

The Oxidation of CO by O₂ and by NO on Supported Chromium Oxide and Other Metal Oxide Catalysts

M. SHELEF, K. OTTO, AND H. GANDHI

From the Scientific Research Staff, Ford Motor Company, Dearborn, Michigan 48121

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The oxidation of CO by NO and by O₂ has been studied on a number of supported transition metal oxide catalysts. On supported chromia the oxidation of CO by NO is faster than by O₂; however, with mixtures of NO and O₂ the reaction is selective towards O₂.

The application of continuous mass-spectrometer monitoring to the study of surface state changes in chromia catalysts is outlined. The method was extended to determine the oxidation state of the surface *in situ* during reaction. In the oxidation-reduction cycle involving alternate passage of He-CO and He-O₂ mixtures at 500°, the majority of the surface atoms undergo a change of oxidation state from Cr⁶⁺ to Cr³⁺. The extent of this change diminishes with decreasing temperature. Mixtures of He and NO oxidize the surface of supported chromia to a lesser extent than He-O₂. During the CO-NO reaction the average surface oxidation state is lower than in the presence of oxygen. A tentative explanation is offered for the selectivity for oxygen over nitric oxide in the oxidation-reduction reactions on commonly employed catalysts.

INTRODUCTION

It was noted in work from this laboratory (1) carried out in connection with automobile exhaust treatment, that with presently known catalysts the catalytic decomposition of NO is a slow process. On the other hand the catalyzed reduction of NO by CO or H₂ is relatively fast (2, 3, 4). Hence it should be possible, in principle, to remove NO from the exhaust using a number of known catalysts provided that there is an excess of reducing agents in the gas stream. These latter, CO and hydrocarbons mainly, are *per se* pollutants and for their removal an oxidizing atmosphere is required. Excess oxygen, achieved by lean carburization or air addition to the exhaust stream, hampers or entirely prevents the catalytic reduction of NO (2). With the above situation in mind a search was made for a catalyst selective towards the CO-NO reaction with respect to the CO-O₂ reaction among the metal oxides of the first transition series. The results of this search warranted a more detailed study of the CO-NO reaction on a chromium oxide catalyst.

EXPERIMENTAL METHODS

a. Reactivity runs. The reaction between CO and NO or O₂ in an integral flow reactor was studied on a series of supported catalysts, consisting of transition metal oxides or platinum on a 95% alumina-5% silica base supplied by the American Cyanamid Co. The catalysts were prepared by impregnation of the support with the corresponding nitrate solution, solutions of ammonium dichromate and copper nitrate in the case of CuCrO₄ catalysts, and with a chloroplatinate solution in the case of platinum. The vanadia catalyst was supplied by the American Cyanamid Co. The catalysts were dried and calcined at 600°C for 8 hr, with the exception of the Pt catalyst which was dried and reduced in a hydrogen stream at 400°C. The support pellets were cylinders 25-30 mm long with an average diameter of 1.5 mm. The pore volume was 0.70-0.75 cc/g. The transition metal content was ~10% by weight (3.7% in the case of Pt). The total surface area of the supported catalyst was 210-230 m²/g. In a typical run 80 cc of the catalyst weighing about 45 g was used and

a mixture containing ~ 1.2 mole % CO, ~ 2.0 mole % NO, and the balance He carrier gas was passed over this catalyst at atmospheric pressure at a flow rate of 1400 cc/min.

The catalysts were confined in a quartz glass tube of 30-mm inner diameter between two quartz glass discs with closely spaced perforations of 1-mm diameter. The length of the catalyst bed of 100–130 mm was preceded by a preheated zone of 100-mm length filled with chips of quartz glass. A Marshall tube furnace (400 mm long and 50 mm in diameter) with its axis in a horizontal position, was employed. A constant temperature within 0.5°C was kept by an electronic controller. The temperature of the catalyst bed was measured at its center by a sheathed chromel-alumel thermocouple in connection with a potentiometer. The temperature difference across the catalyst bed did not exceed 5°C .

