JOURNAL OF CATALYSIS **116**, 498–505 (1989)

Study of Phosphate-Modified TiO_2 (Anatase)

KONSTANTIN I. HADJIIVANOV, DIMITAR G. KLISSURSKI, AND ANATOLY A. DAVYDOV*

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia 1040, Bulgaria; and
**Institute of Catalysis, Siberian Division of the USSR Academy of Sciences, Novosibirsk 630090, USSR*

Received March 14, 1988; revised November 2, 1988

Pure and phosphate-modified titanium dioxide (anatase) have been studied by IR spectroscopy of probe molecules, X-ray photoelectron spectroscopy, X-ray phase analysis, electron microscopy, etc. It is established that the phosphate anions are strongly bonded to the anatase surface and are stable even at the temperature of anatase–rutile transition. The phosphates cannot be removed by washing with water or diluted acids, but are extracted by basic solutions. The active sites for phosphate adsorption are hydroxyl groups and Lewis acid sites on the anatase surface, whereas part of the c.u.s. Ti^{4+} ions, which exhibit a weak acidity, remains free. Thermal treatment of samples modified by phosphoric acid leads to their dehydroxylation due to the recombination of hydrogen-bonded hydroxyl groups. For samples modified by NaH_2PO_4 part of the hydrogen ions are substituted by Na^+, which leads to "dilution" of the hydroxyls and hinders their recombination. As a result, isolated OH groups, stable at 723 K, exist on the surface. The disappearance of the Lewis acidity on anatase after modification with phosphates allows the assumption that the role of phosphorus as a promoter in some titania-supported catalysts is to block the Ti^{4+} Lewis acid sites.

INTRODUCTION

The surface properties of titania (anatase) strongly depend on the presence of impurities (*1–9*). Thus, a Lewis type acidity is characteristic of pure anatase (*1, 2, 10, 11*), whereas sulfated anatase has strong Brønsted acid sites and belongs to the small number of known superacid catalysts (*3, 9*). A number of investigations deal with phosphorus-containing samples, but there are just a few detailed studies of the effect of adsorbed phosphates (*4, 5*). It is established that phosphate adsorption on TiO_2 from aqueous solutions of H_3PO_4, NaH_2PO_4, and Na_2HPO_4 follows the Langmuir equation (*12*). The maximum coverage depends on the sample used, and the values reported range from 1.27 to 2.34 $PO_4H_2^-/nm^2$. The authors (*12*) are of the opinion that the modification is achieved by an exchange reaction between part of the surface hydroxyl groups and the $H_2PO_4^-$ ions. This point of view is impeached by Munuera *et al.* (*5*) who have observed replacement of part of the adsorbed water by phosphate ions. They explain the results with phosphate adsorption on the (111) anatase face and similar structures. However, this interpretation presupposes exposure of the (111) face mainly, which is not characteristic of the anatase crystals (*13*) and cannot account for surface concentration above 2 $PO_4H_2^-/nm^2$. Elucidation of the localization of phosphate ions and their effect on the surface acidity of anatase can help in clarifying the nature of the active sites on pure anatase as well as some other problems which are important for heterogeneous catalysis, e.g., the mechanism of action of some promoters in titania-supported catalysts.

The present paper represents a comparative study of the surface properties of pure and phosphate-modified anatase by IR spectroscopy of probe molecules, XPS, X-ray phase analysis, atomic absorption analysis, scanning electron microscope, etc.

EXPERIMENTAL

Hydrated titania was prepared by hydrolysis of titanium tetrachloride (Merck, for synthesis) (*14*), prepurified by distillation under argon. After filtering, washing, and

0021-9517/89 $3.00

drying, the precipitate was calcined in air at 573 K for 4 h, washed with hot water to remove residual chlorine ions, and dried at 423 K. The substance obtained (which will further on be denoted by TI-0) had a specific surface area of 190 m^2/g and, according to X-ray data, the structure of anatase.

Samples of TI-0 (5 g each) were suspended in 300 ml 0.1 *M* NaH_2PO_4 solution buffered at pH 4 and 300 ml 0.1 *M* H_3PO_4 solution, respectively. After 20 h the samples were filtered, washed with 5 ml water each, then dried again at 423 K. Part of these samples was calcined in air at 723 K for 1 h, others were pressed into pellets of 20–30 mg/cm^2 to be used in IR experiments. The pellets were treated in an analogous manner in the IR cell: 1 h heating in air at 723 K followed by 1 h treatment *in vacuo* at the same temperature.

