

The Low-Temperature Catalytic Oxidation of CO with N₂O by Molybdenum Oxide Supported on Silica Gel

AKIO KAZUSAKA AND JACK H. LUNSFORD

Department of Chemistry, Texas A&M University, College Station, Texas 77843

Received May 3, 1976

On the surface of partially reduced molybdenum oxide supported on silica gel the O⁻ ion was formed from adsorbed N₂O and reacted with CO to give the CO₂⁻ ion. The latter ion was thermally stable to temperatures in excess of 100°C. Preadsorption of CO inhibited the formation of the O⁻ and CO₂⁻ ions, but the preadsorption of CO₂ had no effect on the formation of the two species. The supported molybdenum oxide was active for the oxidation of CO to CO₂ at temperatures as low as 0°C. At all pressures and temperatures studied, the reaction rate was zero order in the partial pressure of CO and CO₂; whereas, the rate was zero or first order with respect to the N₂O partial pressure, depending upon the pressure and temperature. Apparent activation energies of 14.9 and 10.8 kcal/mole were determined for the zero and first order reactions, respectively. In view of the thermal stability of CO₂⁻ and the inhibiting effect of CO, it is concluded that the O⁻ ion is not an intermediate in the low-temperature reaction. Rather, the reaction appears to involve molecular complexes of N₂O and CO on clusters of metal ions.

INTRODUCTION

Kinetic studies interpreted in light of conductivity measurements and electron paramagnetic resonance (EPR) spectroscopy have led to a model in which O⁻ on the surface is an important intermediate in the catalytic oxidation of CO with N₂O or O₂ (1-4). It has been demonstrated that the O⁻ ion on MgO reacts with CO, forming CO₂⁻ at low temperatures (5, 6). Kazankii and co-workers (4) have further shown that over V₂O₅ supported on silica gel the O⁻ ion rapidly reacts with CO, and at 20°C CO₂ was detected in the gas phase (4). The number of CO₂ molecules formed was approximately equal to the original number of O⁻ ions. The amount of CO₂ produced in the gas phase was two to three times greater when a mixture of CO and O₂ was added to the catalyst, but the reaction was not catalytic at 20°C. On the basis of these results and kinetic data obtained at

460°C, the authors conclude that the oxidation of CO does not involve lattice oxide ions, but rather adsorbed oxygen in the form of O⁻ ions.

The purpose of the present study was to determine whether the O⁻ ion is in fact an intermediate in the catalytic oxidation of CO to CO₂. A partially reduced molybdenum oxide catalyst supported on silica gel was chosen since it has been demonstrated that the O⁻ ion may be readily formed upon adsorption of N₂O (7, 8). The O⁻ ion, which is thermally stable at temperatures below 100°C, was detected by EPR spectroscopy. Its oxygen-17 hyperfine structure was used to confirm the identification (8). From the molybdenum hyperfine structure it is evident that each O⁻ ion was bonded to a molybdenum ion. One may also deduce from the spectrum that the molybdenum ion was diamagnetic and probably in the +6 oxidation state. These

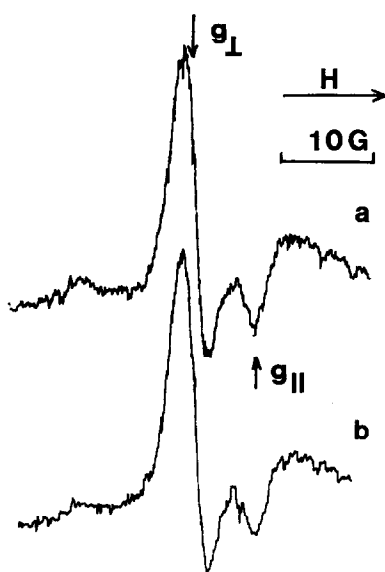


FIG. 1. EPR spectra of CO_2^- on partially reduced $\text{MoO}_3/\text{SiO}_2$: (a) formed by the reaction of O^- with CO (58 Torr) at 26°C , (b) after heating at 60°C for 30 min.

observations, however, do not preclude the possibility that other O^- ions may be bonded to molybdenum in lower oxidation states. Photoelectron spectroscopy studies by Cimino and DeAngelis (9) suggest that the +4 oxidation state is prevalent on the surface of molybdenum oxides supported on silica gel after partial reduction with H_2 at 400°C .

