JOURNAL OF CATALYSIS 61, 256–263 (1980)

A Study of the Selective Oxidation of Propene over a Series of Ternary Tungsten Oxides

S. DE ROSSI,* E. IGUCHI,†[1] M. SCHIAVELLO,*[2] AND R. J. D. TILLEY†

* *Centro di Studio sulla Struttura ed Attività Catalitica di Sistemi di Ossidi del CNR ed Istituto di Chimica del l'Università di Roma, Roma, Italy, and † School of Materials Science, University of Bradford, Bradford BD7 1DP, Yorkshire, England*

Received September 29, 1977; revised June 11, 1979

The oxidation of propene over a series of M–W–O ternary systems, with M = Ti, Ta, Nb, Ge, Sb, Sn, has been studied in the temperature range 623–763°K. Samples were examined by recording their reflectance spectra and also by transmission electron microscopy and powder X-ray diffraction in order to gain information on the original structures of the catalysts and on their changes during reaction. Only Sb- and Sn-containing specimens were found to be selective for acraldehyde production. They were also the only systems having bronze-like properties and reasonable stability during catalytic tests. The other systems were easily oxidized and nonselective. Attempts are made to correlate structural and electronic properties with the selective behavior of the Sb- and Sn-containing systems.

INTRODUCTION

The oxidation of propene has previously been studied (*1*) over a series of binary tungsten oxides which included the stoichiometric oxides, WO_3, which has an ReO_3-related structure, and WO_2, which has a structure similar to the rutile type, and in addition some nonstoichiometric oxides, WO_{3-x}. Among these latter oxides, $WO_{2.96}$ and $WO_{2.90}$, which have structures containing crystallographic shear (*CS*) planes, and $WO_{2.72}$, which is a more complex tunnel structure, were investigated. The results of this work showed that only the WO_{3-x} phases were to some extent selective toward the formation of acraldehyde above 673–693°K, and that the same phases oxidized fairly readily to WO_3 during the course of the reaction and the selectivity consequently disappeared (*1*). Therefore it was concluded that such phases containing *CS* planes or tunnels possess structural and electronic features of interest in the selective process investigated, but they have too great a tendency to incorporate oxygen, which destroys the original structure and deactivates the catalyst for acraldehyde production. Hence it was hoped to find systems with similar structures in which the oxidation to WO_3 might be reduced, thereby increasing the effective lifetime of the catalyst.

Within this framework, the following ternary systems were studied: Ti–W–O, Ta–W–O, Nb–W–O, Ge–W–O, Sb–W–O, and Sn–W–O. Although the phase relations in all these systems are not completely clear, structural aspects are understood in outline and structures analogous to those in the binary system are found. Moreover it was thought of some interest to compare Group IV and Group V transition metal and nontransition metal systems, viz. Ti vs Ge and Sn, and Nb and Ta vs Sb.

EXPERIMENTAL

Catalyst preparation. All ternary oxide samples were prepared by heating mixtures

---

[1] On leave from Department of Metallurgical Engineering, Yokohama National University, Tokiwadai, Hodogaya-ku, Yokohama, 240 Japan.

[2] Correspondence to be addressed to M. Schiavello, Istituto di Chimica Generale, Università di Roma, Roma, Italy.

0021-9517/80/010256-08$02.00/0

of WO_3, W metal turnings, and the appropriate metal or metal oxide in silica ampoules sealed under vacuum. The heating temperatures were in the range 1173–1273°K and heating times were usually 2 to 3 weeks in duration. All chemicals used were of "specpure" quality (Johnson-Matthey Ltd.).

The bulk compositions of the specimens studied are listed in Table 1.

Structural characterization. Electron microscope examination was carried out using a JEM 100B electron microscope operated at 100 kV and fitted with a goniometer stage. Samples were prepared by crushing the crystals in an agate mortar under *n*-butanol and allowing a drop of the resultant suspension to dry on a net-like carbon support film on a copper grid. Only crystals projecting over holes in the support film were studied.