For analytical determination of the elemental composition, the samples were dissolved in concentrated H_2SO_4 with addition of $(NH_4)_2SO_4$ during heating. The reagents used (excepting $TiCl_4$) were A.R. The adsorbates also had the necessary purity.

The infrared spectra were recorded with UR-20 and SPECORD-75-IR spectrometers. The X-ray spectra were obtained by a Dron-3 diffractometer using Cu*K*α radiation. The XPS measurements were made with an ESCALAB-MkII (VG Scientific Ltd.) electron spectrometer using a Mg anode as the radiation source ($h\nu$ = 1254.6 eV). The electron microphotographs were taken with a JEOL JSM-T200 scanning electron microscope. The thermal analysis was carried out by a Derivatograph 1500. Atomic absorption measurements were performed by a Zeeman 3030 Perkin–Elmer apparatus with HGA 600 and AS-60, a Zeeman correction of the nonselective absorption being used. The specific surface area was determined by the BET method using conventional low-temperature nitrogen adsorption.

RESULTS

Since the impurities strongly affect the surface properties of anatase, high-purity samples had to be used. The surface composition was checked by XPS. The analysis showed no sulfur and no chlorine impurities. Phosphorus(V) was detected for both modified samples (P 2*s* and P $2p_{3/2}$ peaks at 189.8 and 132.0 eV, respectively). The sample modified by NaH_2PO_4 showed Na^+ (Na KLL Auger peak at 265.0 eV). This indicated that the sodium ion had replaced part of the hydrogen ions on the surface, probably in the hydroxyl groups formed after the modification.

In further consideration we shall use the following symbols: TI-1, anatase; PTI-2, anatase modified by H_3PO_4; and PTI-3, anatase modified by NaH_2PO_4, all of them calcined at 723 K. Some characteristics of the samples used are presented in Table 1.

The Ti : P atomic ratio for the two modified samples is about 14. The much lower ratio of these elements according to XPS analysis shows that phosphorus is located mainly on the oxide surface. The calculated surface concentration of phosphates (according to atomic absorption analysis data) is 4.5 and 3.4 phosphate ions/nm^2 for PTI-2 and PTI-3, respectively. These values are higher than those available in the literature (*4, 5, 12*) concerning the phosphate concentration on the anatase surface.

Irrespective of the relatively high concentration of phosphorus, the X-ray phase analysis of the four samples showed the presence of anatase alone. This confirms the localization of phosphorus on the surface without detectable amounts of a three-dimensional phosphate phase. A similar behavior was shown by anatase samples with a monolayer V_2O_5 coverage (*15*). The assumption for a distribution of the phosphates on the surface is also supported by the electron microphotographs which revealed no existence of two phases in the samples.

The IR spectra of the modified samples, as recorded in a KBr disk (Fig. 1), exhibit, in addition to anatase absorption, a broad peak with a maximum within the range 1030–1010 cm^{-1} and a shoulder at about 1120 cm^{-1}. These bands characterize the

TABLE 1

Some Characteristics of the Samples Investigated

Sample	X-ray phase analysis	S (m^2/g)	P content (%)	Ti : P ratio in the surface layers[a]	Modifier
TI-0	Anatase	190	below 0.05	—	—
TI-1	Anatase	120	below 0.05	—	—
PTI-2	Anatase	116	2.66	3.8	H_3PO_4
PTI-3	Anatase	160	2.70	4.0	NaH_2PO_4

[a] Determined from the ratio between the areas of the Ti $2p_{3/2}$ peak and P $2s$ peak using the corresponding XPS cross sections.

phosphorus–oxygen stretching modes in the phosphate anion (*16*).

It is of interest to trace the stability of adsorbed phosphates in water. There are data that reveal that after washing with water the major part of phosphorus present on anatase is removed (*17, 18*). For that purpose, 0.1 g of PTI-2 was washed with 100 ml water portions and the phosphorus amount in the filtrates was determined by atomic absorption. Analysis showed the presence of a very small amount of phosphorus in the first filtrate only (ca. 1.0 P atoms/nm^2 of the anatase surface). The IR spectrum of the washed sample, recorded in a KBr disk, showed no substantial changes. Sintering of the sample during the thermal treatment probably caused a reduction of the number of active sites for strong phosphate adsorption, and the liberated ions passed into the solution. The remaining phosphate was impossible to remove by extraction according to the method described.

