JOURNAL OF CATALYSIS 50, 220–227 (1977)

Reaction of Carbon Monoxide with Nitrous Oxide on Vanadium Pentoxide Catalysts Containing Alkali Metal Sulfate Additives

BORDAN W. KRUPAY AND ROBERT A. ROSS[1]

Department of Chemistry, Lakehead University, Thunder Bay, Ontario, Canada P7B 5E1

Received December 14, 1976; revised June 27, 1977

The kinetics of the catalyzed reaction between carbon monoxide and nitrous oxide to yield carbon dioxide and nitrogen from 673 to 773 K has been studied on vanadium pentoxide and on a series of vanadium pentoxide melts containing individually 9.09 mol% of the sulfates of lithium, sodium, potassium, rubidium, and cesium. The additive activity series was

$$V_2O_5 \text{ (pure)} < Li_2SO_4 < Na_2SO_4 < K_2SO_4 < Rb_2SO_4 < Cs_2SO_4$$

and exhibited a compensation effect which is associated with changes in surface oxygen mobility which influence catalytic site activity. A Langmuir–Hinshelwood treatment has been used to interpret the kinetic data and a mechanism is proposed which is related to the presence of two types of oxygen species on the catalyst surface, only one of which may be directly involved in the oxidation process of carbon monoxide.

INTRODUCTION

In studies of the reduction of nitric oxide by a variety of reducing agents (*1–3*), the reaction with carbon monoxide on various transition metal oxides (*4*) has been reported to produce nitrous oxide as an intermediate which can be detected at high space velocities (*5*). The oxide activity series for the CO/NO reaction was found (*4*) to exhibit a pattern different from that expected for catalytic oxidation reactions (*6–9*). In the latter case, the oxides of cobalt, copper, manganese, and nickel are expected to be the most active whereas, for the CO/NO reaction, Fe_2O_3, $CuCr_2O_4$, Cu_2O, and Cr_2O_3 were most active. Since nitrous oxide has been reported as an intermediate in the CO/NO reaction and since there are few available data in the literature on the surface interactions between carbon monoxide and nitrous oxide, this latter reaction has been examined on a series of oxides including vanadium pentoxide and preparations of this oxide containing 9.09 mol% of alkali metal sulfate additives.

Previously, the addition of alkali metal sulfates to vanadium pentoxide was shown (*9*) to influence the catalytic activity in sulfuric acid production (*10*) by altering the mobility of the oxygen in vanadium pentoxide (*9, 11*), and the promoting action of the sulfate additives was found to be (none) $< Li_2SO_4 < Na_2SO_4 < K_2SO_4 < Rb_2SO_4 < Cs_2SO_4$. This same trend has been observed in studies of the catalytic oxidation of sulfur dioxide (*12*). The present study of the CO/N_2O reaction on vanadium pentoxide and melts containing the alkali metal sulfates was undertaken in conjunction with studies currently being conducted here on the isotopic exchange of carbon dioxide on these surfaces.

EXPERIMENTAL METHODS

The all-glass flow system and quartz reactor have been described previously (*13*).

---

[1] To whom reprint requests should be addressed.

ISSN 0021-9517

High-purity helium was used as the carrier gas at atmospheric pressure in the flow system and Beckman GC-5 gas chromatograph. Carbon monoxide, nitrogen, carbon dioxide, and nitrous oxide were analyzed by a thermal conductivity bridge using stainless-steel columns, 72 × 0.125 in., o.d., packed with 24-in. Carbosieve B and the remainder with Poropak Q at a column temperature of 353 K which was sufficient to resolve all components.

All reaction rate measurements were made after steady catalyst activity was attained, usually within 5 h. In all cases, the inlet reaction gas consisted of carbon monoxide and nitrous oxide each at a partial pressure of 40 Torr (5.33×10^3 N m^{-2}). The temperature range of the experiments was determined by the activity of the catalysts: The highest temperature was that at which the conversion was less than 5%, and the lowest was determined by the limits of accurate analysis.