Powder X-ray diffraction patterns of specimens were recorded using a Guinier–Hägg focusing camera and fully monochromatic Cu$K\alpha_1$ radiation, using KCl (a_0 = 0.62923 nm) as an internal standard. Other details can be found elsewhere (*2*).

The reflectance spectra were recorded at room temperature using a Beckman DK-1A spectrophotometer in the 300–2500 nm region using MgO as reference.

Catalytic procedure. The reaction was carried out in a flow system using a vertically positioned Pyrex reactor, in the 623–773°K temperature range. Oxygen and helium/propene mixtures (9/1 by volume), all of high purity (99.95%), were used as reactants. The gas analysis was performed by gas chromatography using a Carlo Erba Fractovap ATC/f, with a molecular sieve column at room temperature for O_2 and CO and a Porapak R column at 419°K for CO_2, C_3H_6, H_2O, and C_3H_4O. Details of the apparatus and procedures are available elsewhere (*1*).

EXPERIMENTAL RESULTS

As will be apparent from the experimental results described below and from the relevant literature cited in these sections, it

TABLE 1

Catalysts and Some Kinetic Parameters

Specimen (nominal composition)	Surface area (m^2 g^{-1})	r^a (693°K) (mol m^{-2} sec^{-1} 10^{-8})	r^a (743°K) (mol m^{-2} sec^{-1} 10^{-8})	$E_a{}^a$ (673–763°K) (kJ mol^{-1})	S (743°K) (%)	Reaction orders[a] (693°K) O_2	(693°K) C_3H_6	(743°K) O_2	(743°K) C_3H_6
$Ti_{0.03}WO_3$	0.5	8.9	25	88	—	0.7	0.1	0.4	0.3
$Ti_{0.06}WO_3$	0.8	7.4	18	79	—	0.5	0	0.3	0.5
$Ta_{0.03}WO_3$	0.4	2.1	7.4	109	—	Not measured			
$Nb_{0.03}WO_3$	0.1	21	69	100	—	Not measured			
$Ge_{0.04}WO_3$	0.5	3.8	11	92	—	0.5	0.1	0.2	0.2
$Ge_{0.08}WO_3$	1.2	4.3	13	92	4	1.0	0	1.2	0.5
$Sb_{0.03}WO_3$	0.6	1.3	4.7	109	35	0.5	0.7	0	1.0
$Sn_{0.01}WO_3$	0.4	2.2	11	134	23	0.8	0	0.8	0.2
$Sn_{0.03}WO_3$	0.2	4.3	17	117	39	0.7	0	0.7	0.2
$Sn_{0.04}WO_3$	0.2	3.7	18	134	26	0.8	0	0.8	0.2
$Sn_{0.06}WO_3$	0.3	8.7	32	113	36	0.9	0.2	0.7	0.3
$Sn_{0.08}WO_3$	0.2	2.6	14	142	11	0.9	0	0.9	0.1
$Sn_{0.10}WO_3$	0.3	1.6	10	159	28	0.9	0	0.9	0.2
$Sn_{0.14}WO_3$	0.4	1.8	10	146	31	1.0	0	0.9	0
$Sn_{0.20}WO_3$	0.5	1.2	6.3	142	20	0.7	0	0.8	0.2

[a] Calculated for total reaction [CO + CO_2 + C_3H_4O (when present)].

is difficult to prepare strictly monophasic samples in an absolute sense. Even heating times of several months yield somewhat disordered mixtures of phases, especially in the crystallographic shear region of the phase diagrams. We have tried, therefore, to produce not single phase materials, but samples containing only one structural type. Within the limits of the characterization techniques used, this approach has been successful.