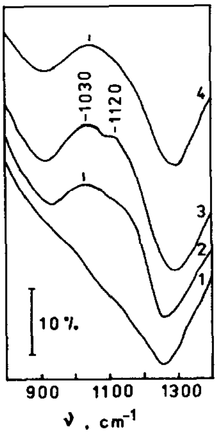


FIG. 1. IR spectra of samples TI-1, PTI-2, and PTI-3, (1), (2), and (3), respectively, and (4), PTI-2 after washing (for the symbols see text). The spectra are recorded in a KBr disk.

Analogous results were obtained during washing with 0.1 *M* H_2SO_4. The amount of phosphorus passing into the solution also corresponds to ca. 1.0 P atoms/nm^2 of the anatase surface.

On the contrary, IR spectroscopy analysis showed that the phosphates were easily extracted with NH_3 solution (lack of the bands at 1030–1010 cm^{-1} in the spectrum of the sample PTI-2 after washing 0.1 g of it with 100 ml 0.1 *M* NH_3 solution). Hence, the phosphate ions can be replaced by OH groups, which indicates that they have been located on c.u.s. Ti^{4+} cations.

The thermal stability was checked by thermal analysis. The DTA curves exhibited no loss of phosphorus up to the temperature of anatase–rutile phase transition (about 1070 K).

The IR spectra of TI-1, PTI-3 (after evacuation at 723 K), and PTI-2 (evacuated at 923 K) samples are presented in Fig. 2. Two types of surface hydroxyl groups are observed on anatase, their maxima being at 3740 and 3700 cm^{-1}. The spectrum of the PTI-3 sample contains a broad band with a maximum centered at 3200 cm^{-1} and a narrow one with a maximum at 3675 cm^{-1}. Both bands characterize O–H stretching modes, the former corresponding to inter-

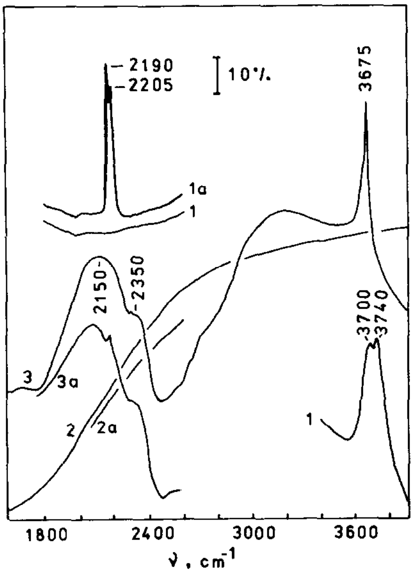


FIG. 2. IR spectra of samples TI-1, PTI-2, and PTI-3, (1), (2), and (3), respectively; spectra (1a), (2a), and (3a) of the same samples are recorded after admitting CO (40 Torr) to them.

acting, and the latter, to isolated hydroxyl groups of the P–O–H type (*19, 20*).

Two other bands with maxima at 2350 and 2150 cm^{-1}, similar in shape to the bands at 1200–1000 cm^{-1} (see also Fig. 1), are observed. They may be assigned to the first overtone of the phosphorus–oxygen stretching modes (*21*). The poor transmittance of the PTI-2 sample in the OH stretching region, due to the strong light scattering, allowed no detailed consideration of the surface hydroxyls in this case.

The CO molecule is very appropriate for the study of the Lewis acidity (*22*). Figure 2 also shows the spectra of the samples after being in contact with 40 Torr (1 Torr = 133.3 N m^{-2}) CO. We found two types of Lewis acid sites on the TI-1 sample (ν_{CO} of the corresponding Ti–CO complexes at 2205 and 2190 cm^{-1}, respectively), which is in agreement with data from the literature (*1, 2, 10, 11*). The surface of both modified samples showed no Lewis acidity (only a very weak peak at 2205 cm^{-1} in the case of PTI-3 being observed). Additional studies revealed the blocking of the Lewis acid sites to be very stable: no Lewis acidity was detected even after 1 h of thermal treatment at 923 K *in vacuo* or reduction under CO (40 Torr) at the same temperature.

