State of iridium supported on SO_4/ZrO_2

*A. V. Ivanov and L. M. Kustov**

*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 117913 Moscow, Russian Federation.
Fax: +7 (095) 135 5328. E-mail: lmk@ioc.ac.ru*

The Ir/ZrO$_2$ and Ir/SO$_4$/ZrO$_2$ systems were studied by diffuse-reflectance IR spectroscopy using CO as a probe molecule. After reduction of 0.5% Ir/ZrO$_2$ in flowing hydrogen at 200 °C, the state of iridium is essentially Ir^0, as in the iridium systems supported on amphoteric oxide supports. For Ir/SO$_4$/ZrO$_2$, the stabilization of ionic forms of the metal, the formation of species with a partial positive charge, and an increase in the frequencies of CO adsorbed on Ir^0 particles, as compared with systems without sulfur, are found. At a concentration as low as 0.1 wt.%, iridium exists substantially as Ir^{3+} ions or small Ir$^{\delta+}$ particles. An increase in the concentration of iridium to 0.5 wt.% leads to the formation of the bulk Ir$_n^0$ phase, whose fraction increases as the iridium content increases. This phase predominates in the samples with 2.5 wt.% iridium.

Key words: iridium, superacids, sulfated zirconia, metal—support interaction; diffuse-reflectance IR spectroscopy.

Among new catalytic systems used for the activation of light alkanes,[1-3] superacidic SO_4/ZrO_2-supported catalysts promoted by different metals are of special interest. However, several key problems related to the nature of their catalytic activity remain unsolved. Therefore, the study of the metal—support interaction can be important for understanding the nature and properties of SO_4/ZrO_2-supported catalysts and their activity in the isomerization of *n*-alkanes.[4,5]

Unlike Pt-, Pd-, and Ni-containing catalysts, oxide, and zeolite systems promoted by iridium are studied insufficiently, although in several reactions they are highly competitive with conventional catalytic systems.[6] In this work, we studied the properties of iridium supported on the superacidic SO_4/ZrO_2 system, and the states of iridium supported on promoted and unpromoted ZrO_2 are compared.

It has been previously shown for ZrO_2 samples containing platinum,[7] rhodium,[8] palladium,[9] and nickel[10] that modification by SO_4^{2-} ions stabilizes positively charged forms M^{n+} ($n > 0$) and favors the formation of partially charged forms of the reduced component ($M^{\delta+}$). The systems become more stable to reduction. The effect of the support can appear as the interaction of active surface sites with supported metals. The starting SO_4 groups, products of their reduction, and superacidic protons affect directly the state of the metal, which results in the formation of metal species with an excess positive charge.

Thus, this work continues the study of the interaction of transition metals with superacidic SO_4/ZrO_2 support.

Experimental

Preparation of Ir/ZrO$_2$. Samples of 0.5% Ir/ZrO$_2$ were prepared by impregnation of the starting Zr(OH)$_4$ (S_{sp} = 150 m^2 g^{-1}, Magnesium Electron Co., grade XZ0706/03) with an aqueous solution of [Ir(NH$_3$)$_5$Cl]Cl$_2$. The catalyst was dried at 120 °C for 6 h and calcined for 2 h in a dry air flow at 500 °C.

Preparation of Ir/SO$_4$/ZrO$_2$. Catalyst samples were prepared by impregnation in two stages. At the first stage, Zr(OH)$_4$ was treated with a 1 N aqueous solution of H$_2$SO$_4$ to attain a concentration of SO$_4^{2-}$ of 5 wt.%. The samples were dried at 120 °C and calcined at 650 °C for 2 h in an air flow. Then 0.1, 0.5, or 2.5 wt.% Ir was added from an aqueous solution of [Ir(NH$_3$)$_5$Cl]Cl$_2$. The catalyst was dried at 120 °C for 6 h and calcined in an air flow at 400 °C for 2 h.