The gas mixture was analyzed by a CEC 21-614 mass spectrometer calibrated for pure gases (1, 5). The He, H_2O , CO, O_2 , and CO_2 concentrations were monitored by peak intensities at $m/e = 4, 18, 28, 32,$ and 44 . In the case of the competitive oxidation of CO by NO and O_2 the composition of the eight-component mixture of He, H_2O , CO, N_2 , NO, O_2 , CO_2 , and N_2O was computed from a set of simultaneous equations using the peak intensities at $m/e = 4, 14, 18, 22, 28, 30, 32,$ and 44 . There was no significant peak observed at $m/e = 46$, indicating the absence of NO_2 formation. The limit of precision of the analysis, as deduced from numerous runs, is $\sim 0.05\%$ of the total gas stream and stems mainly from the small coefficients contributed to the simultaneous equations by the intensities at the secondary m/e peaks 14 and 22, the use of which is necessary to distinguish, respectively, between N_2 and CO, and N_2O and CO_2 . The conversion figures obtained refer in all cases to a steady state of the catalyst surface which is indicated by the constancy of the mass spectrometer reading.

b. Chromium oxide catalyst preparation. Sample A, used in the major part of this investigation, was the same as used in the reactivity runs. The Cr content of sample A

was 10%. The X-ray diffraction showed lines belonging to $\alpha\text{-Cr}_2\text{O}_3$.

Sample B was prepared following the procedure of Chapin and Johnston (6) by impregnation of the above support with a CrO_3 solution. The filtered and washed catalyst was dried at 110° , calcined in air for 3 hr at 350° and for 8 hr at 600° . The Cr content of Sample B was 0.55% Cr.

Sample C of pure chromia was made by adding a solution of 1 *N* NH_4OH to a hot ($80\text{--}90^\circ$) solution of 1 *N* $\text{Cr}(\text{NO}_3)_3 + 1 \text{N}$ NH_4NO_3 during constant stirring until a pH of 8.0 was attained. The precipitated gel was repeatedly washed, dried at 100° , and calcined at 400° for 6 hr. After this treatment the BET surface area was $25.2 \text{ m}^2/\text{g}$.

c. Determination of the oxidation state of the catalyst surface. The oxidation state of the surface of chromium oxide catalysts was established by using a modified method of Weller and Voltz (7). Instead of employing a recirculation or a static apparatus and following the volume changes, the same flow-through reactor of the catalytic reaction experiments was used. At a given temperature the sample was treated by a metered flow of He with a constant concentration of oxygen, fixed in the 1.5–2.5% range. Following 1 hr of treatment the reactor was flushed out with He for ~ 5 min until the mass spectrometer scan of the outlet indicated the absence of oxygen. The He flow then bypassed the reactor, a constant concentration of CO was metered into it and fixed in the range of 2.5–3.5% and the mass spectrum recorded. The mass spectrometer chart was set to an appropriate speed and the monitoring of the outlet gas was started at the time when the flow of the He-CO mixture was directed into the reactor. Instead of monitoring continuously one particular peak the mass spectrum was scanned at 1–2 min intervals to enable the construction of complete material balances. The reduction of the surface was manifested by the disappearance of CO (m/e peak 28) and the appearance of CO_2 (m/e peak 44) and was considered as complete when the CO peak recovered to its original value in the inlet composition and the CO_2 peak subsided. This took 30 to 60 min depending on the

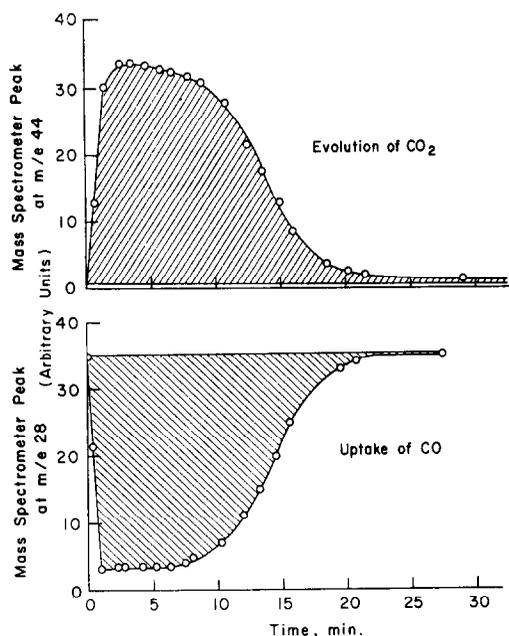


FIG. 1. Example of CO uptake and CO₂ evolution in the reduction half-cycle of a reduction-oxidation experiment; 46 g (80 cm³) of catalyst A, 345°C.

temperature. The reactor was then flushed out by He until elimination of the CO peak from the recorder trace and the same procedure was repeated with a He-O₂ mixture. The whole oxidation-reduction cycle was repeated at least twice at each temperature. In the passage of the He-O₂ mixture there usually appeared a CO₂ peak which was monitored and ascribed to CO (or CO₂) chemisorbed on the reduced surface in the previous reduction half cycle.