DISCUSSION

The cleavage planes (001), (011), and (101) are characteristic of anatase crystals, but the planes (100), (010), (110), (111), (112), (113), and (107) can also be exposed on the surface to a lower extent (*13*). It is believed that the surface arrangement of the ions on the anatase is the same as in the bulk (*23*), which allows modeling the surface. Table 2 shows the concentration of c.u.s. titanium ions on different planes characteristic of anatase.

Obviously, the mean concentration of c.u.s. Ti^{4+} on the anatase surface is 5–6 Ti^{4+}/nm^2. The phosphate concentration in our PTI-2 sample, after extraction of the weakly bound ions, is 3.5 $PO_4H_2^-/nm^2$, i.e., less than one phosphate ion per c.u.s. Ti^{4+} from the surface. If one phosphate ion forms bonds with two c.u.s. Ti^{4+} simultaneously, the phosphate concentration should be ca. 2.5 $PO_4H_2^-/nm^2$. This is lower than the concentration measured for our samples and considerably higher than that reported by Flaig-Baumann *et al.* (*12*) and Munuera *et al.* (*5*). Most likely one phosphate ion is connected to one c.u.s. Ti^{4+} and phosphates located on definite anatase planes. Thus, the phosphorus uptake concentration will strongly depend on the sample morphology.

Using IR spectroscopy data concerning the kind and concentration of surface compounds on anatase and their dependence on the sample morphology (*2*), and taking into account the effect of the coordination state of the ligands on the electron acceptor properties of the c.u.s. cations (*24*), in previous papers we divided the Ti^{4+} ions on the anatase surface into several groups (see Fig. 3.).

1. Five-coordinated Ti^{4+} forming acid–basic rows with the c.u.s. oxygen anions.

TABLE 2

Concentration of c.u.s. Ti^{4+} on Some Anatase Planes

Plane	(001)	(101), (011)	(110)	(100), (010)	(111)	(113)
Ti^{4+}/nm^2	7.0	5.3	4.1	6.0	5.8	5.8

They are situated mainly on the (001) and (112) faces and are inactive toward CO adsorption at room temperature.

2. Five-coordinated Ti^{4+} belonging to acid–basic pairs.[1] They lie on the (101), (011), (100), and (010) faces and represent the first type of Lewis acid sites (ν_{co} of adsorbed CO at 2190 cm^{-1}).

3. Four-coordinated Ti^{4+}. These are the c.u.s. cations from the (110) face and from some edges as well as part of the cations from (111) and (113) faces. They are second type Lewis acid sites (ν_{co} of the corresponding Ti–CO complexes at 2205 cm^{-1}).

4. Titanium ions which are sites for the localization of surface hydroxyl groups. They are situated mainly at the edges of the (001) face and at some crystal lattice defects.

As a result of our IR spectroscopy studies on CO adsorption, complete blocking of the Lewis acid sites by phosphates was established. This means that the latter are localized on faces with Lewis acidity. Since the phosphates do not cover the whole anatase surface, the inert (001) and (112) faces and their analogous structures remain free. This is also confirmed by results obtained by other authors. Using the TPD technique, Munuera *et al.* (*5*) studied the water desorption from pure and KH_2PO_4-modified anatase. Two forms of adsorbed water, with maxima of the TPD peaks at 125 and 325°C (398 and 598 K), respectively, are observed on the pure anatase surface. The modification leads to the complete disappearance of the high-temperature peak, whereas the position, shape, and size of the low-temperature one remain the same. These results can only be due to the fact that water adsorption proceeds on two types of faces differing in surface acidity. The disappearance of the high-temperature peak after modification shows that the phosphates have been adsorbed on the faces characterized by a strong Lewis acidity, and as a result the active sites have been blocked. In view of the low thermal stability of the weakly bound water (its evolution beginning at ca. 300 K), as well as the fact that after modification the Lewis acid sites able to form stable M–CO type complexes at room temperature are absent, we are of the opinion that the low-temperature peak is produced by water adsorbed on the (001) and (112) faces. Hence, the phosphates are localized on some of the side crystal faces, such as (101), (011), (110),

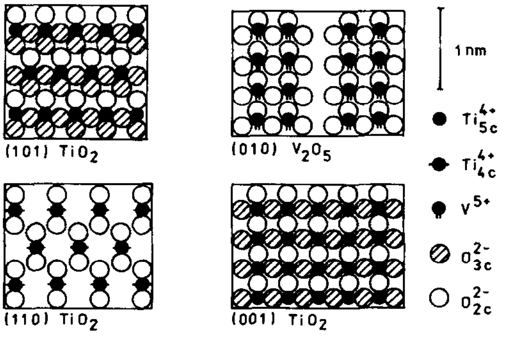


FIG. 3. Scheme of some crystallographic planes of anatase and V_2O_5. The subscripts indicate the coordination number of the corresponding ion.

