Surface and Catalytic Properties of Cerium Oxide

Tsutomu Yamaguchi, Norimasa Ikeda, Hideshi Hattori, and Kozo Tanabe

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, Japan

The acid–base and oxidizing–reducing properties of cerium oxide evacuated or treated with hydrogen after evacuation at various temperatures and the catalytic activity for the isomerization of 1-butene were studied. No correlation was found between the oxidizing or reducing property and the catalytic activity. On the other hand, the activity was lost by the additions of both acidic carbon dioxide and basic ammonia molecules. The ratio of cis-2-butene to trans-2-butene was found to be high (4–6). The active sites have been concluded to be acid–base pair sites, though basic sites play a main role. The experiment on coisomerization of cis-2-butene-d_0/d_8 revealed that the isomerization proceeds intramolecularly via π-allylic carbanion intermediates. The two activity maxima appearing on pretreatment at 600 and 800°C are considered due to the dehydration and/or decarboxylation and the structural change of cerium oxide, respectively.

INTRODUCTION

In a series of lanthanide oxides, CeO_2 has the highest activity in the catalytic oxidation of butane (*1*), and the result has been interpreted in terms of the lowest stability of the tetravalent ion of cerium, which has the lowest fourth ionization potential. Though the CeO_2 catalyst prepared from its nitrate was active for the hydrogenation of 1,3-butadiene at room temperature (*2*) but not for the hydrogenation of ethylene (*3*), the catalyst prepared from its chloride did not catalyze the former reaction, while it did when cyclohexadiene was used as a hydrogen donor (*4*). The hydrogenation activity was enhanced by reducing the catalyst with hydrogen (*2, 3*). For these reactions, the oxidizing–reducing property on CeO_2 is supposed to play an important role.

On the other hand, high selectivity of CeO_2 for the formation of α-olefin was found in the dehydration of 2-butanol (*5*) and a mechanistic work was reported in which a deuterium tracer method (*6*), which indicates the cooperation of acidic and basic sites of the catalyst, was used.

Cerium oxide seems to be an interesting compound for which to investigate a corre-

lation between acid–base or oxidizing–reducing properties and catalytic activities. However, no surface property of CeO_2 has been measured up to the present. The present work deals with the role of an acid–base property of CeO_2 for the isomerization of butene and with the contribution of a redox property to the reaction. A tracer study has also been made to elucidate the nature of the active site and the reaction mechanism.

EXPERIMENTAL

Cerium hydroxide was prepared by hydrolysis of cerium nitrate by ammonia water. The precipitate was washed and dried in air at 100°C for 24 h. This was used for the reaction after evacuation at desired temperatures for 2 h (designated by CeO_2-E), or successive treatment with 10 Torr of H_2 for 2 h and the following evacuation at the same temperatures for 2 h (designated by CeO_2-H).

Surface area was measured by BET method by using N_2 as an adsorbent. X-Ray diffraction patterns were recorded on a Toshiba ADG-301 diffractometer with a powdered sample, using $CuK\alpha$ as a radiation source.

1-Butene was purified by passing through 4-A molecular sieves kept at −78°C. Perdeuterated cis-2-butene was prepared by the exchange of the light butene with D_2 over MgO. Perylene and nitrobenzene were used without further purifications. Oxygen, CO_2, and NH_3 gases were purified by passing through 4-A molecular sieves.

The isomerization reaction of 1-butene was carried out at 50°C in a closed recirculation reactor with 300 ml of inside volume. The reaction rate and the selectivity were obtained from the initial rate of the disappearance of 1-butene and by extrapolating the ratio of cis-2-butene/trans-2-butene (cis/trans) to zero conversion, respectively.

A microcatalytic pulse reactor was employed for the coisomerization of cis-2-butene-d_0/d_8 at 80°C. The butenes produced were separated gas chromatographically and subjected to a mass spectrometric analysis. The exchange reaction between 1-butene and D_2 was carried out in a closed recirculating reactor at 50°C by using 50 Torr of both butene and D_2.

In poisoning experiments, the catalyst was exposed to 10 Torr of O_2, CO_2, or NH_3 for 10 min at room temperature, followed by evacuation for 30 min at the same temperature, and then the isomerization reaction was started.

EPR study was carried out for CeO₂-H on which O_2, perylene, or nitrobenzene was adsorbed. Oxygen and perylene were adsorbed at room temperature and nitrobenzene was admitted at 100°C.