To establish the experimental conditions for which the reaction rate was not influenced by external or internal diffusion, preliminary experiments were conducted in the usual manner (*14*), and as a result, kinetic measurements were performed at a total gas flow rate of 350 ml min^{-1} (NTP). "Blank" runs showed that reaction on the quartz wool and reactor walls reached 1% conversion at 853 K.

Surface areas were determined by low-temperature krypton adsorption (BET, 77 K; $\sigma = 21.5$ Å^2).

Vanadium pentoxide (Ventron, $>99.9\%$ pure) and the preparations containing 9.09 mol% of alkali metal sulfates (Ventron, $>99.9\%$ pure) were prepared (*9*) by melting a mixture of vanadium pentoxide powder and the corresponding sulfate additive in a quartz dish at 993 K for 4 h: X-ray powder diffraction photographs, taken after heating for 2- and 4-h intervals, were identical. The liquid melts were cooled rapidly, ground, and tableted in a 1.27-cm die at a pressure of 3 tons for 2 min. Samples were calcined at 793 K for 10 h except for cesium and rubidium sulfate melts which were calcined at 703 K. The tablets were crushed, and sieved material with a particle diameter between 1 and 2 mm was used for the catalytic studies.

Carbon monoxide (C.P.; 99.5% minimum), carbon dioxide (Coleman; 99.99%),

TABLE 1

Carbon Monoxide Rate-Order Data for Alkali Metal Sulfate Additives with Nitrous Oxide Partial Pressure at 40 Torr

P_{CO}	Rate × 10^8 (mol m^{-2} s^{-1})					
	None	Li_2SO_4	Na_2SO_4	K_2SO_4	Rb_2SO_4	Cs_2SO_4
30	8.07	4.53	25.9	23.8	1.29	4.82
40	10.1	5.79	35.7	36.2	1.72	5.98
50	19.5	6.52	43.1	44.4	2.08	7.23
60	—	7.98	53.9	55.2	2.55	8.87
70	17.4	8.88	62.9	66.8	2.92	10.3
80	—	10.4	78.4	79.8	3.56	12.7
100	26.9	13.6	97.6	100	4.67	16.5
120	35.6	—	—	—	—	—
Temperature (K)	723	713	713	713	703	703
Order	0.94	0.80	1.0	1.1	1.3	1.1

TABLE 2

Carbon Dioxide Rate-Order Data for Alkali Metal Sulfate Additives with $P_{CO} = P_{N_2O} = 40$ Torr Held Constant

P_{CO_2}	Rate × 10^8 (mol m^{-2} s^{-1})				
	None	Li_2SO_4	Na_2SO_4	K_2SO_4	Cs_2SO_4
54.3	—	—	20.2	—	—
43.4	7.63	4.84	21.1	23.8	3.78
32.6	—	4.89	22.4	26.2	3.99
21.7	7.89	5.06	23.7	27.6	4.19
10.9	9.40	5.29	25.8	28.6	4.33
5.43	—	5.57	—	32.4	4.60
Temperature (K)	723	713	713	713	703
Order	−0.2	−0.2	−0.2	−0.2	−0.2

nitrogen (super-pure; 99.99%), nitrous oxide (99.9% minimum), and helium (high purity; 99.995%) were used as supplied.

RESULTS

Carbon Monoxide Reaction Rate Order

Table 1 summarizes the dependence of the rate of reaction results upon the carbon monoxide partial pressure in the region from 30 to 120 Torr. Pure vanadium pentoxide exhibited the lowest activity of the series, and hence rate-order data had to be obtained at a higher temperature, 723 K. Catalysts containing rubidium and cesium sulfate melted at ~745 K and this necessitated rate-order determinations at the lower temperature, 703 K. Samples containing the sulfates of lithium, sodium, and potassium were examined for rate-order relationships at 713 K.