Before measurements, samples with particle sizes of 0.2—0.5 mm were loaded in a quartz reactor with CaF$_2$ window for recording IR spectra and activated *in vacuo* at 400 °C. After the residual pressure of 10^{-4} Torr was achieved, the samples were treated with O$_2$ (30 Torr) at 400 °C to prevent reduction of iridium and SO$_4^{2-}$ ions. Then the system was evacuated again and cooled to room temperature.

To obtain iridium in the reduced form, the catalysts were treated in a hydrogen flow (30 mL min^{-1}) at 200—300 °C for 2 h. Then the samples were evacuated at the temperature of reduction to a pressure of 10^{-4} Torr and cooled to room temperature.

Recording IR spectra. Carbon monoxide (20 Torr) was adsorbed on the pre-activated and evacuated samples. IR spectroscopic studies were carried out using a Nicolet Impact 410 spectrophotometer equipped with a diffuse-reflectance attachment.[11] After recording the spectrum, the sample was evacuated at a stepwise temperature increase with an increment of 50 °C, and the spectra were recorded at each temperature of evacuation.

The spectra were processed using the Kubelka—Munk equation by the OMNIC® program according to the known procedures.[12,13] The computer simulation also included smoothing the spectra, subtraction of the background, and deconvolution of the spectra by their approximation with doublets, which represented a combination of mixed Gauss—Lorentz functions.

Results and Discussion

Ir/ZrO₂ system

The diffuse-reflectance IR spectra of CO (20 Torr) adsorbed on the 0.5% Ir/ZrO₂ sample reduced at 200 °C are presented in Fig. 1. After adsorption of CO on the surface, absorption bands (AB) at νCO 2190, 2075, and 2010 cm⁻¹ appear. The first band is characteristic of CO complexes with Lewis acid sites (LAS) at the ZrO₂ surface.[14] The other bands are assigned to various CO complexes with Ir. The asymmetry of the high-frequency AB at 2075 cm⁻¹ indicates its complex character. The deconvolution of the spectrum in the frequency range of iridium carbonyls makes it possible to distinguish three components with maxima at 2075, 2050, and 2010 cm⁻¹. According to the published data,[15,16] the AB at 2050 cm⁻¹ can be assigned to CO complexes with bulk metal Ir_n^0 particles. The bands at 2075 and 2010 cm⁻¹ can be attributed to antisymmetric and symmetric vibrations of the dicarbonyl fragments, which have been observed previously for the $Ir_4(CO)_{12}$ clusters.[17] An alternative explanation of the appearance of the AB involves the formation of a geminal dicarbonyl $Ir^+(CO)_2$ complex.[15,18] However, it has been shown that this complex is formed due to secondary redox processes of interaction of the Ir_n^0 particles with CO and OH groups on the oxide support surface rather than due to the incomplete reduction of iridium.[15] After the 0.5% Ir/ZrO₂ sample was reduced at 200 °C, all iridium exists as Ir^0 species.
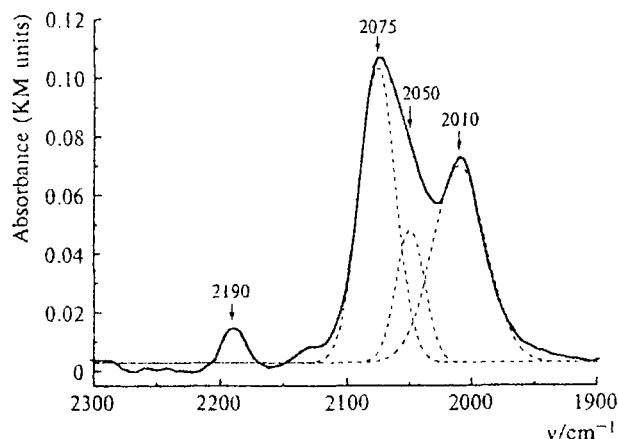

Fig. 1. IR spectrum of CO (20 Torr) adsorbed on the 0.5% Ir/ZrO₂ sample reduced at 200 °C. Dotted line shows the deconvolution of the spectrum into components.