The peak heights were plotted versus time in a manner shown on Fig. 1, and the area corresponding to the appearance or

disappearance of a given component was traced by a planimeter and converted into the amount of that component taken up (or given off) by a unit weight of catalyst using the known flow rate and inlet composition of the gas mixture and mass spectrometer sensitivity for the given gas constituent. When the peak under consideration also had contributions from secondary peaks of another component the necessary corrections were applied. For instance, the CO peak at $m/e = 28$ has a contribution also from CO₂ which amounts to 8.01% of the peak of CO₂ at $m/e = 44$. Therefore the CO uptake has to be increased by an amount equivalent to 8.01% of the evolved CO₂ corrected by the small factor 1.09/1.08 representing the ratio of mass spectrometer sensitivity for CO to that for CO₂.

It is apparent from Fig. 1 that there is a certain error associated with the tail of the integrated area. From the material balances referred to subsequently the total error including the tail area, flow changes, mass spectrometer peak reading, etc., is estimated to be below 10%.

To compare the extent of surface oxidation by NO to that by O₂, oxidation runs of a reduced surface were made in a similar manner using a He-NO mixture with a NO concentration fixed in the 3.0-4.0% range.

In addition to the mass spectrometer measurements, the oxidation state after oxidation by O₂ at each temperature was determined iodometrically. A weighed amount of the sample (~0.5 g) was put into an Erlenmeyer flask together with 100 cc of distilled H₂O, 30 cc of HCl, and 1.2 g of KI; the flask was flushed with Ar, stoppered, and left

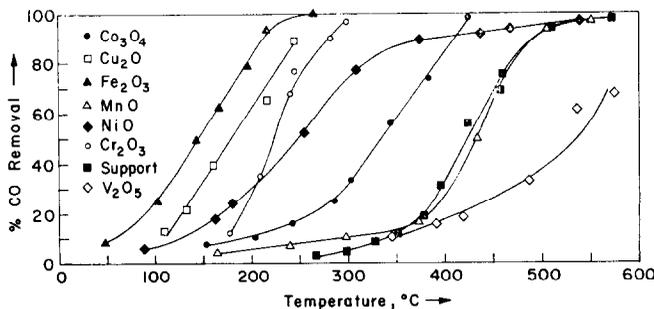


FIG. 2. Relative reactivity curves for the CO-NO reaction. Conditions: 45-46 g (80 cm³) of catalyst; gas composition, CO ~1.2%, NO ~2.0%, balance He; gas rate ~1400 cm³/min.

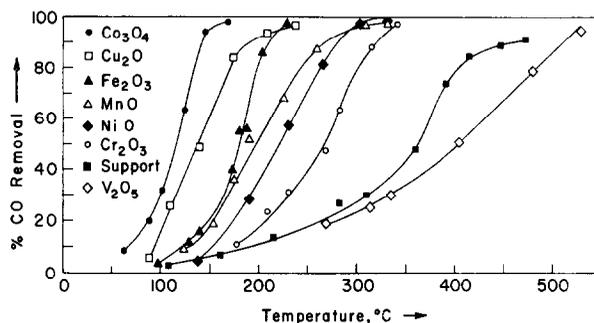


Fig. 3. Relative reactivity curves for the CO-O₂ reaction. Conditions: 45-46 g (80 cm³) of catalyst A, gas composition, CO~1.2%, O₂~1.2%, balance He; gas rate~1400 cm³/min.

standing for 2 hr. It was established by preliminary experiments that an extraction time of less than 1 hr produces low results and standing in air caused oxidation of the KI by oxygen. The flask contents were titrated with 0.05 N Na₂S₂O₃, adding starch solution near the end point.