All kinetic results are summarized in Table 1 where the following details are given: (a) the catalysts, designated by their nominal composition; (b) the surface area values measured by the BET method using krypton as adsorbate ($P_0 = 363$ N m^{-2}, $\sigma = 0.194$ nm^2); (c) the specific rates of propene conversion, r, at two temperatures (693 and 743°K) expressed as mol m^{-2} sec^{-1}; (d) the apparent activation energy values, E_a, calculated from the rate and for the ratio, R, $O_2/C_3H_6 = 1$; (e) the selectivity to acraldehyde, S, in percentage calculated for R = 1 and for the temperature 743°K; (f) the reaction orders for O_2 and C_3H_6 at two temperatures (693 and 743°K), calculated for the total conversion, including also acraldehyde when present. These results refer to steady-state conditions.

The reflectance spectra are similar to those already published (*1*). They are characterized by a broad and intense peak, whose intensity maximum varies for different specimens within large wavelength values (560–950 nm) and by a second small peak between 350 and 400 nm which is characteristic of WO_3 (*1*). From the spectra taken on the specimens used for the catalytic reaction it appears that for some specimens the intense broad peak shifts to higher wavelengths and eventually disappears, while for others it remains constant or shifts slightly to higher wavelengths. The second small peak, due to WO_3, sometimes increased in intensity to become the only one present, while for other samples it increased only slightly. Table 2 summarizes

TABLE 2

Wavelength and Intensity Changes of the Absorption Bands in the Reflectance Spectra of the Specimens Studied

Specimen (nominal composition)	Before catalysis		After catalysis		After catalysis	
	First band (nm)	Second band[a]	(up to 693°K) First band (nm)	Second band[a]	(up to 763°K) First band (nm)	Second band[a]
$Ti_{0.03}WO_3$	790	X	=	X(+)	=	X(+)
$Ti_{0.06}WO_3$	660	X	660(−)	X(+)	660(−)	X(+)
$Ta_{0.03}WO_3$	=	X	=	X(+)	=	X(+)
$Nb_{0.03}WO_3$	=	X	=	X(+)	=	X(+)
$Ge_{0.04}WO_3$	800	X	950	X	=	X(+)
$Ge_{0.08}WO_3$	580	X	650(−)	X	650(−)	X(+)
$Sb_{0.03}WO_3$	910	X	940	X	1070	X(+)
$Sn_{0.01}WO_3$	=	X	=	X	=	X
$Sn_{0.03}WO_3$	950	X	1000	X	1050	X(+)
$Sn_{0.04}WO_3$	880	X	890	X	1000	X(+)
$Sn_{0.06}WO_3$	800	X	830	X	910	X(+)
$Sn_{0.08}WO_3$	760	=	790	=	800(−)	X
$Sn_{0.10}WO_3$	740	=	Not recorded		810	X
$Sn_{0.14}WO_3$	580	=	Not recorded		650	X
$Sn_{0.20}WO_3$	560	=	570	=	830	X

[a] Between 350 nm and 400 nm (WO_3): X when present; (+) increase in intensity of absorption; (−) reduction in intensity of absorption; = absent.

the reflectance spectra both before and after catalysis. It must be noted that as already reported (*1*, *3*), the lower the wavelength of the broad peak the higher is the oxygen deficit. Thus the shift of the maximum to higher wavelengths, due to the catalytic reaction, indicates a decrease of the oxygen deficiency. The increase of the small peak at 350–400 nm similarly indicates an increase of the WO_3 content of the sample. A discussion of the origin of the absorption bands is outside the scope of this paper (*4*, *5*). The reflectance spectra must, therefore, be considered as a fingerprint for the characterization of the specimens.

Ti–W–O System

Electron microscope studies show that the Ti-containing samples are disordered. In the $Ti_{0.03}WO_3$ sample *CS* planes are present. These are mainly of the {103} type, but regions of {001} *CS* are also present and disordered regions with indices somewhere between these two were also observed. In the $Ti_{0.06}WO_3$ sample the same *CS* phases are present and also a disordered oxide of approximate composition $WO_{2.82}$ (*6*).