RESULTS AND DISCUSSION

The variations of the catalytic activity, the selectivity, and the surface area of CeO₂ with pretreatment temperatures are shown in Figs. 1, 2, and 3, respectively. Hydrogen treatment enhanced the reaction by more than one order of magnitude, while little change was observed in the selectivity.
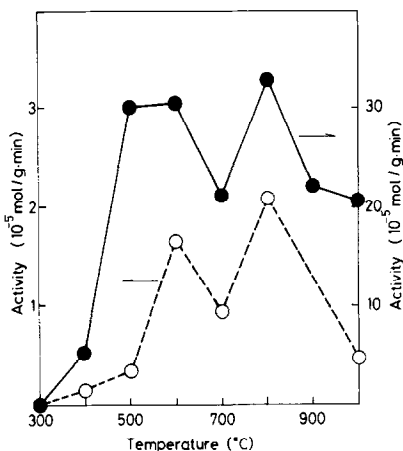
Two maxima were observed at around

FIG. 1. Variation of catalytic activity with pretreatment temperature. ○, CeO₂-E; ●, CeO₂-H (CeO₂-E, CeO₂-H: see text).

600 and 800°C in the variation of the catalytic activity. From thermal desorption data (Fig. 4), most of the water and CO_2 was removed at around 600°C. The loss of water and/or CO_2 from the catalyst surface results in the increase of the surface area up to 500°C and the successive loss leads to the decrease in the surface area by sintering or rearrangement of surface structure. The first maximum in the catalytic activity change may correspond to a dehydration or a decarboxylation process. It is evident from comparison of Fig. 1 with Fig. 3 that the change of the catalytic activity is not
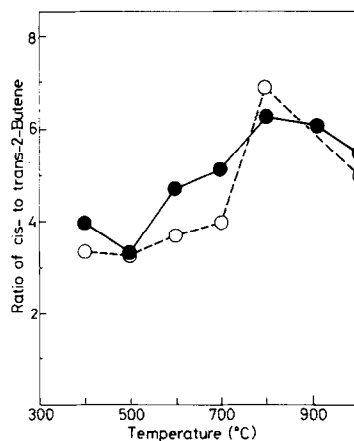

FIG. 2. Variation of selectivity with pretreatment temperature. ○, CeO₂-E; ●, CeO₂-H.
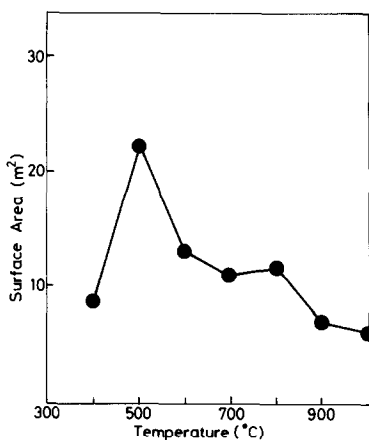
FIG. 3. Variation of surface area with evacuation temperature.

FIG. 5. Variation in relative intensity of EPR signals on CeO_2-E with pretreatment temperature. $\bigcirc$, O_2^-; $\bullet$, anion radical of nitrobenzene; $\blacktriangle$, cation radical of perylene.

simply due to the change of the surface area.

The selectivity varies slightly from 4 at lower temperature to 6 at higher temperature. Hydrogen treatment did not result in a significant change in the selectivity. A high ratio of *cis/trans* indicates that the active site is basic, since the high values were reported for base-catalyzed isomerizations (7–11). The small change in the ratio but the large enhancement in the activity by hydrogen treatment suggests that the number of basic sites is increased by hydrogen treatment.
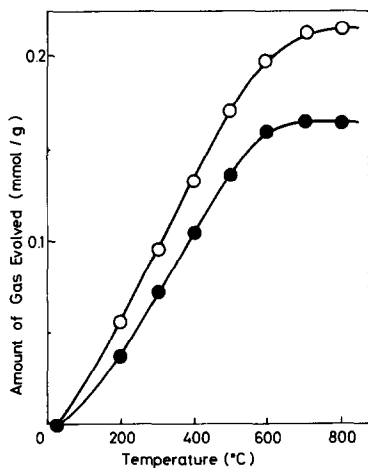
Figures 5 and 6 show the variations in the

relative intensities of the EPR signals on CeO_2-E and -H, respectively. Adsorption of O_2, perylene, and nitrobenzene gave the typical signals of O_2^-, cation radical of perylene, and anion radical of nitrobenzene. Cation radicals of perylene were observed only when CeO_2-E was evacuated at 300°C (Fig. 5). A maximum intensity of the O_2^- signal was obtained on CeO_2-E-500 (evacuated at 500°C) but not on CeO_2-H. On the other hand, a maximum intensity of anion radicals of nitrobenzene was found on both CeO_2-E and CeO_2-H pretreated at