Carbon Dioxide Reaction Rate Order

Rate-order dependencies for carbon dioxide were determined in the partial pressure range of 5.43 to 54.3 Torr at the same temperatures used in the carbon monoxide experiments. These results are presented in Table 2. All exhibited a negative rate-order dependence on the carbon dioxide partial pressure. In the case of catalysts containing rubidium sulfate, introduction of 5.43 Torr carbon dioxide into the inlet stream resulted in a progressive decrease in the reaction rate until a steady level was reached which did not change when the carbon dioxide partial pressure was increased in steps up to 54.3 Torr. Since all other catalysts exhibited a carbon dioxide rate-order dependence of −0.2, this value was later assumed for the V_2O_5 melts containing rubidium sulfate to obtain comparative kinetic data.

The Effect of Temperature on the Reaction Rate

In all cases, the reacting gas mixture consisted of 40 Torr each of carbon monoxide and nitrous oxide. After steady catalyst activity was attained at the highest temperature, the rate of reaction was determined at progressively decreasing temperatures. For vanadium pentoxide and catalyst melts containing the sulfates of lithium, sodium, and potassium, the temperature was decreased from 773 K in 6 K intervals to approximately 673 K, while for the melts containing cesium and rubidium sulfates, the highest temperature was 723 K, and reaction rates were determined at 4 K intervals to approximately 673 K. Rate constants were determined by integration of the rate expression $r = k(P_{CO})^n/(P_{CO_2})^m$, and the Arrhenius plots derived are shown in Fig. 1. The activation energy progressively increased from 28 ± 1 kcal mol^{-1} (117 ± 4 kJ mol^{-1}) for pure vanadium pentoxide to 38 ± 1 kcal mol^{-1} (159 ± 4 kJ mol^{-1}) for V_2O_5 containing cesium sulfate. Further, the latter oxide melts and those containing sodium sulfate gave apparent activation energy values of 24 ± 1 and 25 ± 1 kcal mol^{-1}, respectively, at the higher temperatures. These data are summarized in Table 3 and Fig. 2 which illustrates a compensation effect for the series of catalysts.

Examination of Catalysts

The catalysts were examined before and after catalysis and revealed distinct color changes for vanadium pentoxide and the melts containing the sulfates of lithium, sodium, potassium, rubidium, and cesium where a definite darkening of color was detected. For example, the melt containing lithium sulfate was blue-black after catalysis, indicative of a nonstoichiometric deficiency of oxygen in the pentoxide (*15*). The samples containing sodium and potassium sulfates were initially black and hence changes in color were not distinct. X-ray powder diffraction and electron diffraction micrographs of the samples before and after catalysis revealed no obvious, long-to-intermediate-range structural changes; however, scanning electron micrographs and optical microscopy indicated that the proportion of crystalline plates was greatest for the melt containing potassium sulfate. Similarly, the hardness of the catalyst pellets was greatest for the potassium sulfate melt and least for vanadium pentoxide

TABLE 3

Apparent Activation Energies and Preexponential Factors from the Arrhenius Plots

Catalyst additive	Apparent activation energy (kcal mol^{-1})	Log (pre-exponential factor)	Temperature range (K)
None	28	6.42	693–773
Li_2SO_4	32	7.33	677–773
Na_2SO_4	25	6.26	737–773
	32	8.09	677–731
K_2SO_4	33	8.29	671–773
Rb_2SO_4	35	8.51	679–723
Cs_2SO_4	24	4.83	703–723
	38	9.27	671–699