As indicated in Table 2 the reflectance spectra recorded on these specimens show that both Ti-containing catalysts oxidize extensively to WO_3 during reaction at 693°K. For $Ti_{0.06}WO_3$ the band at 660 nm, present in the as-prepared specimen, could still be observed after catalytic experiments up to 763°K, but with a much reduced intensity. Considerable changes in the original structure were confirmed by electron microscopy which showed only WO_3-like crystals to be present after reaction tests up to 763°K.

The catalytic results indicate that both specimens behave similarly. There is no substantial difference in activity in reaction orders and activation energy. In addition selectivity to acraldehyde was never observed on either specimen. This latter result agrees with the fact that both catalysts oxidize rapidly to WO_3, which is not selective under our conditions (*1*).

Ta–W–O and Nb–W–O Systems

Previous experiments have shown that samples with an overall composition Nb_xWO_3 or Ta_xWO_3 in which x is small consist of two phases, a fully oxidized phase of the tetragonal tungsten bronze type and reduced tungsten oxides which may contain a very small amount of Nb or Ta (*7*). The present studies indicate that our samples are similar, and contain both structure types.

The reflectance spectra of both are similar to that of WO_3 and do not change after the catalytic experiments. This suggests that the original specimens are very close in stoichiometry to WO_3, and may even be superficially oxidized to WO_3. The electron microscope studies on the specimens used in catalysis up to 763°K showed only WO_3-like diffraction patterns.

The $Nb_{0.03}WO_3$ specimen was found to be more active than the Ta specimen but no selectivity to acraldehyde was found for either catalyst.

Ge–W–O Systems

The samples of overall composition Ge_xWO_3 decompose during reaction to form $x GeO_2$ and WO_{3-2x}. $Ge_{0.04}WO_3$ therefore produced a sample which was predominantly WO_{3-2x} and contained {102} and {103} *CS* structures. $Ge_{0.08}WO_3$ consisted almost entirely of an oxide of approximate formula W_5O_{14}, isostructural with Mo_5O_{14} (*8*), which does not appear to form in the binary W–O system. In addition this sample also contained a small amount of {103} CS phases (*9*).

From the reflectance spectra, it was concluded that the specimen $Ge_{0.04}WO_3$ was fully oxidized after the catalytic experiments up to 763°K as the band at 800 nm found in the as-prepared specimen was absent in the spectrum recorded at the end of the kinetic study, leaving only absorption attributed to WO_3. The oxidation was confirmed by electron microscopy, which revealed the presence of only WO_3-like crystals. Oxidation also occurred for $Ge_{0.08}WO_3$, whose spectra show a shift of the band from 580 nm, from the original sample, to 650 nm with some reduction in intensity.

The catalytic properties for both specimens are very similar, as shown in Table 1. They are also similar to those of the other catalysts already mentioned, the only difference being that the sample $Ge_{0.08}WO_3$ produced a very small amount of acraldehyde.

Sb–W–O System

Electron microscope studies indicate that the Sb_xWO_3 system is rather complex. However, below a composition of approximately $Sb_{0.07}WO_3$ the system forms a series of perovskite-related bronzes (*10*), and the sample studied here, of composition $Sb_{0.03}WO_3$, was of this type.

The reflectance spectra recorded at various stages of the catalytic study show a little shift of the band at 910 nm in the original sample, without any decrease in intensity (see Table 2). This indicates that only a small degree of oxidation occurred during the reaction and that the original structure or a similar one is maintained in the surface layers.

Transmission electron microscope analysis on the sample used in catalysis up to 763°K is not easy. The diffraction patterns and electron microscope contrast from WO_3 or a perovskite bronze are very similar. X-Ray diffraction is of more use here, and this suggested that little or no oxidation had taken place.