Ir/SO₄/ZrO₂ system

The IR spectra of CO adsorbed on the Ir/SO₄/ZrO₂ samples containing 0.1—2.5 wt.% Ir and reduced at 200 °C are presented in Fig. 2. After adsorption of CO, the spectrum of the 0.5% Ir/SO₄/ZrO₂ system (see Fig. 2, a) contains two AB at 2195 and 2080 cm⁻¹. The low-frequency band is complex, and after deconvolution of the spectrum, four components with maxima at 2165, 2135, 2105, and 2075 cm⁻¹ can be distinguished.

The comparison of the frequencies of vibrations of CO adsorbed on the Ir/SO₄/ZrO₂ sample with our earlier results on Ir/ZrO₂ and the published data shows that the presence of SO₄ groups affects the behavior of iridium. The spectra of CO adsorbed on the Ir/SO₄/ZrO₂ sample exhibit strong AB in the high-frequency region (>2120 cm⁻¹), whereas no AB is present in the frequency region below 2030 cm⁻¹, which is characteristic of $Ir_4(CO)_{12}$ and $Ir_6(CO)_{16}$ clusters with CO occupying positions of bridged ligands.[17,19] This probably indicates that no formation of the Ir_4 and Ir_6 clusters in the classic form occurs. The absence of AB in the 2030—2000 cm⁻¹ region is a consequence of the fact that no $Ir^+(CO)_2$ complexes are formed. This indicates the specificity of the formation of the charged SO₄/ZrO₂-supported iridium carbonyl complexes.

The preliminary analysis shows that bands with νCO >2120 cm⁻¹ can characterize surface CO complexes with iridium ions carrying a charge higher than 1+. At the same time, the vibrations of CO adsorbed on the Ir^{m+} particles ($0 \le m < 1$) contribute to the formation of a broad AB in the region of 2075—2120 cm⁻¹.

To investigate in more detail the compounds formed, we studied the effect of the metal concentration, temperature of reduction, and conditions of thermal evacuation on the spectral parameters of CO adsorbed on the Ir/SO₄/ZrO₂ samples.

The comparison of Figs. 2, b and c shows that an increase in the metal content to 2.5 wt.% results in an increase in the intensity of AB at 2135 and 2075 cm⁻¹; and the ratio of intensities of the bands at 2100 and 2075 cm⁻¹ changes toward an increase in the relative intensity of AB at 2075 cm⁻¹.

By contrast, a decrease in the metal concentration to 0.1 wt.% (see Fig. 2, c) leads to a decrease in the intensity of AB at 2075 cm⁻¹ as compared to that of other bands. The spectrum exhibits a broad AB at ~2100 cm⁻¹, and AB at 2195 and 2165 cm⁻¹ predominate. At the same time, it must be noted that the iridium concentration affects the ratio between the intensities of AB at 2195 and 2165 cm⁻¹ and AB at 2075 cm⁻¹, on the one hand, but the absolute intensity of the bands at 2195 and 2165 cm⁻¹ remains approximately the same for all systems regardless of the metal content, on the other hand.