EXPERIMENTAL RESULTS

A. The Relative Activity of Various Supported Catalysts in the CO-NO and CO-O₂ Reactions

To determine the relative activity and selectivity the results of the conversion runs were plotted in percent conversion-temperature coordinates as shown in Figs. 2 and 3. The temperature of 50% CO removal serves as a comparative reactivity index and is tabulated in Table 1. Values for a Pt cata-

TABLE I
RELATIVE REACTIVITY OF SUPPORTED TRANSITION METAL CATALYSTS (~10% METAL) IN THE CO-NO AND CO-O₂ REACTIONS^a

Catalyst ^b	Temperature of 50% CO removal (°C)	
	In CO-NO reaction	In CO-O ₂ reaction
Fe ₂ O ₃	145°	180°
CuCr ₂ O ₄	155°	115°
Cu ₂ O	175°	140°
Cr ₂ O ₃	220°	265°
NiO	250°	220°
Pt (3.75%)	285°	215°
Co ₃ O ₄	350°	115°
Bare Support	425°	365°
MnO	435°	195°
V ₂ O ₅	560°	405°

^a Conditions of Figs. 2 and 3.

^b The active oxide as written pertains only to the phase identified by X-rays after catalyst preparation.

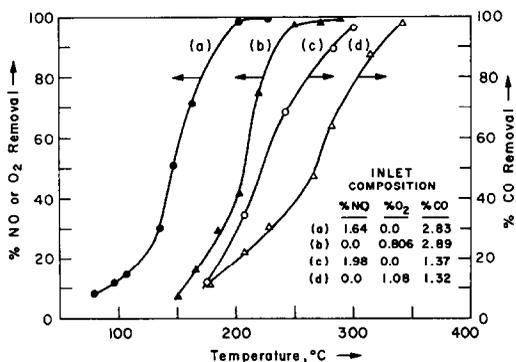


Fig. 4. Reactivity curves for the CO-NO and CO-O₂ reactions carried out separately on supported chromia. Conditions: 46 g (80 cm³) of catalyst A; Gas rate~1400 cm³/min.

lyst (3.57%) and a copper chromite catalyst, both on the same support, are also included in the table. With the exception of the position of Fe₂O₃ the reactivity sequence in the CO-O₂ reaction of the first row transition metal oxides follows the well-established activity series of these oxides with respect to oxidation-reduction catalytic reactions (8, 9, 10), the oxides of Co, Cu, Mn, and Ni being the most active. On the other hand the sequence for the CO-NO reaction: Fe₂O₃ > CuCr₂O₄ > Cu₂O > Cr₂O₃ > NiO > Pt > Co₃O₄ > Al₂O₃ (5% SiO₂) > MnO > V₂O₅, is altogether different. Only in the case of two oxides, Fe₂O₃ and Cr₂O₃, was there an apparent selectivity in favor of the CO-NO

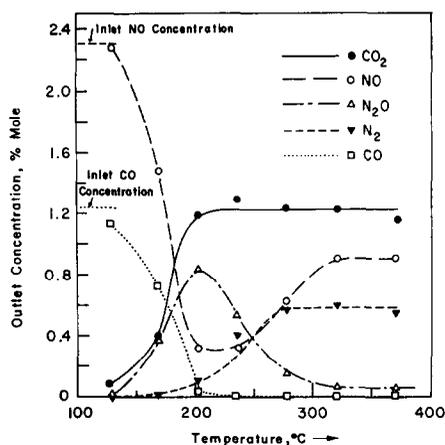


FIG. 5. Change in the outlet composition with temperature in the CO-NO reaction on supported chromia under overall oxidizing conditions. Conditions: 46 g (80 cm³) of catalyst A; gas rate ~1400 cm³/min.

reaction, as is seen from Table 1. The subsequent work in this paper pertains only to the use of Cr₂O₃ as a catalyst for the interaction between CO and NO.

B. Relative Activity of Supported Chromia in the CO-O₂ and CO-NO Reactions Carried Out Separately

The relative activity of the chromia catalyst in the CO-CO₂ and CO-NO reactions is exemplified by the curves in Fig. 4. Curves (c) and (d) are the corresponding ones from Figs. 2 and 3 and represent the relative activity under overall oxidizing conditions; curves (a) and (b) represent the reactions under overall reducing conditions. Under oxidizing conditions the extent of reaction is given by the percent of removal of CO and under reducing conditions by that of NO (or O₂). It is seen from Fig. 4 that the CO-NO and CO-O₂ reactions are both faster under reducing conditions but that their relative position remains the same: in both cases the CO-NO reaction is faster, its curve lying to the left of that of the CO-O₂ reaction.