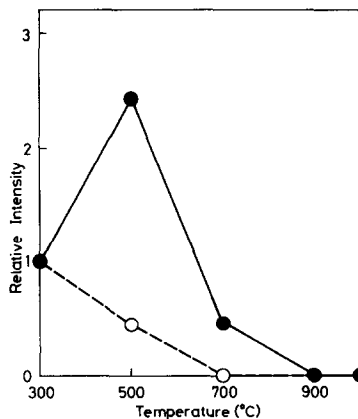FIG. 4. Evolution of H_2O ($\bullet$) and CO_2 ($\bigcirc$) at various temperatures.

FIG. 6. Variation in relative intensities of EPR signals on CeO_2-H with pretreatment temperature. See Fig. 5 for definition of symbols.

500°C. Since the signal intensity was measured in such a way that the sample weights were set equal for all the experiments (80 mg) and the peak-to-peak heights were compared for those samples, the data may be qualitative. However, the changes in the relative intensity with pretreatment temperature do not seem to correspond to the activity variations in Fig. 1: EPR results showed only one maximum at 500°C and they lack the second maximum which appeared in the activity variations. Therefore, it seems unlikely that the catalytic activity can be attributed to the action of the reducing (one electron donating) or the oxidizing (one electron accepting) sites on CeO$_2$-E and CeO$_2$-H.

The effect of hydrogen treatment on the signal intensities of anion radicals of nitrobenzene and oxygen and cation radicals of perylene was found to be small compared with that on the catalytic activity. This suggests again that the sites responsible for the formation of these radicals are not important for the isomerization of 1-butene.

The fact that most of the H$_2$O and CO$_2$ was removed at 600°C, at which an activity maximum was obtained, indicates that the active sites are generated by the removal of CO$_2$ and/or H$_2$O. Evacuation at such a temperature causes Ce cations and oxygen anions to be exposed.

Though basic oxygen anions are considered to be involved in active sites from the results of the reaction kinetics, as in the case of alkaline earth metal oxides, the catalytic activity was poisoned completely, not only with acidic carbon dioxide molecules but also with basic ammonia molecules. The catalytic activities of ThO$_2$ (12) and ZrO$_2$ (13) were also poisoned completely by irreversibly adsorbed ammonia or carbon dioxide at 100°C. On these catalysts, the activity was gradually recovered by removing the poison by elevation of the evacuation temperature. Infrared spectroscopic investigation of ammonia adsorbed on ZrO$_2$ (14) indicated that no physically adsorbed ammonia was found after the

evacuation of 100°C. Though no attempt has been carried out to characterize the adsorbed poisons on CeO$_2$, most of the ammonia or carbon dioxide remaining after the evacuation at 50°C is supposed to be chemically adsorbed species. Thus, it seems plausible to conclude that the active site is an acid–base pair site, since if either part of a pair site is blocked, the reaction does not take place. The concept that acid–base pair sites are responsible for the isomerization was also proposed for η-Al$_2$O$_3$ catalyst on the basis of the experiments on the activity of substituted olefins (15).

The coisomerizations of cis-2-butene-d_0/d_8 over CeO$_2$-E-700 and CeO$_2$-H-700 were carried out to elucidate the reaction mechanism. Isotopic distribution of butene isomers is listed in Table 1. The number of H (or D) atoms exchanged per molecule (AEM value) was calculated from the equation (16),

$$\text{AEM} = \sum_{i=0}^{4} i \cdot N_i + \sum_{i=5}^{8} (8 - i) \cdot N_i,$$

where N_i is the fraction of isotopic species containing i D atoms. The low AEM value in the coisomerization and the negligible deuterium incorporation in the exchange reaction between 1-butene and D$_2$ (Table 2) on the catalysts which are evacuated or treated by hydrogen at different temperatures reveal that the isomerization takes place intramolecularly via a π-allylic carbanion intermediate on acid–base pair sites. A basic site abstracts a hydrogen ion from a butene molecule to initiate the reaction and a π-allylic carbanion may be adsorbed on an acidic site. Such sites are not changed in nature by both an evacuation and a hydrogen reduction at different temperature. The π-allylic carbanion intermediate was postulated for the isomerization reaction over alkaline earth metal oxides (10, 17), La$_2$O$_3$ (18), ThO$_2$ (12), and ZrO$_2$ (13) from the observation of the intramolecular hydrogen transfer and the high cis/trans ratios. Lombardo et al. (19) have discussed exten-