---

[1] The acidity of these ions is higher than that of the previous type irrespective of their equal coordination numbers. This is due to the fact that their charge is compensated by ligands with a weaker electronegativity; i.e., there is only one c.u.s. oxygen ion in their first coordination sphere. For details see Ref. (*24*).

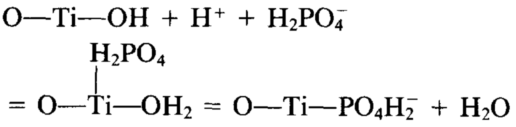
(111), (113), (100), and (010), while the (001) and (112) faces and their analogous structures are not occupied by them. The disappearance of the hydroxyl groups typical of our TI-1 sample (bands at 3740 and 3700 cm^{-1}) after modification shows that the titanium cations, to which they had been bonded, were also sites for phosphate adsorption.

The IR spectra of the modified samples show no bands in the 1300–1200 and 2600–2400 cm^{-1} regions where the P=O double bond and the corresponding overtones are expected (*25*). Hence, the electrons in the phosphates are delocalized. The band at 3675 cm^{-1}, attributed to P–O–H groups, is not observed in the spectrum of the PTI-2 sample. It seems reasonable to assume that the exchange of part of the H$^+$ from the hydroxyls with Na$^+$ leads to "dilution" of the OH groups and hinders their recombination according to the reaction

$$2\ OH^-_{surf.} \rightarrow O^{2-}_{surf.} + H_2O$$

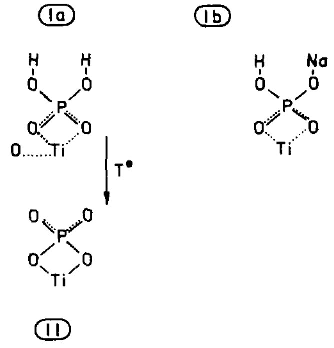
The band at 3200 cm^{-1} in the spectrum of PTI-3 indicates that some residual hydrogen-bonded hydroxyl groups are present on the sample surface. Most likely they are of the (POH). . .(TiOH). . .(POH). . . type, since the geminal hydroxyls, P(OH)$_2$, are thought to absorb near 3600 cm^{-1} (*19*).

The structures of phosphates adsorbed on anatase are still not clear. Flaig-Baumann *et al.* (*12*) proposed an adsorption mechanism consisting in an exchange reaction between the surface hydroxyl groups and the H$_2$PO$_4^-$ in the solution (at pH ≤7 the phosphoric acid is dissociated to the first degree only). The interaction can be presented as



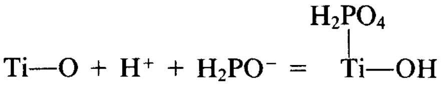
$$\begin{aligned} &O{-}Ti{-}OH + H^+ + H_2PO_4^- \\ &= O{-}\overset{\overset{\displaystyle H_2PO_4}{|}}{Ti}{-}OH_2 = O{-}Ti{-}PO_4H_2^- + H_2O \end{aligned}$$

The structures in Scheme 1 can be proposed in this case, both before and after dehydration during the thermal treatment and with different degrees of exchange with Na$^+$.



SCHEME 1

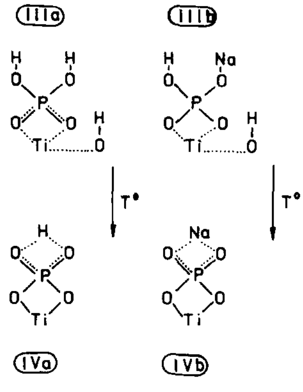
In the case when the phosphates block the Lewis acid sites, the adsorption has to proceed according to the mechanism



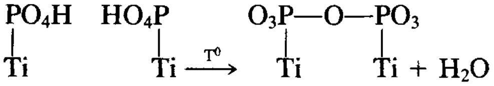
$$Ti{-}O + H^+ + H_2PO^- = \overset{\overset{\displaystyle H_2PO_4}{|}}{Ti}{-}OH$$

The respective structures are shown in Scheme 2.