A decrease in the coverage of the surface with CO molecules during evacuation of the samples results in considerable changes in the spectral pattern (see Fig. 2,
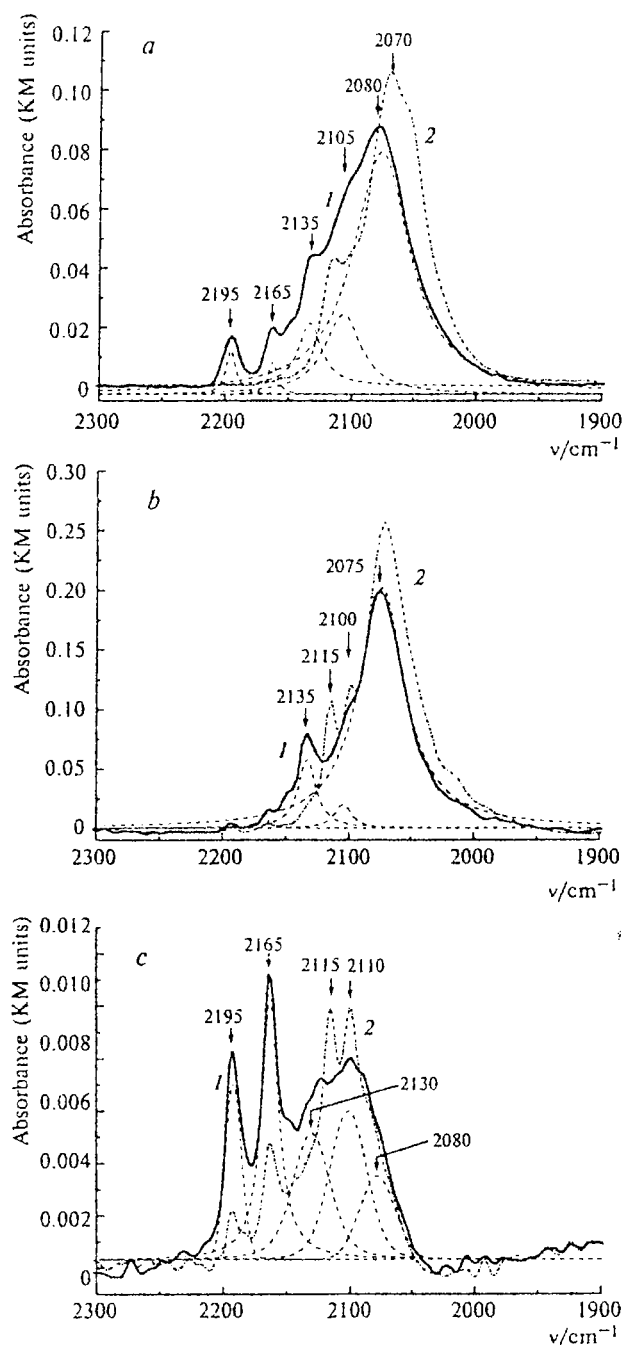
Fig. 2. IR spectrum of CO (20 Torr) adsorbed on the 0.5% Ir/SO$_4$/ZrO$_2$ (a), 2.5% Ir/SO$_4$/ZrO$_2$ (b), and 0.1% Ir/SO$_4$/ZrO$_2$ (c) catalysts reduced at 200 °C before (1) and after (2) evacuation at 20 °C. Dotted line shows the deconvolution of the spectrum into components.

a—c, spectra 2). After evacuation at 20 °C, the spectra of all samples exhibit a decrease in the intensity of AB at 2195, 2165, and 2135 cm^{-1}, which is characteristic of CO complexes with metal ions.[20] The presence of the

AB at 2195 cm^{-1} after evacuation indicates that this band belongs mainly to CO complexes with Ir ions, since AB of vibrations of CO with LAS of SO$_4$/ZrO$_2$, which are also observed in this region, disappear already after evacuation at 20 °C.[7] The constant ratio of the intensities of AB at 2195 and 2165 cm^{-1} allows us to assign them to an adsorption complex, in particular, the Ir^{3+}(CO)$_2$ complex described previously for the zeolite systems.[21] Since the intensity of AB of the Ir^{3+}(CO)$_2$ complexes is almost independent of the metal concentration, it can be assumed that surface acid sites associated with sulfate ions are responsible for the formation of these species. The formation of geminal dicarbonyl complexes indicates the small size of the particles (in the limiting case with the appearance of single Ir^{3+} ions).