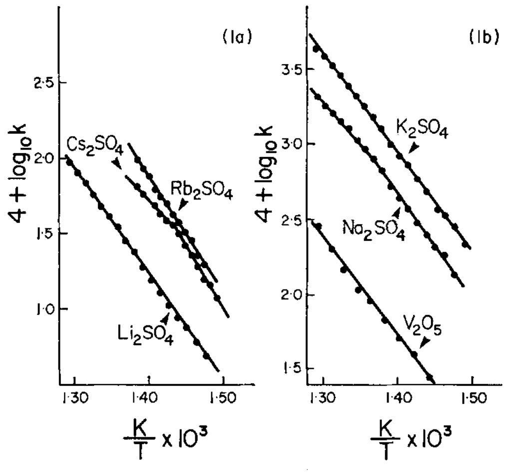


FIG. 1. Arrhenius plots of the rate constants of the reaction between carbon monoxide and nitrous oxide for V_2O_5 and melts containing the indicated sulfate.

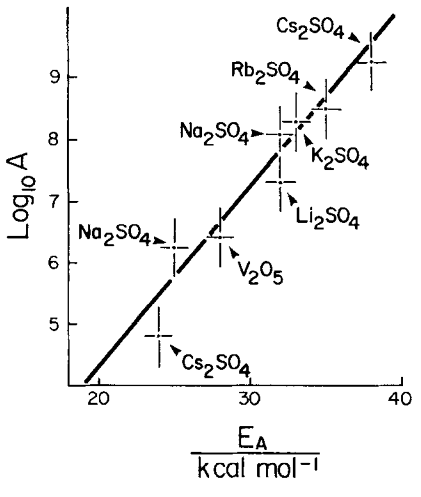


FIG. 2. Compensation effect for V_2O_5 and melts containing sulfate additives.

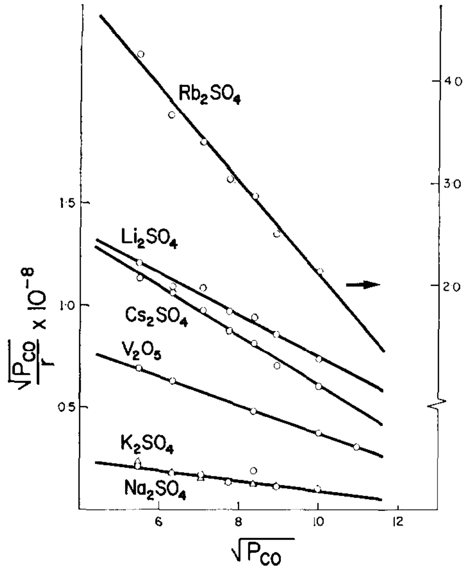


FIG. 3. Plots of the carbon monoxide rate-order data according to Eq. (3) for V_2O_5 and melts containing the indicated sulfate.

which disintegrated fairly readily under slight pressure.

DISCUSSION

In the V_2O_5 structure, three types of oxygen atoms can be distinguished. These are designated as O_1, O_2, and O_3 and are attached to one, two, and three vanadium atoms, respectively (*16*), in the V_2O_5 network. The number of oxygen atoms of each type and the corresponding V–O bond lengths (in Å) are: one O_1 (1.54); one O_2 (1.77); two O_3 (1.88); one O_3 (2.02). The next nearest oxygen neighbor of vanadium in V_2O_5 lies in the adjacent layer (*17*) at a distance of 2.81 Å and, with the other five, completes a very distorted octahedron. Two types of vanadium-to-oxygen bonds have been detected (*18*) by isotopic oxygen exchange where, initially, exchange begins mainly at the V=O groups common to all the surface planes. The exchange in the V–O–V plane, however, proceeds as the fastest of all the exchange processes in the bulk of the oxide. Although the exchange between V=O groups and the V–O–V groups is comparatively slow, this may be a contributory process during catalytic oxidation reactions.