The structure IVa, characterized by a delocalized proton, is not directly evidenced by our experimental data. Its presence may be accepted by analogy with structures with a delocalized proton, which have been proposed for sulfates (*3*) and for monolayer vanadia coverage (*17*) on anatase. It is possible that further dehydroxylation would lead to bridged structures according to the reaction



SCHEME 2



$$\begin{array}{cc} \text{PO}_4\text{H} & \text{HO}_4\text{P} \\ | & | \\ \text{Ti} & \text{Ti} \end{array} \xrightarrow{T^0} \begin{array}{ccc} \text{O}_3\text{P} & \text{—O—} & \text{PO}_3 \\ | & & | \\ \text{Ti} & & \text{Ti} \end{array} + H_2O$$

Figure 4 shows a probable scheme for structures IVa on a row of c.u.s. titanium ions from the (101) anatase plane, the symmetry of the phosphate ions and the distances between the atoms being taken into account.

The results obtained allowed us to propose a new hypothesis for the mechanism of action of phosphorus as a promoter in vanadia–titania catalysts. Recent investigations on the V_2O_5/TiO_2 system by high-resolution electron microscopy (*26*) have shown that V_2O_5 is not uniformly distributed on the anatase surface. IR spectroscopy of probe molecules on a grafted vanadia–titania catalyst has shown that a large part of its surface area belongs to the support (*8*). Titanium cations are present on the surface in a considerable concentration even with a vanadia coverage close to a monolayer (*27*) or exceeding in quantity a monolayer (*28*). Since the c.u.s. Ti^{4+} ions favor the complete combustion of the partial oxidation products in *o*-xylene conversion (*15*), the system described should have a low selectivity. The addition of phosphorus would lead to blocking of the Ti^{4+} Lewis acid sites and will be accompanied by an increase in selectivity of the catalysts. The alkali metals probably neutralize the Brønsted acidity generated after modification (*4*), which could also lead to parasitic reactions. Similar replacement of the H^+ from the POH groups in the zirconium phosphate catalyst by Cs^+ has led to complete poisoning of the catalyst with respect to the isomerization of but-1-ene (*19*).

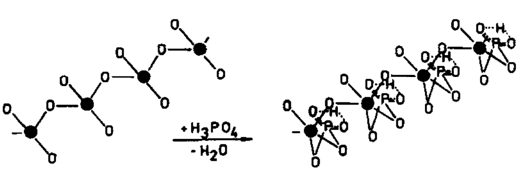


FIG. 4. Scheme of phosphate ions adsorbed on the (101) anatase plane.

Vejux and Courtine (*29*) noted the similarity between the (010) plane of V_2O_5 and the anatase surface, but this similarity is most pronounced with the (001) plane of anatase (Fig. 3). In the case of an industrial catalyst, the epitaxial growth of V_2O_5 probably occurs predominantly on this plane, while the Ti^{4+} Lewis acid sites on the other faces are blocked by the promoters. Only this distribution would have a positive effect. This also could explain the low selectivity of V_2O_5/TiO_2 catalysts when the promoters are distributed in vanadia (*18, 30*). The above hypothesis satisfactorily explains our previous results (*31*) on the decrease in selectivity, after reduction of phosphorus concentration, of vanadia–titania catalysts for the oxidation of *o*-xylene to phthalic anhydride.

ACKNOWLEDGMENTS

The authors thank Dr. I. Karadjova and Dr. G. Tyuliev for their help with the atomic absorption and XPS experiments.

REFERENCES

1. Busca, G., Saussey, H., Saur, O., Lavalley, J. C., and Lorenzelli, V., *Appl. Catal.* **14,** 245 (1985).

2. Hadjiivanov, K., Klissurski, D., and Davydov, A., *Kinet. Katal.* [In Russian] **29,** 161 (1988); *in* "Proceedings, 6th International Symposium on Heterogeneous Catalysts, Sofia, 1987," Part I, p. 365.