EXPERIMENTAL

Catalysts were prepared which contained 2.1 or 6.6% Mo by weight supported on silica gel. A solution containing ammonium paramolybdate and silica gel was evaporated to dryness while being stirred. After drying at 90°C for several hours, the impregnated catalyst was heated in air at 500°C for 20 hr to decompose the ammonium paramolybdate. The sample was subsequently treated in 150 Torr of O_2 for 1 hr at 500°C and degassed *in vacuo* at 500°C for 1 hr.

The O_2 , CO , CO_2 , and N_2O gases were obtained from commercial sources. The

O_2 was used without further purification, and the CO was purified by passing through a cold trap at -196°C . The CO_2 and N_2O were purified by freezing at -196°C and collecting the gases that sublimed up to a temperature of -78°C . This procedure was repeated twice.

The apparatus used in the kinetic study was a conventional closed recirculating system, having a total volume of 200 cc. The CO , N_2O , and CO_2 gases were analyzed using an on-line gas chromatograph with a silica gel column at 0°C .

For the EPR study the samples were contained in a conventional fused quartz reactor which had a side arm 4 mm in diameter. A Model E-6S Varian spectrometer was employed to obtain the EPR data. Spectra were recorded with the sample either at 26 or -196°C .

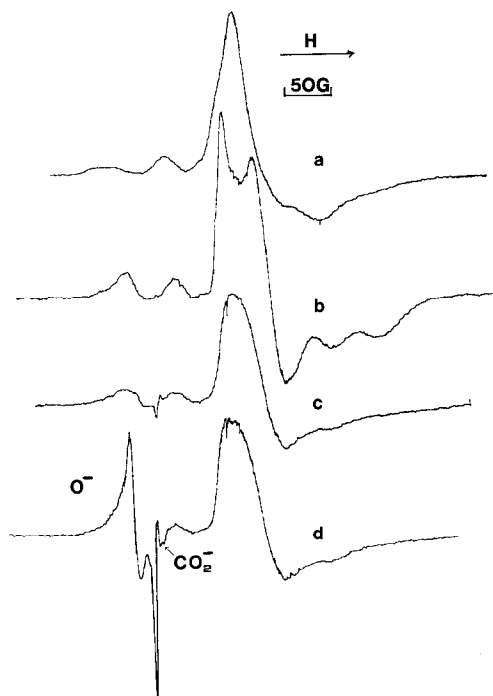


FIG. 2. EPR spectra of partially reduced $\text{MoO}_2/\text{SiO}_2$: (a) Mo^{5+} spectrum, (b) after the addition of CO (59 Torr) at 26°C , (c) after removal of gas phase CO in (b) and addition of N_2O , (d) after 10 hr at 26°C .

RESULTS

EPR Experiments

Most of the experiments were carried out on the sample which contained 2.1% Mo by weight. Following the pretreatment with O₂ and evacuation at 500°C, the sample was reduced in 150 Torr of CO for 30 min at 500°C. The CO was then evacuated at 500°C for an additional 30 min, and the sample was cooled. Upon exposing the sample to 30 Torr of N₂O at room temperature, the EPR spectrum of the O⁻ ion, as previously reported, was observed. In a pulse experiment it was determined that the amount of N₂ formed was an order of magnitude greater than the O⁻ spin concentration.

The O⁻ signal disappeared rapidly upon admitting 58 Torr of CO to the catalyst at 26°C, and a new signal was observed as shown in Fig. 1a. This spectrum, attributed to the CO₂⁻ ion, is characterized by $g_1 = 2.0020$ and $g_{11} = 1.9976$. The spectrum remained unchanged upon heating the sample in CO to 60°C for 30 min, and it was still observable, though less intense, after heating the sample to 200°C for 15 min.

