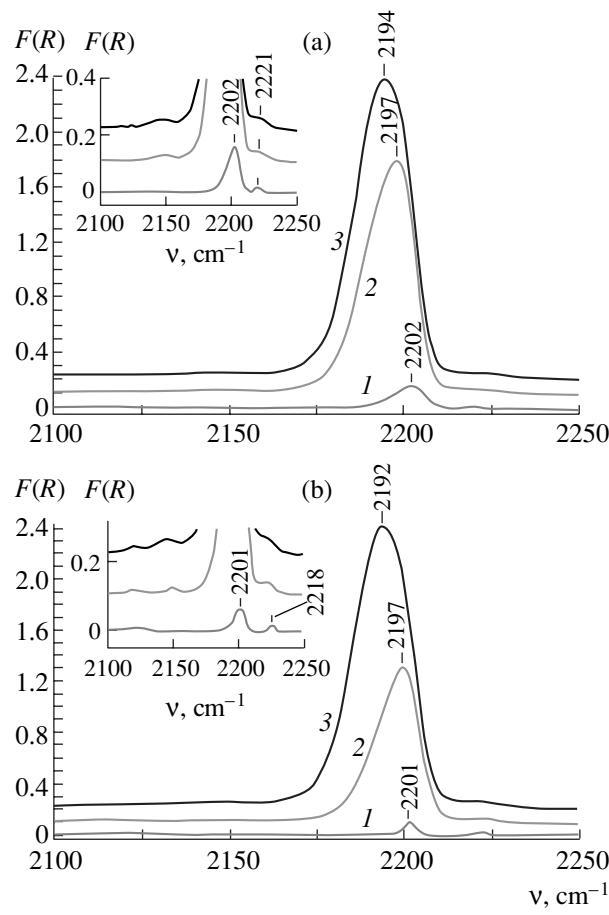


Fig. 4. IR spectra of CO adsorbed on the surface of the samples (a) 3InZr and (b) 5InZr at room temperature. The pressure of CO, torr: (1) 0.5, (2) 5, or (3) 20.

ized in the intercrystallite space. At the same time, the presence of the modifier component affects the predominant crystallographic orientation and the defect structure of the surface formed.

Electron-Acceptor Properties

The electron-acceptor properties of the systems prepared based on zirconium dioxide were studied with the use of carbon monoxide as a probe molecule. An intense absorption band at $2192\text{--}2204\text{ cm}^{-1}$ makes a predominant contribution to the IR spectrum of adsorbed CO (Fig. 4). A band shape analysis indicates that this band is complex and adequately approximated by two components with maximums at $2195\text{--}2206$ and $2180\text{--}2190\text{ cm}^{-1}$.

These absorption bands are characteristic of carbonyl complexes formed as a result of CO adsorption at two types of electron-acceptor sites on the surface of ZrO_2 (coordinatively unsaturated Zr^{4+} cations). The frequencies of adsorbed CO equal to $2202\text{--}2204\text{ cm}^{-1}$ cor-

respond to the strongest Lewis acid sites (LASs) of samples prepared by coprecipitation. This was observed previously [12] in LASs on the surface of tetragonal ZrO_2 . At the same time, a new type of stronger LASs was formed on the surface under the action of the modifier component, and the spectrum exhibited an absorption band at $2218\text{--}2221\text{ cm}^{-1}$, which corresponds to CO complexes with coordinatively unsaturated In^{3+} cations on the surface. The intensity of this band is low compared with the intensities of bands due to CO complexes with Zr^{4+} ; this suggests that the concentration of sites of this kind is comparatively low.

Thus, complex binary systems with a highly thermally stable phase of tetragonal ZrO_2 can be prepared by modifying zirconium dioxide with indium oxide. The surface of the complex binary systems is characterized by a higher concentration of structural defects. The electron-acceptor properties of the surface of the complex systems primarily depend on the electron-acceptor properties of the ZrO_2 phase. At the same time, new stronger LASs are formed on the surface under the action of the modifier component; however, the concentration of these sites is low.

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