An increase in the intensity of AB at 2115 and 2100 cm^{-1} is observed in the spectra of the samples, and for the systems containing >0.5 wt.% Ir, the intensity of AB at 2070—2075 cm^{-1} increases. This phenomenon was often observed in the spectra of CO adsorbed on metals.[22,23] This is related to the redistribution of adsorbed molecules between various adsorption centers. Most probably, such a redistribution occurs through the transfer of the CO molecules adsorbed on positively charged ions to metal particles to form more stable complexes. CO molecules can be also abstracted from polycarbonyl fragments to form linear monocarbonyl complexes. It can be assumed that similar transformations occur in the case of iridium. Thus, all AB in the 2070—2115 cm^{-1} range are assigned to vibrations of CO on iridium particles with the charge varying from 0 to +1. In this case, AB at 2070—2090 cm^{-1} can be assigned to monomolecular linear CO complexes with particles of the bulk iridium; at the same time, AB at 2100 and 2115 cm^{-1} can be related to polycarbonyl Ir^0(CO)$_n$ complexes (n = 2 or 3). The latters are formed when CO interacts with small particles such as Ir$_4$ or Ir$_6$ clusters, which are the subject to the strong influence of the surface acid sites. This assignment is supported by the fact that an increase in the temperature of evacuation results in an increase in the intensity of AB of the monocarbonyl CO complexes due to a decrease in the concentration of the polycarbonyl complexes.

Higher frequencies of vibrations of the CO complexes with Ir^0 in the Ir/SO$_4$/ZrO$_2$ systems (vCO 2080—2090 cm^{-1}), as compared with the published data (vCO 2050—2070 cm^{-1}),[15,16,18] may indicate the presence of a partial positive charge on the iridium particles, with the magnitude varying with the particle size.

The maximum of the AB at 2135 cm^{-1} lies between the maxima of the bands for the Ir^0(CO)$_n$ and Ir^{3+}(CO)$_2$ complexes; therefore, this AB can be assigned to iridium species with an intermediate oxidation state.

The data on the state of iridium collected from the results of analysis of the IR spectra of CO adsorbed on the Ir/ZrO$_2$ and Ir/SO$_4$/ZrO$_2$ samples are summarized in Table 1. For the SO$_4$/ZrO$_2$-supported iridium sys-

Table 1. Assignment of AB of iridium carbonyl complexes supported on ZrO_2 and SO_4/ZrO_2

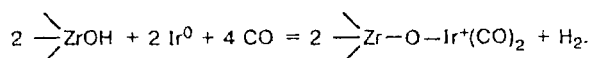| System	vCO/cm^{-1}	State of Ir	Carbonyl complex
Ir/SO$_4$/ZrO$_2$	2195, 2165	3+	Ir^{3+}(CO)$_2$
	2135	2+	Ir^{2+}(CO)
	2115	δ+	Ir$_{4-6}$$^{δ+}(CO)_n$
	2100	δ+	Ir$_{4-6}$$^{δ+}(CO)_n$
	2090	δ+	Ir$_n$$^{δ+}$(CO)
	2070—2075	0	Ir$_n$^{0}(CO)
Ir/ZrO$_2$	2075, 2010	1+	Ir$^+$(CO)$_2$
	2050	0	Ir$_n$^{0}(CO)

tems, as for those with other metals, the stabilization of charged metal forms, the appearance of the Ir$^{δ+}$ particles ($0 < δ < 1$), and an increase in the frequencies of vibrations of CO adsorbed on the Ir^0 particles are observed, as compared to the systems containing no sulfur.