For both isotopic exchange and hydrogen oxidation (*19*), the rate-limiting stage was associated with the exchange of adsorbed oxygen ions with the oxide oxygen ions as a result of electron transfer, leading to exchange without displacement of oxygen atoms. The new anion formed as a result of such transfer would be expected to exchange rapidly with other oxide anions or gas phase oxygen. Further, the coordination state of the surface atoms has been shown to be an important factor (*20*), since tetrahedrally coordinated vanadium is more reactive during electron transfer reactions than square, pyramidal, or octahedral coordinations, and for the straight decomposition of N_2O, the process has been formulated as:

$$V_{\text{tetr.}}^{4+} + N_2O \xrightarrow{-78^\circ C} [V^{4+}\cdots N_2O] \xrightarrow{20^\circ C} [V^{5+}\cdots O^-] + N_2 \quad (1)$$

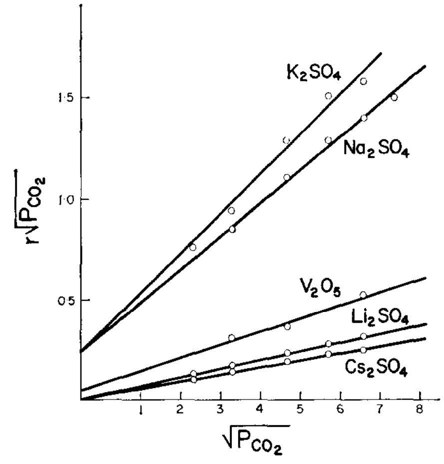


FIG. 4. Plots of the carbon dioxide rate-order data according to Eq. 4 for V_2O_5 and the melts containing the indicated sulfate.

Various Langmuir–Hinshelwood kinetic expressions (*21, 22*) were used to analyze the present rate-order data (Tables 1 and 2), within the context of previous discussions concerning the use of such equations (*23, 24*), to formulate mechanisms for the surface reaction. The relationship between the rate of reaction, r (mol m^{-2} s^{-1}), and surface coverage by carbon monoxide, θ_{CO}, and carbon dioxide, θ_{CO_2}, was best expressed as:

$$r = k(\theta_{CO}/\theta_{CO_2}), \tag{2}$$

where

$$\theta_{CO} = a(P_{CO})^{\frac{1}{2}}/[1 + a(P_{CO})^{\frac{1}{2}}] \tag{3}$$

and

$$\theta_{CO_2} = b(P_{CO_2})^{\frac{1}{2}}/[1 + b(P_{CO_2})^{\frac{1}{2}}]. \tag{4}$$

Figures 3 and 4 show that Eqs. (3) and (4), respectively, accommodate the data for all vanadium pentoxide samples. The interpretation associated with these equations is that both carbon monoxide and carbon dioxide in the adsorbed state occupy two surface sites. Since the rate of reaction is independent of nitrous oxide partial pressure, the adsorption of nitrous oxide was not considered to be rate-determining.

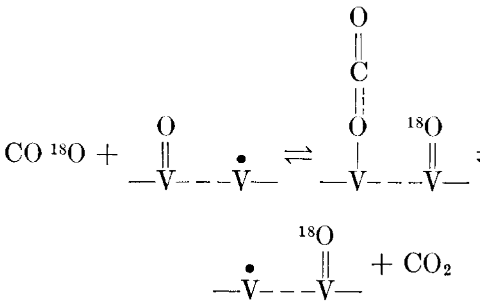
Thus a reaction scheme consistent with the above surface and kinetic features may be:

$$\mathrm{CO\ (ads)} + [\mathrm{O}]_A + [\mathrm{O}]_B \rightleftarrows (\mathrm{CO_3}) \tag{5}$$

$$(\mathrm{CO_3}) \rightarrow \mathrm{CO_2(g)} + [\ ]_A + [\mathrm{O}]_B \tag{6}$$

$$\mathrm{N_2O\ (ads)} + [\ ]_A \rightarrow \mathrm{N_2(g)} + [\mathrm{O}]_A, \tag{7}$$