The spectrum of Mo⁵⁺ in the reduced sample is shown in Fig. 2a. The addition of 59 Torr of CO to this sample resulted in a substantial modification of the spectrum as depicted in Fig. 2b. Since both ¹²CO and ¹³CO produced the same spectrum, one may conclude that the new spectrum is due to a modification in the symmetry of Mo⁵⁺ rather than the formation of a new radical involving CO. Removal of the CO by brief evacuation at 26°C resulted in a spectrum very similar to that depicted in 2c, suggesting that part of the CO remained coordinated to the Mo⁵⁺ ions.

Subsequent addition of 30 Torr N₂O at 26°C did not immediately result in the formation of O⁻ as shown by the spectrum of Fig. 2c. A very weak signal was observed at $g = 2.002$. After keeping the sample for

10 hr at 26°C, both the spectrum of the O⁻ ion and the spectrum of the CO₂⁻ ion, though less intense, were observed (Fig. 2d). The O⁻ signal was not detected following the introduction of mixtures of CO (59 Torr) and N₂O (31 or 195 Torr) to a reduced sample which was maintained at 60°C. In general it was found that the presence of CO inhibited the formation of both the O⁻ and CO₂⁻ ions which were observed by EPR spectroscopy.

The addition of CO₂ at a pressure of 50 Torr to a freshly reduced sample resulted in the formation of a very weak signal with $g = 2.002$. The spectrum of the Mo⁶⁺ was unperturbed. Upon the addition of 28 Torr of N₂O at 59°C, the O⁻ signal appeared with essentially the same amplitude as obtained for a sample which had not been exposed to CO₂.

Kinetic Experiments

Three gram samples of the catalyst containing 2.1% by weight of molybdenum were pretreated as described for the EPR experiments. The CO and N₂O gases were introduced over the catalyst after mixing them for 20 min by circulation through a bypass. After each kinetic run the catalyst was reduced again at 500°C. For the first four cycles the catalytic activity increased, but thereafter it remained stable.

A typical time course of the reaction is shown in Fig. 3. The initial pressure of CO was about 60 Torr, while the initial pressure of N₂O was 58 and 117 Torr for the experiments depicted by Fig. 3a and b, respectively. Except for the initial stage of the reaction, the sum of the partial pressures of N₂O and CO₂ remained constant as long as CO was present, but the sum may have decreased slightly after the CO was depleted. The constant value for the sum of the partial pressures indicates that all of the oxygen atoms from N₂O were transferred to CO without any net oxidation of the catalyst.