The product distributions in the CO-NO reaction are given in Fig. 5 for a typical run under oxidizing conditions and in Fig. 6 for a run under reducing conditions. The N₂O concentration passes as expected (5)

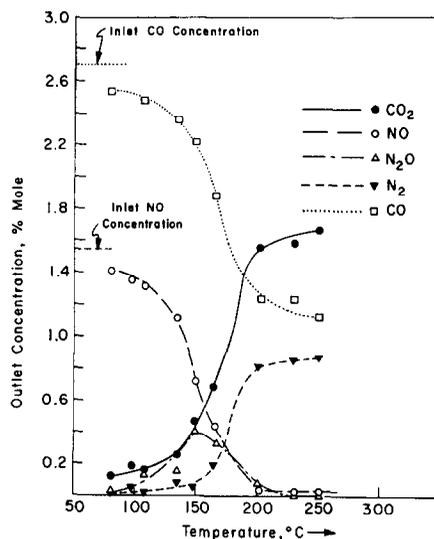


FIG. 6. Change in the outlet composition with temperature in the CO-NO reaction on supported chromia under overall reducing conditions. Conditions: 46 g (80 cm³) of catalyst A; gas rate ~1400 cm³/min.

through a maximum with the increase of the temperature. Under reducing conditions the peak is smaller and shifted, together with the whole reaction, towards lower temperatures.

Additional experiments were carried out using the same amount of catalyst at a constant temperature of 200°C and a gas flow rate of ~500 cc/min, changing the ratio between CO and NO, and CO and O₂ over wide limits. Under overall oxidizing conditions, the CO content in the inlet was kept constant at 1.7–2.0% and the NO/CO and O/CO ratios were varied. The results of these experiments are given in Table 2, showing that the degree of conversion is not sensitive to the O/CO ratio or the NO/CO ratio. At higher NO/CO ratios N₂O is formed predominantly compared with N₂. It is worth mentioning that in runs under overall reducing conditions in which the NO was kept constant at the inlet in the 1.7–2.0% range, the amounts of N₂O in the outlet are sharply reduced. At NO/CO = 0.59% and 93.6% conversion, the N₂O/N₂ ratio was 0.02 and decreased still further with the decrease of the NO/CO ratio.

TABLE 2
EFFECT OF INCREASING THE NO/CO OR O/CO RATIO ON THE
CONVERSION OF CO ON SUPPORTED CHROMIA^a

NO/CO ratio at inlet	CO-NO reaction		CO-O ₂ reaction	
	% CO Conversion	N ₂ O/N ₂ ratio at outlet	O/CO ratio at inlet	% CO conversion
5.2	94.4	10.1	14.8	41.7
3.23	89.3	Almost all N ₂ O	5.91	39.0
1.13	95.8	1.17	2.36	38.9

^a Conditions: 200°C; 46 g of catalyst; space velocity \sim 400 hr⁻¹.

C. Reaction of CO on Supported Chromia with O₂-NO Mixtures

Although the CO-NO reaction on supported chromia was faster than the CO-O₂ reaction there is almost a complete selectivity in favor of the second reaction when CO-NO-O₂ gas mixtures are contacted over the catalyst. This is true both in reducing and oxidizing conditions, as seen in Fig. 7. Under reducing conditions the removal of NO is very small until practically all the oxygen is depleted. Under oxidizing conditions, with oxygen present in almost the stoichiometric amount to oxidize CO to CO₂, there is only a small participation of NO in the oxidation in the low-temperature range; as the temperature increases, even this small amount of the NO-CO reaction vanishes.

D. Oxidation-Reduction of the Supported Chromia Catalyst

The observed experimental results, together with the well-known propensity of chromium oxide surfaces to change their oxidation state with changes in the environment, suggest that the average oxidation state in the absence of oxygen is different, presumably lower, than when oxygen is present. In that case, reaction of CO with NO would occur on an altogether different surface than with O₂. To verify this assumption the oxidation-reduction behavior of catalyst A was investigated.

The sample of catalyst A, on which the surface oxidation-reduction runs were carried out, was well stabilized by prolonged use in the catalytic studies and also by preliminary oxidation-reduction cycling. No shrinkage of the overall surface of the catalyst was noted. Thus, the BET area, as determined

by N₂ adsorption at -196°, was 216 m²/g both for a freshly calcined catalyst and for a catalyst after use. The surface of the chromia on the sample, however, shrunk by \sim 14% during the course of the investigation. This was established by iodometric titration of the Cr⁶⁺ which is present on the surface after oxidation by air. The fresh sample after treatment in air at 600° had excess charges corresponding to 0.88 mg atom O/g and the stabilized sample after similar treatment, 0.76 mg atom O/g.