where $[O]_A$ and $[O]_B$ designate oxygen sites of distinct chemical reactivities and $[\ ]_A$ is an oxygen vacancy. An unspecified intermediate structure, designated (CO_3), is indicated. "Carbonate" formation is generally accepted for the oxidation of carbon monoxide on n-type oxides (*20*). Previously, the mechanism for the isotopic exchange of carbon dioxide (*25*) has been formulated according to the scheme:



$$\mathrm{CO\,{}^{18}O} + \underset{\text{—V— — —V—}}{\overset{\mathrm{O}}{\|}\qquad\bullet} \rightleftarrows \underset{\text{—V— — —V—}}{\overset{\overset{\overset{\mathrm{O}}{\|}}{\overset{\mathrm{C}}{\|}}}{\overset{\mathrm{O}}{|}}\qquad\overset{{}^{18}\mathrm{O}}{\|}} \rightleftarrows \underset{\text{—V— — —V—}}{\bullet\qquad\overset{{}^{18}\mathrm{O}}{\|}} + \mathrm{CO_2} \tag{8}$$

Since the catalytic rate of reaction is independent of nitrous oxide partial pressure, the rapid decomposition of N_2O would appear to be related to the desorption of carbon dioxide and the consequent formation of the oxygen vacancy $[\ ]_A$. During steady catalysis, replenishment of the oxygen species, designated $[O]_A$, may proceed via the V–O–V network as suggested (*18*) in a manner similar to that for the adsorption of formic acid on V_2O_5 (*26*). The inhibitory effect of carbon dioxide would then be associated with "blockage" of the N_2O decomposition sites.

In the temperature range of 573 to 723 K, the oxidation of carbon monoxide by molecular oxygen on V_2O_5 has been proposed (*27*) to proceed via an associative mechanism where the oxidation and reduction reactions occur in a concerted manner. On this basis, reactions (5) (surface reduction) and (7) (surface oxidation) would be interpreted as occurring simultaneously at relatively close proximities to enable surface complex formation in a manner similar to that proposed for catalysis on copper chromite (*28*). However, the rapid exchange of oxygen in the V–O–V network (*18*) would facilitate a greater separation between the surface reduction and oxidation sites, and, since catalysis is occurring at temperatures well above the surface Tamman temperature of the solids, the active surface species will be expected to possess high mobility, and hence, a two-step mechanism for the redox reaction cannot be excluded.

The plot of log A vs E_A for the series of vanadium pentoxide catalysts, Fig. 2, shows that a compensation effect is operative which, together with the rate-order data, suggests a surface mechanism, common for all the catalysts examined, that may be influenced by the different reactivities of the oxygen surface sites. The observed activation energies and the temperature range of the catalysis for the reaction of carbon monoxide with nitrous oxide are much higher than those for CO oxidation (*29*) but comparable to those for the decomposition of nitrous oxide and the isotopic oxygen exchange (*9*). On this basis, the decomposition of nitrous oxide might be expected to influence the catalytic rate even though a zero-order rate dependence upon nitrous oxide partial pressure was observed. Since the presence of V^{4+} sites is likely to facilitate the decomposition of nitrous oxide, as shown (*20*) in reaction (1), the activation energy would be expected to decrease with increasing numbers and mobilities of V^{4+} sites. Previously, considerable loss of oxygen from vanadium pentoxide on melting (*19*) has been reported, while the V^{4+}/V^{5+} ratio in V_2O_5 glasses can be as high as 0.5 (*30*). Further, the addition of alkali metal sulfates is related (*9, 19*) to the mobility of the catalyst oxygen with the presence of V^{4+} ions. Hence, a progressive decrease in the apparent activation energy for the CO/N_2O reaction would be expected in the series from the pure oxide to the melt containing Cs_2SO_4 if nitrous oxide decomposition were rate-controlling; however, the experimental data (Table 3) cannot support this proposal since the apparent activation energy increases rather than decreases.