TABLE 1

Isotopic Distribution of Product Isomers in Coisomerization of cis-2-Butene-d_0/d_8 over CeO_2

Catalyst	Amount of each product (%)		Isotopic distribution (%)									AEM[a]	IE[b]
			d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8		
CeO_2-E-700	1	3.1	55.5	5.8	0.6	0	0	0	0.7	7.1	30.2	0.16	1.6
	trans	12.6	49.5	4.0	1.3	0	0	0	1.3	3.6	40.1	0.13	1.2
	cis	84.3	33.8	0.6	0.6	0	0	0	0.4	1.4	63.1	0.04	0.54
	1	3.1	47.5	4.0	0.6	0	0	0	0.8	4.5	42.5	0.11	1.1
	trans	5.6	49.4	8.2	1.2	0	0	0	1.6	10.5	29.0	0.24	1.4
	cis	91.3	33.1	0.8	0.6	0	0	0	0.2	1.4	63.9	0.04	0.53
CeO_2-H-800	1	2.1	34.6	12.7	1.8	0	0	0	1.1	5.4	44.4	0.24	1.0
	trans	9.0	48.4	8.2	1.4	0	0	0	1.9	5.6	34.6	0.20	1.4
	cis	88.9	40.1	0.8	0.5	0	0	0	0.1	1.3	57.2	0.03	0.71

[a] Calculated from $\sum_{i=0}^{4} i \cdot N_i + \sum_{i=5}^{8} (8-i) N_i$.

[b] Calculated from $\left(\sum_{i=0}^{3} N_i + 0.5N_4 \right) / \left(\sum_{i=5}^{8} N_i + 0.5N_4 \right)$, where N_i represents a fraction of the isomer containing i D atoms.

sively the nature of the intermediate species in the n-butene isomerization over ZnO and Al_2O_3 and concluded that the mechanisms for n-butene isomerization over these oxides are the same or very similar at temperatures below 100°C, i.e., π-allylic carbanion being operative. Though additional information will be needed over CeO_2 to make the picture more quantitative, the qualitative picture seems to be the same for ZnO, Al_2O_3, La_2O_3, ThO_2, ZrO_2, and alkaline earth metal oxides.

TABLE 2

Isotopic Distribution of Product Isomers in Exchange Reaction between 1-Butene and D_2

H_2 treatment temp. (°C)	Product	Amount of each product (%)	Isotopic distribution (%)		
			d_0	d_1	d_2
600	1	62.5	98.5	1.5	0
	trans	4.9	100	0	0
	cis	30.9	100	0	0
800	1	60.1	100	0	0
	trans	5.1	100	0	0
	cis	34.4	100	0	0

A successive evacuation at higher temperatures results in a decrease of the surface area or a rearrangement of the surface structure, and this causes a slight decrease in catalytic activity at 700°C.