The catalytic studies showed that this catalyst had low activity for the total reaction ($CO + CO_2 + C_3H_4O$), but exhibited a rather good selectivity in the temperature range 450–490°K, especially with propene-rich feeds. For instance, the selectivity to acraldehyde at 763°K is 43% with $O_2/C_3H_6 = 14$ and 56% with $O_2/C_3H_6 = 0.4$. Other experiments, some of which are reported in Fig. 1, carried out with rather low propene concentration, indicated that selectivity was independent of oxygen partial pressure. Moreover the reaction orders for the overall reaction, including all products, are zero for O_2 and one for C_3H_6 (see Table 1).

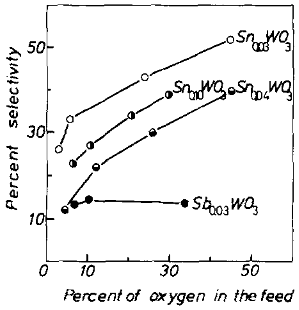

FIG. 1. Percentage selectivity at 743°K vs oxygen percentage in the feed at constant C_3H_6 concentration for some Sn_xWO_3 specimens and for $Sb_{0.03}WO_3$.

Sn–W–O System

From a structural viewpoint these specimens have complex crystal structures, whose unit cells have orthorombic, pseudohexagonal, or tetragonal symmetry according to the tin concentration. These are fairly fully described in the literature (*11–14*). They are also known to have bronze-like properties. The electron microscope results showed that the structures of the present samples were in agreement with those expected from the previous studies.

The reflectance spectra of the specimens before their use as catalysts indicate that the higher the tin content the lower is the wavelength of the broad band, as expected. The only exception to this was in the $Sn_{0.01}WO_3$ which showed only a diffuse absorption between 1000 and 2500 nm. The second band centered at about 380 nm, decreased in intensity from $Sn_{0.01}WO_3$ to $Sn_{0.06}WO_3$, and was not present for higher Sn concentrations. As shown in Table 2, after the catalytic experiments, for all the catalysts, the broad band was shifted to higher wavelengths while the second band increased if it was present or else it appeared. This indicated that, although a moderate oxidation occurs on the catalyst, the original structure is maintained virtually intact. The electron microscope studies performed on the specimens after catalysis showed the same structural features as in the original specimens.

The kinetic study showed that the *r* values, the activation energies, and the percent selectivity values do not vary in a regular fashion in proportion to the tin concentration. Moreover the E_a values are higher than for the other systems. The reaction orders for total oxidation are almost the same for all the catalysts of this series: about zero for C_3H_6 and 0.7–1 for O_2 at 693°K and about 0.2 for C_3H_6 and 0.7–0.9 for O_2 at 743°K. In Fig. 1 the percent selectivity vs the O_2 percentage in the feed is reported, from which it can be seen that the selectivity also increases with increase of oxygen in the feed. Thus the behavior of the Sn–W–O system seems to be quite opposite to that of Sb–W–O with respect to the influence of the reactant composition on selectivity.

DISCUSSION

Among the catalysts studied only those containing Sb and Sn were able to selectively oxidize propene to acraldehyde. These solids have rather different crystallographic structures varying from essentially WO_3 (in Sb_xWO_3) via the planar fault and intergrowth structures of the lower Sn_xWO_3 bronzes to the tetragonal bronze structures for $Sn_{0.20}WO_3$. This is an indication that the structural aspect may be important but, in this case, is not a limiting factor for the selective process. The key features determining the occurrence of selectivity toward acraldehyde must therefore be sought in other characteristics which are common to both Sb and Sn but absent from Ti, Ta, Nb, and Ge-containing catalysts. In this context the most obvious characteristic of the selective catalysts is in the presence of bronze-like properties of high oxygen mobility and electron conductivity coupled with a resistance to further oxidation under the reaction conditions. Although the nonselective catalysts, which are in part constituted of reduced tungsten oxide *CS* shear or tunnel phases, also share the property of high oxygen mobility (*22*), they all oxidize fairly readily to WO_3 and so develop insulating properties. It would thus appear that the presence of a partially reduced oxide and/or electron conductivity is crucial for the appearance of acraldehyde among the reaction products.