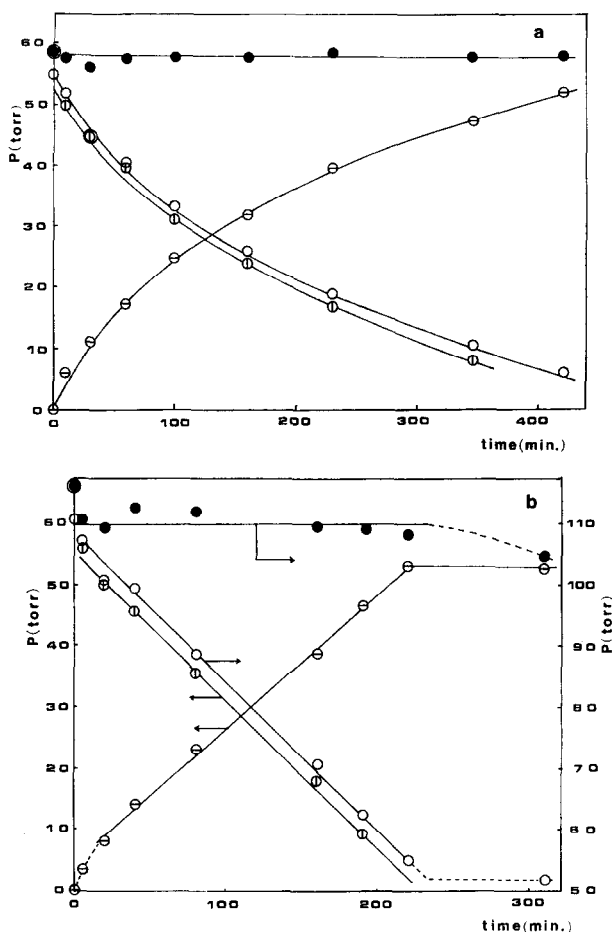


FIG. 3. Partial pressures of the gas phase during the oxidation of CO with N₂O at 60°C: ○, N₂O; ⊕, CO; ⊖, CO₂; ●, sum of the partial pressures of N₂O and CO₂. Initial pressure of N₂O was 58 Torr in (a) and 117 Torr in (b).

As shown in Fig. 4, the reaction order with respect to N₂O depended upon the N₂O pressure at 60°C. Zero order was observed in the range of 60 to 150 Torr of N₂O; whereas, first order was observed for pressures less than 60 Torr. At 26°C the reaction was first order with respect to N₂O even in the range of 60 to 120 Torr, as shown in Fig. 4c. It may be observed from Fig. 4a and b that the rate did not depend on the pressure of CO. The initial CO pressures were approximately 30 and 60 Torr.

The effect of CO₂ on the reaction rate was tested both in the regions where the

reaction was first order and zero order with respect to N₂O. In the former case the CO₂ partial pressure was abruptly changed from 18 to 59 Torr, and after a perturbation in the reaction rate over a period of several minutes the original rate was recovered. At the higher pressures of N₂O, the initial addition of 37 Torr of CO₂ did not alter the steady state reaction rate.

We can summarize the kinetic data by the following rate equations:

$$\text{Rate} = kP_{\text{N}_2\text{O}}^1 P_{\text{CO}}^0 P_{\text{CO}_2}^0$$

Low pressure of N₂O, $T \geq 60^\circ\text{C}$;
low and high pressure of N₂O,
 $T = 26^\circ\text{C}$ (1)

$$\text{Rate} = k' P_{\text{N}_2\text{O}}^0 P_{\text{CO}}^0 P_{\text{CO}_2}^0$$

High pressure of N_2O , $T \geq 60^\circ\text{C}$ (2)

where k and k' indicate the rate constants and $P_{\text{N}_2\text{O}}$, P_{CO} , and P_{CO_2} the partial pressures of N_2O , CO , and CO_2 , respectively.

The Arrhenius plots of the reaction rate constants over the temperature range from 26 to 120°C are shown in Fig. 5. The

calculated activation energies were 10.8 and 14.9 kcal/mole for Eqs. 1 and 2, respectively, with an estimated error of ± 1 kcal/mole. As indicated in the figure caption, the data for the first-order reaction was taken at a low pressure of N_2O , and the data for the zero-order reaction was taken at a high pressure of N_2O .