Nature of the metal—support interaction

It has been shown previously[6—9] that processes of three types can occur on the SO_4/ZrO_2 surface in the presence of the metal. First, at a low temperature of reduction, metal microparticles can interact with superacidic protons of the surface. Second, acidic sites of the SO_4/ZrO_2 surface can react with metal compounds (oxides, chlorides, etc.) during oxidative and reductive pre-treatments. This can result in the replacement of superacid protons by metal atoms. The latters can remain bound to other atoms in the M$^{δ+}$ species or exist as ions. The processes of the third type are caused by redox reactions between the SO$_4$ groups, the metal, and the reducing agent (hydrogen) and by the formation of surface metal sulfides. However, their influence becomes noticeable only at reduction temperatures higher than 300 °C.

Analysis of the results of study of the Ir/ZrO$_2$ and Ir/SO$_4$/ZrO$_2$ systems by IR spectroscopy using CO as a probe molecule (see Figs. 1 and 2) suggests the following model of interaction of the SO_4/ZrO_2 surface with supported iridium.

The Ir/ZrO$_2$ system is characterized by the presence of only Ir^0 metal particles, whose interaction with OH groups and CO can form charged Ir$^+$(CO)$_2$ complexes via the reaction[15]

$$2 \;\; \underset{/}{\overset{\backslash}{-}}ZrOH + 2\; Ir^0 + 4\; CO = 2\;\; \underset{/}{\overset{\backslash}{-}}Zr-O-Ir^+(CO)_2 + H_2.$$
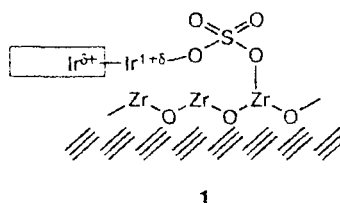
The AB at 2020 cm^{-1} is absent in the spectra of the Ir/SO$_4$/ZrO$_2$ system, which indicates that this process is impossible for oxides promoted by sulfate ions. This can be due to blocking OH groups by the surface SO$_4$
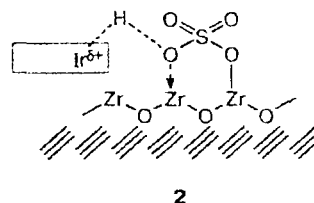
groups. The metal particles on the SO_4/ZrO_2 surface are stabilized, and the main effect of the support, under conditions of mild reduction, is manifested at the metal—support interface. Depending on the particle size and the proximity of acid sites of the support surface, this effect can lead to the formation of various charged iridium forms.

Isolated Ir^{3+} ions are also present on the surface of the reduced Ir/SO$_4$/ZrO$_2$ samples. The low concentration of these ions and the fact that it is almost independent of the metal content are the result of the low concentration of centers of localization of these particles, i.e., acid surface sites.

Large metal particles can interact with the adjacent surface HSO$_4$ groups to form various charged forms of iridium. For example, complexes 1, which are characterized by AB at 2135 cm^{-1}, can appear.

1

When the direct interaction is absent, the effect of acidic protons of the active sites, the formation of complex 2, and the electron-withdrawing effect of the [O=S=O] fragment of the active site are decisive factors. This results in a decrease in the electron density on the metal particles and the formation of metal states with a partial positive charge (Ir$^{δ+}$). This effect is indicated by an increase in the frequency of vibrations of CO adsorbed in the linear form on the metal particles, as compared to vibrations of CO on the Ir/ZrO$_2$ sample.

2

In addition, the samples contain a phase of metallic iridium, which remains virtually unaffected by the surface active sites.

Thus, different states of iridium on the surface, depending on the metal concentration, are observed for the Ir/SO$_4$/ZrO$_2$ system. When the concentration of Ir is of the order of 0.1 wt.%, nearly all iridium is in the state of a strong interaction with the surface and exists in the form of Ir^{3+} ions or small Ir$_n$$^{δ+}$ particles. An increase in the iridium concentration to 0.5 wt.% results in the formation of the free metal phase, whose fraction becomes predominant at a concentration of iridium equal to 2.5 wt.%.