The desorption of carbon dioxide has been related (*31–33*) to the binding energy of surface oxygen as demonstrated in the case of nickel(II) oxide where carbon dioxide desorption becomes progressively more difficult with increased surface oxygen mobility, as in "black" NiO, becoming relatively more facile for the near-stoichiometric "green" NiO. Because the oxygen mobility for the vanadium pentoxide melts containing alkali metal sulfate increases in the order (*9*)

$$\text{(none)} < Li_2SO_4 < Na_2SO_4 < K_2SO_4 < Rb_2SO_4 < Cs_2SO_4,$$

the observed compensation effect, Fig. 2, can be related to the desorption of carbon dioxide from the surface, whereupon nitrous oxide can migrate to the vacated site and decompose. Indeed, the graph of $r(P_{CO_2})^{\frac{1}{2}}$ versus $(P_{CO_2})^{\frac{1}{2}}$ shows that the capacity to retain carbon dioxide increases in the series: $Li_2SO_4 < Na_2SO_4 < K_2SO_4$, where rate-order data were obtained at the same temperature. Thus, the compensation effect observed for the series of vanadium pentoxide/alkali metal sulfate catalysts would appear to be related to the mobility of the surface oxygen which may influence the rate of carbon dioxide desorption and, in turn, the apparent activation energy.

Whether the sequence of reactions (5) to (7) proceeds in an exclusive, concerted, or stepwise manner is not certain. Although a concerted process has been proposed for carbon monoxide oxidation by molecular oxygen on V_2O_5 (*27*), increased surface oxygen mobility has been shown (*33*) to favor a stepwise process. Also, the oxidation of carbon monoxide on V_2O_5 (*35*) has been reported to proceed at low temperatures via a concerted reaction which changes in the temperature region of 733 to 863 K to a two-step process. Since the V_2O_5/Cs_2SO_4 catalyst possesses the highest oxygen mobility in the present series, any change in mechanism would be expected to occur at a lower temperature on this than with the others. Thus the change in the apparent activation energy from 24 to 38 kcal mol^{-1} at ~670 K for the cesium sulfate melt may be associated with the nature of the surface mechanism. A similar proposal cannot be made unequivocally for the sodium sulfate melt, where the change in apparent activation from 25 to 32 kcal mol^{-1} occurs at $\sim$744 K, since the addition of sodium sulfate to vanadium pentoxide is known (*35*) to form "vanadium bronzes".

Thus for the series of melts containing alkali metal sulfate, a common reaction mechanism is indicated proceeding via a "carbonate"-like intermediate bound to the surface via two chemically different surface oxygen species, and the observed compensation effect may be associated with the progressive increase in the oxygen mobility of the catalyst with the consequences that this has on surface site activity and, in turn, on the apparent activation energy.

ACKNOWLEDGMENTS

We thank Imperial Oil Enterprises Ltd., Toronto, Canada, for financial assistance and Mr. K. Heckley for the preparation of the vanadium pentoxide melts used in this study.