Evacuation at the temperature higher than 700°C or a hydrogen treatment may cause a formation of nonstoichiometric cerium oxide. Bysse et al. (20) reported that cerium oxide changed its chemical composition from $CeO_{1.985}$ (evacuated) to $CeO_{1.945}$ by a hydrogen treatment, even at 450°C, without changing its surface area. Bevan (21) described the phase change during the partial reduction of CeO_2. The reduction of a typical fluorite structure of CeO_2 (α phase) leads to a new β phase, which has a rhombohedral structure arising from a distortion of the cube along its body diagonal. X-Ray diffraction patterns of CeO_2-E-800 (evacuated at 800°C), CeO_2-H-800, and CeO_2-H-1000 (treated by H_2 at 800 and 1000°C, respectively) are shown in Fig. 7. The diffraction patterns of the oxide treated below 700°C showed a typical CeO_2 structure. As seen in Fig. 7, though CeO_2-E-800 shows typical CeO_2 lines, CeO_2-H-800
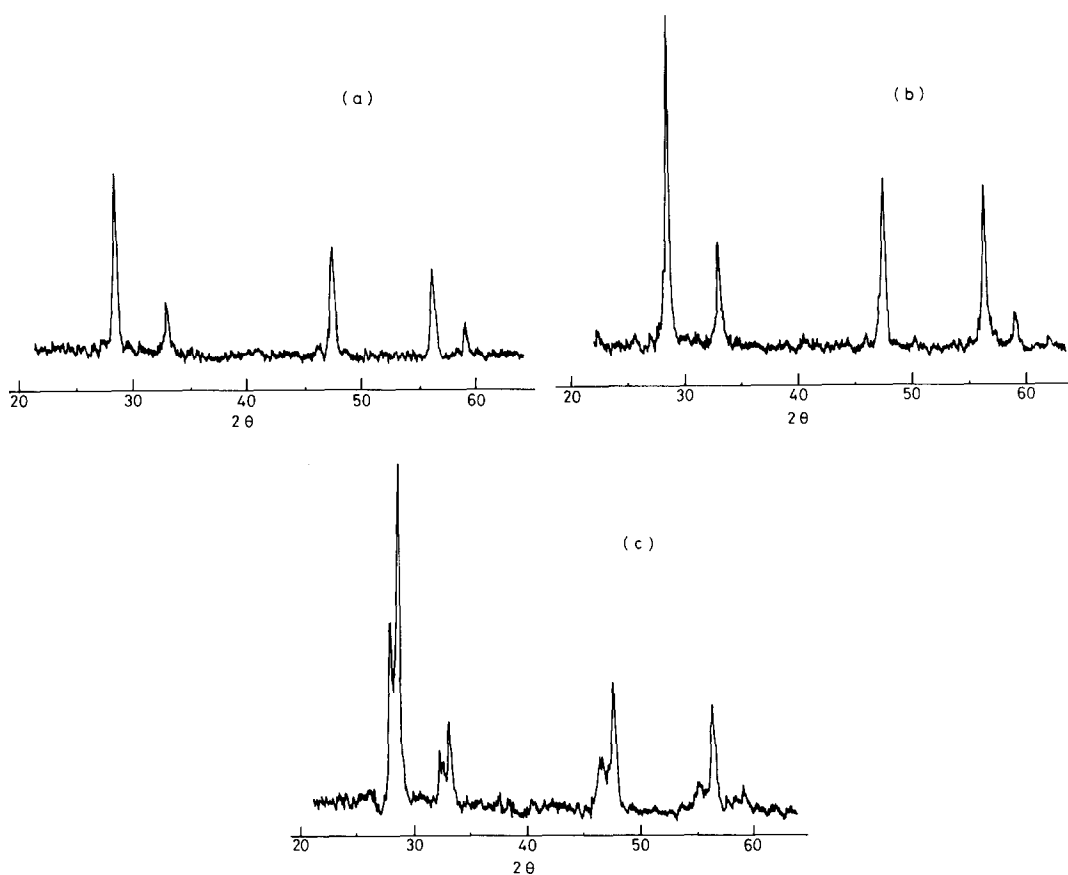
FIG. 7. X-Ray diffraction patterns of CeO_2. (a) CeO_2-E-800; (b) CeO_2-H-800; (c) CeO_2-H-1000.

gives a shoulder at a lower diffraction angle on each line and the tendency is more pronounced in CeO_2-H-1000, in which one can see the distinct doublet on each diffraction line. Taking into consideration Bevan's statement that β phase $(CeO_{1.812})$ is an ordered structure which is derived from eight-unit cells of the CeO_2 structure by the ordered omission of six O^{2-} ions (20), the doublet may be brought about from the slight distortion of the structure, which leads to a change in the atomic distances. The hydrogen reduction is considered to cause the removal of oxygen ions from the fluorite structure and to give anion vacancies, and in extreme cases it gives an ordered structure of β phase. In fact, an addition of 10 Torr of O_2 for 10 min at room temperature to the pretreated catalyst and the following evacuation for 30 min at the

same temperature brought about a complete inhibition of the isomerization. Though a crystallographic investigation was not attempted on the structural reversibility before and after the admission of O_2 to the pretreated catalyst, the poisoning experiment may suggest the importance of the surface irregularities, which were derived from the removal of oxygen atoms by the evacuation at elevated temperatures or by the hydrogen treatment.