A three gram sample of the catalyst containing 6.6% by weight molybdenum

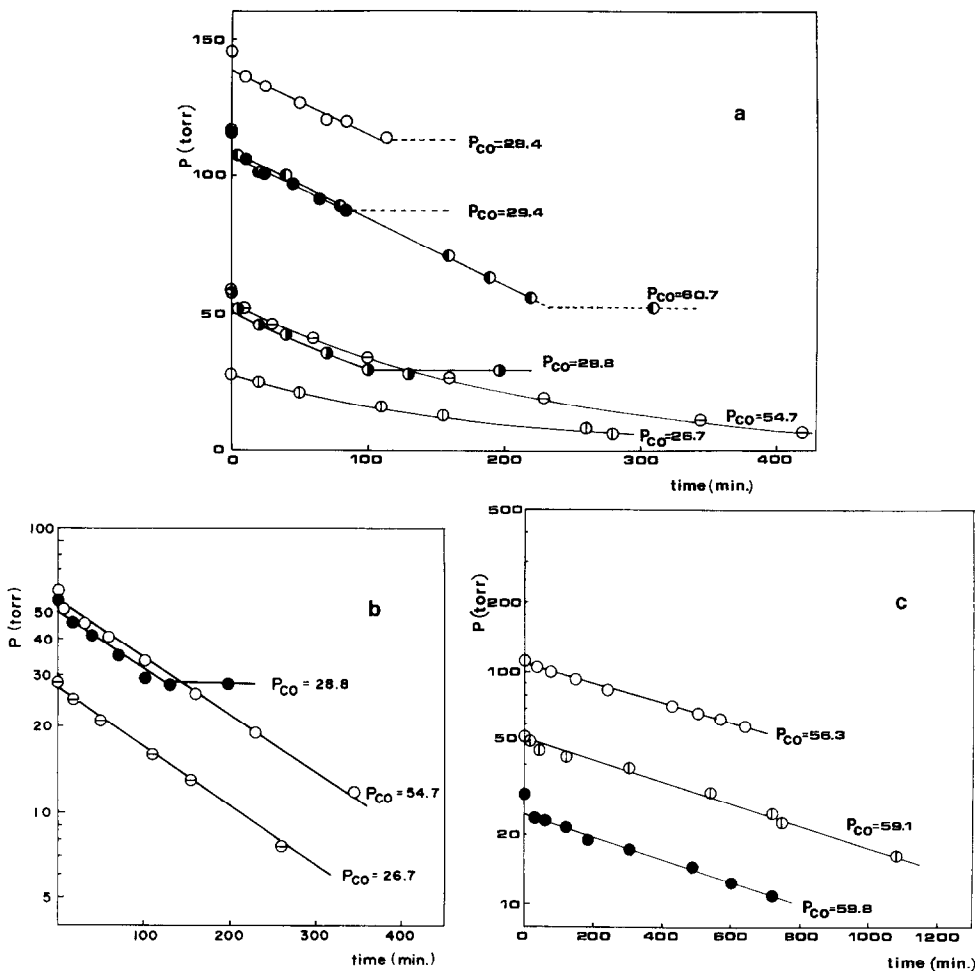


FIG. 4. Dependence of reaction rates on temperature and the partial pressure of CO and N_2O . (a) Initial pressures: $P_{\text{N}_2\text{O}} = 145.5$ Torr (\circ), $P_{\text{CO}} = 28.4$ Torr; $P_{\text{N}_2\text{O}} = 116.8$ Torr (\bullet), $P_{\text{CO}} = 60.7$ Torr; $P_{\text{N}_2\text{O}} = 115.2$ Torr (\blacklozenge), $P_{\text{CO}} = 29.4$ Torr; $P_{\text{N}_2\text{O}} = 57.9$ Torr (\ominus), $P_{\text{CO}} = 28.8$ Torr; $P_{\text{N}_2\text{O}} = 58.4$ Torr (\oplus), $P_{\text{CO}} = 54.7$ Torr; $P_{\text{N}_2\text{O}} = 28.1$ Torr (\diamond), $P_{\text{CO}} = 26.7$ Torr. Reaction temperature: 60°C . (b) Initial pressures: $P_{\text{N}_2\text{O}} = 58.4$ Torr (\circ), $P_{\text{CO}} = 54.9$ Torr; $P_{\text{N}_2\text{O}} = 57.9$ Torr (\bullet), $P_{\text{CO}} = 28.8$ Torr; $P_{\text{N}_2\text{O}} = 28.1$ Torr (\ominus), $P_{\text{CO}} = 26.7$ Torr. Reaction temperature: 60°C . (c) Initial pressures: $P_{\text{N}_2\text{O}} = 112.0$ Torr (\circ), $P_{\text{CO}} = 56.3$ Torr; $P_{\text{N}_2\text{O}} = 52.9$ Torr (\oplus), $P_{\text{CO}} = 59.1$ Torr; $P_{\text{N}_2\text{O}} = 29.6$ Torr (\bullet), $P_{\text{CO}} = 59.8$ Torr. Reaction temperature: 26°C .