References

1. A. Corma, *Chem. Rev.*, 1995, **95**, 559.
2. X. Song and A. Sayari, *Catal. Rev. Sci. Eng.*, 1996, **38**, 329.
3. T. Okuhara, N. Mizuno, and M. Misono, *Adv. Catal.*, 1996, **41**, 113.
4. L. M. Kustov, T. V. Vasina, A. V. Ivanov, O. V. Masloboishchikova, E. G. Khelkovskaya-Sergeeva, and P. Zeuthen, *Stud. Surf. Sci. Catal.*, 1996, **101**, 821.
5. A. V. Ivanov, T. V. Vasina, O. V. Masloboishchikova, E. G. Khelkovskaya-Sergeeva, L. M. Kustov, and P. Zeuthen, *Kinet. Katal.*, 1998, **39** [*Kinet. Catal.*, 1998, **39** (Engl. Transl.)].
6. M. Hino and K. Arata, *Catal. Lett.*, 1995, **30**, 2.
7. A. V. Ivanov, L. M. Kustov, T. V. Vasina, V. B. Kazansky, and P. Zeuthen, *Kinet. Katal.*, 1997, **38**, 416 [*Kinet. Catal.*, 1997, **38** (Engl. Transl.)].
8. A. V. Ivanov, A. Yu. Stakheev, and L. M. Kustov, *Kinet. Katal.*, 1997, **38**, 718 [*Kinet. Catal.*, 1997, **38** (Engl. Transl.)].
9. A. V. Ivanov and L. M. Kustov, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 57 [*Russ. Chem. Bull.*, 1998, **47**, 55 (Engl. Transl.)].
10. A. V. Ivanov and L. M. Kustov, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 409 [*Russ. Chem. Bull.*, 1998, **47**, 394 (Engl. Transl.)].
11. L. M. Kustov, A. A. Alekseev, V. Yu. Borovkov, and V. B. Kazansky, *Dokl. Akad. Nauk SSSR*, 1981, **261**, 1374 [*Dokl. Chem.*, 1981 (Engl. Transl.)].
12. V. Yu. Borovkov, Doct. Sci. (Chem.) Thesis, Institute of Organic Chemistry of the USSR Acad. Sci., Moscow, 1989 (in Russian).
13. A. S. Medin, Ph. D. (Phys.-Math.) Thesis, Institute of Organic Chemistry of the USSR Acad. Sci., Moscow, 1990 (in Russian).
14. C. Morterra, R. Aschieri, and M. Volante, *Mater. Chem. Phys.*, 1988, **20**, 539.
15. F. Solymosi, E. Novak, and A. Molnar, *J. Phys. Chem.*, 1990, **94**, 7250.
16. F. J. C. M. Toolenaar, A. G. T. M. Bastein, and V. Ponec, *J. Catal.*, 1983, **82**, 35.
17. T. Beutel, S. Kawi, S. K. Purnell, H. Knözinger, and B. C. Gates, *J. Phys. Chem.*, 1993, **97**, 7284.
18. P. Gelin, A. Auroux, Y. Ben Taarit, and P. C. Gravelle, *Appl. Catal.*, 1989, **46**, 227.
19. S. Kawi, J.-R. Chang, and B. C. Gates, *J. Am. Chem. Soc.*, 1993, **115**, 4830.
20. A. A. Davydov, *IK-spektroskopiya v khimii poverkhnostnykh okislov* [*IR Spectroscopy in the Chemistry of Surface Oxides*], Nauka, Sib. Otd., Novosibirsk, 1984 (in Russian).
21. T. V. Voskobojnikov, E. S. Shpiro, H. Landmesser, N. Jaeger, and G. Schulz-Ekloff, *J. Mol. Catal., A., Chem.*, 1995, 299.
22. R. M. Hammaker, S. A. Francis, and R. P. Eischens, *Spectrochim. Acta*, 1965, **21**, 1295.
23. M. Scheffler, *Surf. Sci.*, 1979, **81**, 562.