The tervalent Ce_2O_3, which is produced by the deep reduction at high temperature, has the rare earth Type-A structure, being isomorphous with La_2O_3. Rosynek and Fox (22) reported the participation of the surface irregularities, such as anion vacancies generated during vacuum calcination of La_2O_3, on the n-butene isomerization. They suggested the existence of such anion va-

cancies on La_2O_3 from the results of infrared (23) and $^{16}O-^{18}O$ isotope exchange studies (24).

Thus we conclude that the sites responsible for the second maximum which appeared at 800°C and for the enhanced activity by hydrogen treatment are acid–base pair sites that arise from the formation of the nonstoichiometric oxide or from the formation of β phase.

REFERENCES

1. Hattori, T., Inoko, J., and Murakami, Y., *J. Catal.* **42**, 60 (1976).
2. Shima, H., unpublished results.
3. Minachev, Kh. M., Khodakov, Yu. S., and Nakhshunov, V. S., *J. Catal.* **49**, 207 (1977).
4. Shima, H., and Yamaguchi, Y., *Chem. Lett.*, 899 (1979).
5. Lundeen, A. J., and Hoozer, R. V., *J. Org. Chem.* **32**, 3386 (1967).
6. Thomke, K., *in* "Proceedings, 6th International Congress on Catalysis, London, 1976" (G. C. Bonds, P. B. Wells, and F. C. Tompkins, Eds.), Vol. 1, p. 303. The Chemical Society, London, 1977.
7. Haag, W. O., and Pines, H., *J. Amer. Chem. Soc.* **82**, 2488 (1960).
8. Foster, N. F., and Cvetanoić, R. J., *J. Amer. Chem. Soc.* **82**, 4274 (1960).
9. Chang, C. C., and Kokes, R. J., *J. Phys. Chem.* **77**, 1957 (1973).
10. Hattori, H., Yoshii, N., and Tanabe, K., *in* "Proceedings, 5th International Congress on Catalysis, Palm Beach, 1972" (J. W. Hightower, Ed.), Vol. 10, p. 233. North-Holland, Amsterdam, 1973.
11. Itoh, M., Hattori, H., and Tanabe, K., *J. Catal.* **43**, 192 (1976).
12. Imizu, Y., Yamaguchi, T., Hattori, H., and Tanabe, K., *Bull. Chem. Soc. Japan* **50**, 1040 (1977).
13. Nakano, Y., Iizuka, T., Hattori, H., and Tanabe, K., *J. Catal.* **57**, 1 (1979).
14. Yamaguchi, T., Nakano, Y., and Tanabe, K., *Bull. Chem. Soc. Japan* **51**, 2482 (1978).
15. Gati, Gy., and Knözinger, H., *in* "Proceedings, 5th International Congress on Catalysis, Palm Beach, 1972" (J. W. Hightower, Ed.), Vol. 1, p. 819. North-Holland, Amsterdam, 1973.
16. Hightower, J. W., and Hall, W. K., *J. Amer. Chem. Soc.* **89**, 778 (1967).
17. Hattori, H., Maruyama, K., and Tanabe, K., *J. Catal.* **44**, 50 (1976); Mohri, M., Tanabe, K., and Hattori, H., *J. Catal.* **32**, 144 (1974).
18. Fukuda, Y., Hattori, H., and Tanabe, K., *Bull. Chem. Soc. Japan* **51**, 3150 (1978).
19. Lombardo, E. A., Conner, W. C., Jr., Madon, R. J., Hall, W. K., Kharlamov, V. V., and Minachev, Kh. M., *J. Catal.* **53**, 135 (1978).
20. Brysse, M., Guenin, M., Claudel, B., and Veron, J., *J. Catal.* **28**, 54 (1973).
21. Bevan, D. J. M., *J. Inorg. Nucl. Chem.* **1**, 49 (1955).
22. Rosynek, M. P., and Fox, J. S., *J. Catal.* **49**, 285 (1977).
23. Rosynek, M. P., and Magnusen, D. T., *J. Catal.* **48**, 417 (1977).
24. Sokolovskii, V. D., Sazonov, L. A., Boreskov, G. K., and Moskvina, Z. V., *Kinet. Katal.* **9**, 130 (1968).