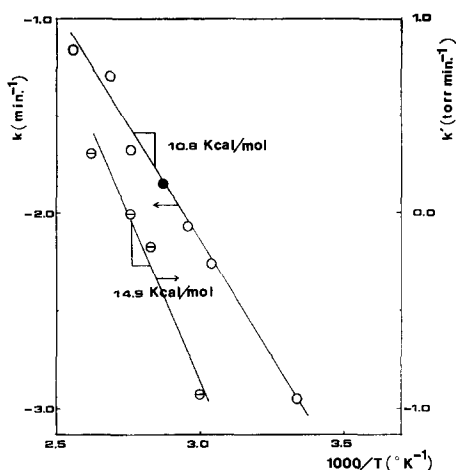


FIG. 5. Arrhenius plots of k and k' . Initial pressures: $P_{N_2O} = 29$ Torr, $P_{CO} = 59$ Torr (O); $P_{N_2O} = 150$ Torr, $P_{CO} = 71$ Torr (\ominus), $P_{N_2O} = 29$ Torr, $P_{CO} = 58$ Torr, $P_{CO_2} = 26$ Torr (\bullet).

was pretreated in the same manner as that described for the sample of lower loading. A stable activity was obtained after four reduction and reaction cycles. The results showed that the activity of the sample containing 6.6% Mo by weight molybdenum was approximately 100 times greater than the sample containing 2.1% Mo by weight. The reaction was carried out over the more active catalyst at 0°C, and the reaction was first order in N_2O and zero order in CO.

In order to determine the rate of reduction of lattice oxide ions the sample containing 6.6% Mo was reduced with 150 Torr of CO at elevated temperatures. The rate of CO_2 formation was very slow at temperatures less than 300°C; thus it is doubtful that the observed catalytic reaction involved extensive reduction and oxidation of the molybdenum oxide.

DISCUSSION

The spectrum of Fig. 1a demonstrates that CO rapidly reacts with O^- to form CO_2^- . The unresolved structure in the region of the low-field maximum (g_1) may be due to line broadening or to motion

perpendicular to the plane of the CO_2^- ion. In any event, the values of $g_1 = 2.0020$ and $g_{11} = 1.9976$ are the same, within experimental error, as those obtained for CO_2^- on MgO^{10} ($g_1 = 2.0017$, $g_2 = 2.0029$, and $g_3 = 1.9974$) if one assumes that g_1 and g_2 are averaged to give g_1 . The stability of the CO_2^- ion on the supported molybdenum catalysts was not surprising in view of its stability on MgO.

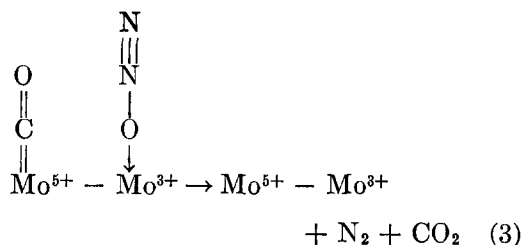
The unexpected result from this study was the remarkable activity of the catalyst for CO oxidation at temperatures as low as 0°C. It seems unlikely that the CO_2^- ion, which was thermally stable in excess of 100°C, could be an intermediate in the low-temperature reaction. On the basis of the large N_2/O^- ratio one could argue that only a small fraction of the CO_2^- was actually observed and that the remainder was less stable. There is little reason to believe, however, that the CO_2^- would be significantly less stable on lower oxidation states of molybdenum.

Additional evidence against the role of O^- in the low temperature oxidation reaction comes from the inhibiting effect of CO on the formation of O^- . As long as CO was present on the surface, no O^- could be formed, as indicated by the results of Fig. 2. It is inferred from Fig. 2 that CO is weakly adsorbed on part of the observed Mo^{5+} , thus modifying the symmetry of the metal ion, but CO is more strongly held on another form of Mo^{5+} . This latter Mo^{5+} is ultimately the site for the formation of $Mo^{6+}-O^-$ ion pairs.