This observation is fully in accord with previous studies (*15–17, 19*) which have indicated that two kinds of sites are involved in the overall process. The first is suitable for the adsorption and the activation of the propene and is acceptor in character. This may be a metal ion in a high oxidation state, on which propene can be bonded in the form of a symmetric π-allyl complex with hydrogen atom abstraction, successively transforming into a σ-complex bonded to an oxygen ion with a loss of another hydrogen atom (*15*). The second site is donor in character and is capable of adsorbing oxygen. This second site can be present at some distances from those in which O^{2-} ions react with the allyl complex to form an adsorbed acraldehyde molecule (*19*). If this is the case there is the necessity of O^{2-} ion diffusion from the second to the first site from which the desorption of the products generate anionic vacancies which must be continuously filled.

A simultaneous electron flow must also take place in the opposite direction in order to avoid the surface complex being too strongly bonded and then completely oxidized and also to restore the donor sites in their original condition (*19, 20*).

Both Sn- and Sb-containing systems are suitable for the reoxidation step of the reaction because of the presence of lower valence cations which may act as donor sites for the oxygen adsorption. Furthermore the good oxygen mobility and the electron transfer ability of these bronzes can support the ion and electron flow between sites of different character. The nonselective catalysts initially also certainly possess donor sites (W^{5+}, W^{4+}) (*21*), which may well be located in the *CS* planes or in the pentagonal columns in the tunnel compounds. They also are characterized by high mobility of oxygen ions (*22*) and by a reasonable facility to conduct electrons. It has been shown (*1*) that similar structures are able to perform to some extent the selective oxidation, but the drawback is that these materials oxidize fairly readily to WO_3 and the selectivity disappears.

Concerning the sites responsible for the propene adsorption, the experimental results do not allow us to arrive at any definite conclusion. However, with respect to the Sn-containing system no relation was found between activity, selectivity, and tin content of the catalysts. It is conceivable that Sn ions in the 4+ oxidation state are involved in the olefin bonding and such a relation has been suggested by various authors (*23, 24*). In this respect, although tin is probably contained as Sn^{2+} in the fresh catalyst (*12*), it is likely that a certain amount of Sn^{4+} ions will be present on the surface during the reaction. The reaction orders found for the tin-containing catalysts (see Table 1) suggest that the reoxidation step is rate controlling, while the propene adsorption step is, in comparison, fast. This is not inconsistent with the idea that the Sn ions are involved in the adsorption of the propene.

With respect to the reaction orders found (see Table 1) and to the behavior of the selectivity toward the feed composition (see Fig. 1), the Sb–W–O system seems to be quite different from the Sn–W–O system, and indicates that the reoxidation step is easy while the interaction with propene is rate limiting.

This suggests that Sb ions are not as suitable for propene adsorption as Sn ions and/or the oxygen diffusion mechanism is different for these two selective systems. However at this stage it is not possible to discriminate between these possibilities. In summary, the studies presented here are consistent with the following reaction model formulated on the basis of two hypotheses: (i) the only oxygen species involved in the selective steps are O^{2-} ions, as suggested by several previous studies (*15–17*), and (ii) the selective oxidation takes place through a redox mechanism (*18*):

$$C_3H_{6(gas)} + O^{2-}{}_{(surf)} \rightarrow C_3H^{\cdot}_{5(ads)} + OH^- + e^- \quad (1)$$

$$C_3H^{\cdot}_{5(ads)} + 2O^{2-}{}_{(surf)} \rightarrow C_3H_4O_{(ads)} + OH^- + 3e^- \quad (2)$$

which constitutes propene adsorption and selective oxidation on an acceptor site. This is followed by

$$C_3H_4O_{(ads)} + 2OH^- \rightarrow C_3H_4O_{(gas)} + H_2O + O^{2-}{}_{(surf)} + 2V_0 \quad (3)$$

where V_0 is an anionic vacancy. This describes desorption of the products. Finally

$$O_{2(gas)} + 2V_0 + 4e^- \rightarrow 2O^{2-}{}_{(surf)} \quad (4)$$

provides for a reoxidation of the catalyst through a donor site.