REFERENCES

1. Caretto, L. S., McElroy, M. W., Nelson, J. L., and Venturini, P. D., *in* "Project Clean Air Task Force Assessments," Vol. 1. Prepared for the University of California, September 1, 1970.
2. Shelef, M., and Kummer, J. T., *Chem. Eng. Progr. Symp. Ser.* **67**, No. 115 (1972).
3. Dwyer, F. G., *Catal. Rev.* **62**, 261 (1972).
4. Shelef, M., Otto, K., and Gandhi, H., *J. Catal.* **12**, 361 (1968).
5. Shelef, M., and Otto, K., *J. Catal.* **10**, 408 (1968).
6. Golodets, G. I., and Roiter, V. A., *Ukr. Khim. Zh.* **29**, 667 (1963).
7. Klier, K., *J. Catal.* **8**, 14 (1967).
8. Boreskov, G. K., *Kinet. Catal.* **8**, 1020 (1967).
9. Bibin, V. N., and Kasatkina, L. A., *Kinet. Catal.* **15**, 653 (1964).
10. Boreskov, G. K., "Catalysis in Sulfuric Acid Production" (in Russian). State Press for Chemical Literature, Moscow, 1954.
11. Dzisyak, A. P., Boreskov, G. K., Kasatkina, L. A., and Kochurikhin, V. E., *Kinet. Catal.* **2**, 727 (1961).
12. Jiru, P., Tomkova, D., Jara, V., and Wankova, J., *Z. Anorg. Allg. Chem.* **121**, 303 (1960).
13. Krupay, B. W., and Ross, R. A., *Canad. J. Chem.* **51**, 3520 (1973); Krupay, B. W., and Ross, R. A., *J. Catal.* **39**, 369 (1975).
14. Satterfield, C. N., "Mass Transfer in Heterogeneous Catalysis." M. I. T. Press, Cambridge, Mass., 1970.
15. Hucknall, D. J., "Selective Oxidation of Hydrocarbons," p. 153. Academic Press, London/New York 1974.
16. Byström, A., *et al.*, *Acta Chem. Scand.* **4**, 1119 (1950).
17. Wells, A. F., "Structural Inorganic Chemistry," p. 686. Clarendon Press, Oxford, 1962.
18. Kera, Y., and Hirota, K., *J. Phys. Chem.* **73**, 3973 (1969).
19. Boreskov, G. K., Kasatkina, L. A., Popovskii, V. V., and Balovnev, Yu. A., *Kinet. Catal.* **1**, 207 (1960).
20. Bond, G. C., "Heterogeneous Catalysis: Principles and Applications," p. 33. Clarendon Press, Oxford, 1974.
21. Yang, K. H., and Hougen, O. A., *Chem. Eng. Progr.* **46**, 146 (1950).
22. Hougen, O. A., and Watson, K. M., "Chemical Process Principles," Part III. Wiley, New York/London, 1966.
23. Boudart, M., *AIChE J.* **2**, 62 (1956).
24. Weller, S. W., "Chemical Reaction Engineering Reviews" (H. M. Hulburt, Ed.), p. 26. American Chemical Society, Washington, D. C., 1975.
25. Hirota, K., Kera, Y., and Teratani, S., *J. Phys. Chem.* **72**, 3133 (1968).
26. Adachi, M., Imanaka, T., and Teranishi, S., *Nippon Kagaku Zasshi* **89**, 446 (1968).
27. Boreskov, G. K., Marshneva, V. I., and Sokolovskii, V. D., *Dokl. Akad. Nauk SSSR* **199**, 1091 (1971).
28. Boreskov, G. K., Gruver, V. Sh., and Yur'eva, T. M., *Kinet. Catal.* **10**, 862 (1969).
29. Thomas, J. M., and Thomas, W. J., "Introduction to the Principles of Heterogeneous Catalysis." Academic Press, London/New York, 1967.
30. Munakata, M., *Solid-State Electron.* **1**, 159 (1960); Nester, H. H., and Kingery, W. D., *in* "VII International Congress on Glass," Brussels. Paper 106 (1965); Rawson, H., "Inorganic Glass-Forming Systems," p. 195. Academic Press, New York, 1967.
31. Boreskov, G. K., Pankrat'ev, Yu. D., and Popovskii, V. V., *Kinet. Catal.* **13**, 1101 (1972).
32. Krupay, B. W., and Ross, R. A., *Canad. J. Chem.* **52**, 3063 (1974).
33. Boreskov, G. K., Mamedov, E. A., and Popovskii, V. V., *Kinet. Catal.* **14**, 451 (1973).
34. Boreskov, G. K., and Marshneva, V. I., *Dokl. Akad. Nauk SSSR* **213**, 926 (1973).
35. Fotiev, A. A., and Slobodin, B. V., *Russ. J. Inorg. Chem.* **10**, 80 (1965).