If one discards the theory that O^- is an important intermediate in the low-temperature catalytic reaction, then the most reasonable alternative appears to be a reaction between molecular complexes of N_2O and CO. The strong dependence of the reaction rate on the concentration of molybdenum suggests that two or more metal ions are necessary for the formation of the active center. At least some of the

ions in the cluster must be in a partially reduced state.

In view of the kinetic data it seems that the N_2O and CO are adsorbed on ions having different oxidation states, and the sites which adsorbed the CO are totally covered. In this respect it should be mentioned that we were unable to observe infrared absorption bands due to either a N_2O or a CO complex, thus the concentration of such complexes must be small. The reaction may be described as



although the oxidation states of the metal ions are a matter of speculation. The rate equations may be understood by assuming that Eq. 3 is the slow step in the reaction mechanism and that the available sites for coordination with N_2O become saturated rather abruptly at N_2O pressures near 60 Torr. The reaction rate would therefore be first order in N_2O at lower pressures but zero order at higher pressures.

Stable complexes involving N_2O are not very common; however, at least two ruthenium ammine complexes with nitrous oxide have been prepared (11, 12). More pertinent to the present discussion is the work of Borello *et al.* (13) on surface complexes of nitrous oxide formed on $\alpha\text{-Cr}_2\text{O}_3$. Two chemisorbed nitrous oxide species were identified by their infrared spectra. The infrared bands were assigned to N_2O adsorbed through the oxygen atom

and through the terminal nitrogen atom. Both forms of adsorbed N_2O rapidly reacted with CO, forming adsorbed CO_2 . These results lend credence to the hypothesis that N_2O can adsorb in a nondissociative manner on transition metal ions in a low oxidation state. Furthermore, such N_2O complexes may in general be reactive with respect to CO.

ACKNOWLEDGMENT

The authors wish to acknowledge the support of the National Science Foundation under Grant No. CHE75-15456.

REFERENCES

1. Amigues, P., and Teichner, S. J., *Discuss. Faraday Soc.* **41**, 362, 404 (1966).
2. Chon, H., and Prater, C. D., *Discuss. Faraday Soc.* **41**, 380, 401 (1966).
3. Tanaka, K., and Blyholder, G., *Chem. Commun.*, 736 (1971).
4. Kazanskii, V. B., Shvets, V. A., Kon, M. Ya., Nikisha, V. V., and Shelimov, B. N., "Catalysis" (J. Hightower, Ed.), pp. 1423-1435. North-Holland, Amsterdam, 1973.
5. Naccache, C., *Chem. Phys. Lett.* **11**, 323 (1971).
6. Mariaudeau, P., Vedrine, J. C., Ben Taarit, Y., and Naccache, C., *J. Chem. Soc. Faraday Trans., II*, **71**, 736 (1975).
7. Shvets, V. A., and Kazanskii, V. B., *J. Catal.* **25**, 123 (1972).
8. Ben Taarit, Y., and Lunsford, J. H., *Chem. Phys. Lett.* **19**, 348 (1973).
9. Cimino, A., and DeAngelis, B. A., *J. Catal.* **36**, 11 (1975).
10. Lunsford, J. H., and Jayne, J. P., *J. Phys. Chem.* **62**, 2182 (1965).
11. Armor, J. N., and Taube, H., *Chem. Commun.*, 287 (1971).
12. Diamantis, A. A., and Sparrow, G. J., *Chem. Commun.*, 819 (1970).
13. Borello, E., Cerruti, L., Ghiotti, G., and Guglieiminotti, E., *Inorg. Chimica Acta* **6**, 45 (1972); Zecchina, A., Cerruti, L., and Borello, E., *J. Catal.* **25**, 55 (1972).