ACKNOWLEDGMENTS

M. S. acknowledges with thanks the "Consiglio Nazionale della Ricerche (Roma)" for financial support. R.J.D.T. and E.I. are indebted to the Science Research Council for an equipment grant and financial support for one of us (E.I.). The authors also wish to acknowledge the constructive help of one of the referees in remodelling the discussion.

REFERENCES

1. De Rossi, S., Iguchi, E., Schiavello, M., and Tilley, R. J. D., *Z. Phys. Chem.* **103,** 193 (1976).
2. Schiavello, M., Tilley, R. J. D., De Rossi, S., and Iguchi, E., *Z. Phys. Chem.* **104,** 165 (1977).
3. Porter, V. R., White, W. B., and Roy, R., *J. Solid State Chem.* **4,** 250 (1972).
4. Faughnan, B. W., Crandall, R. S., and Heyman, P. M., *RCA Rev.* **36**(1), 177 (1975).
5. Goodenough, J. B., "Progress in Solid State Chemistry" (H. Reiss, Ed.), Vol. 5, p. 319. Pergamon Press, Oxford, 1972.
6. Ekström, T., and Tilley, R. J. D., *Mater. Res. Bull.* **9,** 705 (1974).
7. Ekström, T., and Tilley, R. J. D., *J. Solid State Chem.* **18,** 123 (1976).
8. Ekström, T., *Chem. Commun.* 7 (1975).

9. Ekström, T., Iguchi, E., and Tilley, R. J. D., *Acta Chem. Scand.* **A30**, 312 (1976).

10. Parmentier, M., and Gleitzer, C., *J. Solid State Chem.* **17**, 255 (1976).

11. McColm, I. J., Steadman, R., and Howe, A., *J. Solid State Chem.* **2**, 555 (1970).

12. Steadman, R., *Mater. Res. Bull.* **7**, 1143 (1972).

13. Steadman, R., Tilley, R. J. D., and McColm, I. J., *J. Solid State Chem.* **4**, 199 (1972).

14. McColm, I. J., Steadman, R., and Dimbylow, C., *J. Solid State Chem.* **14**, 185 (1975).

15. Haber, J., *Z. Chem.* **13**, 241 (1973).

16. Schuit, G. C. A., *J. Less Common Metals* **36**, 175 (1974).

17. Hucknall, D. J., "Selective Oxidation of Hydrocarbons," p. 36, Academic Press, London, 1974.

18. Mars, P., and Van Krevelen, D. W., *Chem. Eng. Sci. Suppl.* **3**, 41 (1954).

19. Weiss, F., Marion, J., Metzger, J., and Cognion, J. M., *Kinet. Katal.* (Eng. transl.), **14**, 32 (1973).

20. Peacock, J. M., Parker, A. J., Ashmore, P. G., and Hockey, J. A., *J. Catal.* **15**, 398 (1969).

21. De Angelis, B. A., and Schiavello, M., *J. Solid State Chem.* **21**, 67 (1977).

22. Schiavello, M., Tilley, R. J. D., Cannizzaro, M., De Rossi, S., and Pepe, F., *Z. Phys. Chem.* **106**, 45 (1977).

23. Onsan, I. Z., and Trimm, D. L., *J. Catal.* **38**, 257 (1975).

24. Firsova, A. A., Khovanskaya, K. M., Isyganov, A. D., Suzdalev, I. P., and Margolis, L. Ya., *Kinet. Katal.* (Eng. transl.) **12**, 708 (1971).