3. Saur, O., Bensitel, M., Mohammed Saad, A. B., Lavalley, J. C., Tripp, C. P., and Morrow, B. A., *J. Catal.* **99,** 104 (1986); Hadjiivanov, K., and Davydov, A., *Kinet. Katal.* **29,** 460 (1988). [In Russian]

4. Cornejo, J., Steinle, J., and Boehm, H. P., *Naturforsch. B* **33,** 1238 (1978).

5. Munuera, G., Moreno, F., and Prieto, J. A., *Z. Phys. Chem.* **78,** 113 (1972).

6. Al-Mashta, F., Sheppard, N., and Davanzo, C.U., *Mater. Chem. Phys.* **13,** 315 (1985).

7. Busca, G., and Ramis, G., *Appl. Surf. Sci.* **27,** 114 (1986).

8. Busca, G., Marchetti, L., Centi, G., and Trifirò, F., *J. Chem. Soc. Faraday Trans. 1* **81,** 1003 (1985).

9. Arata, K., and Hino, M., *in* "Proceedings, 7th Soviet–Japan Symposium on Catalysis, Irkutsk, 1-7 July, 1983," p. 7. Novosibirsk, 1983.

10. Primet, M., Pichat, P., and Mathieu, M., *J. Phys. Chem.* **75,** 1216, 1221 (1971).

11. Davydov, A., *Adsorpts. Adsorbenty* **5,** 83 (1977). [In Russian]
12. Flaig-Baumann, R., Hermann, M., and Boehm, H. P., *Z. Anorg. Allg. Chem.* **372,** 296 (1970).
13. Kostov, I., "Mineralogy." Nauka i Izkustvo, Sofia, 1973.
14. "Handbook of Inorganic Synthesis" (G. Brauer, Ed.), Vol. 4. Mir, Moscow, 1985.
15. Wasch, I. E., Saleh, R. Y., Chan, S. S., and Chersich, C. C., *Appl. Catal.* **15,** 339 (1985).
16. Nakamoto, K., "IR Spectra of Inorganic and Coordination Compounds." Mir, Moscow, 1966.
17. Bond, C. C., Zurita, J. P., Flamerz, S., Gellings, P. J., Bosch, H., van Ommen, J. G., and Kip, B. J., *Appl. Catal.* **22,** 361 (1986).
18. van Hengstum, A. J., Pranger, J., van Ommen, J. G., and Gellings, P. J., *Appl. Catal.* **11,** 313 (1984).
19. Busca, G., Lorenzelli, V., Galli, P., La Ginestra, A., and Patrono., *J. Chem. Soc. Faraday Trans. 1* **83,** 853 (1987).
20. Busca, G., Centi, G., Trifirò, F., and Lorenzelli, V., *J. Phys. Chem.* **90,** 1337 (1986).
21. Busca, G., and Lavalley, J. C., *Spectrochim. Acta, Part A* **42,** 443 (1986).
22. Davydov, A., "IR Spectroscopy Applied to Surface Chemistry of Oxides." Nauka, Novosibirsk, 1984.
23. Ziolkowski, J., *J. Catal.* **84,** 317 (1983).
24. Hadjiivanov, K., Klissurski, D., and Davydov, A., *J. Chem. Soc. Faraday Trans. 1* **84,** 37 (1988).
25. Smith, A., "Applied IR Spectroscopy." Mir, Moscow, 1982.
26. Kang, Z. C., and Bao, Q. X., *Appl. Catal.* **26,** 251 (1986).
27. Busca, G., *Langmuir* **2,** 577 (1986).
28. Miyata, H., Nakagawa, Y., Ono, T., and Kubokawa, Y., *Chem. Soc. Japan Chem. Lett.*, 1141 (1983).
29. Vejux, A., and Courtine, P., *J. Solid State Chem.* **23,** 93 (1978).
30. Haase, R., Illgen, U., Scheve, J., and Schulz, I. W., *Appl. Catal.* **19,** 13 (1985).
31. Nikolov, V., Klissurski, D., and Hadjiivanov, K., *in* "Proceedings, 4th International Symposium Catalyst Deactivation, Antwerp, Sept. 29–Oct. 1, 1987" (B. Delmon and G. F. Froment, Eds.), p. 173. Elsevier, Amsterdam, 1987.