In the bulk, the trivalent state of Cr is the most stable in the temperature range of this study, as was noted on the basis of previous publications by Weller and Voltz (?). This has been confirmed by recent data of Kubota (11) according to which the higher oxides Cr₃O₈, Cr₂O₅, and CrO₂ decompose spontaneously in air into Cr₂O₃ at 325°, 380°, and 450°, respectively. The free energy changes are given by Klier (9) for the reaction $\text{Cr}_2\text{O}_3 + \frac{1}{2}\text{O}_2 \rightarrow 2\text{CrO}_2$, $\Delta F^\circ_{600^\circ\text{K}} = -690$ cal/mole and for the reaction $\frac{1}{3}\text{Cr}_2\text{O}_3 + \frac{1}{2}\text{O}_2 \rightarrow \frac{2}{3}\text{CrO}_3$, $\Delta F^\circ_{600^\circ\text{K}} = +11\ 668$

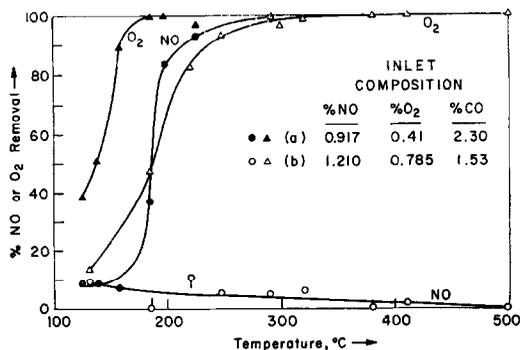


FIG. 7. Selective removal of oxygen in the simultaneous reaction of CO with NO and O₂. Conditions: 46 g (80 cm³) of catalyst A; gas rate \sim 1400 cm³/min.

cal/mole. For the first reaction the equilibrium oxygen pressure is calculated to be 0.3 atm at 600°K and will increase with temperature. To prevent the possibility of formation of higher valency oxides in the bulk during the oxidation cycle, the oxygen pressure was maintained below 0.03 atm as described in the experimental section. The second reaction is thermodynamically excluded at any temperature >300°.

There is no reduction of the bulk to the divalent state in a reducing atmosphere at temperatures <500°C, as shown by the ESR studies of O'Reilly and McIver (12) in which the bulk of chromia, supported on alumina and reduced at 500°C in H₂, was found to be in the trivalent oxidation state. The changes in the oxidation state of Cr occurring in the treatment by the He-O₂, He-NO, and He-CO mixtures can be considered as confined to the surface only.

The results of the oxidation-reduction cycles using sample A in the temperature range 300-500°C are summarized in Table 3. Two full cycles were performed at each temperature (four cycles at 345°). In the oxidation step of one of these cycles a He-O₂ mixture was passed directly on the reduced surface (columns 10-12) and in the other a He-NO mixture (columns 6-9). There was no uptake of NO on a surface oxidized by the He-O₂ mixture.

The following are deduced from the data of Table 3. (a) The NO oxidizes the reduced

surface only partially and the passage of the He-O₂ mixtures on the partially oxidized surface completes the oxidation. (b) The amount of oxygen transferred in a cycle increases with the temperature, which was also noted by Weller and Voltz (7). (c) There is apparently very little chemisorption of NO on the partially oxidized surface at >300°C as the evolved N₂ accounts within the experimental error for the NO uptake. (d) Considerable retention of CO (CO₂) on the reduced surface is observed. (e) The passage of NO over a reduced surface with retained CO(CO₂) results in the evolution of the major part, but not all, of the retained CO. (f) The material balances were calculated by dividing the amount of oxygen taken up in the oxidation half-cycle by the CO taken up in the reduction half-cycle. The maximum deviation from the expected value of 1.0 is ~17%, and for most cases the deviations are within 10%.

The data of Table 3 are combined with those of the iodometric titration and shown in Fig. 8. Curve (a) gives the amount of excess positive charges over oxidation state 3⁺, as determined by the iodometric titration after oxidation in a He-O₂ mixture and expressed in mg atoms O/g catalyst, as a function of temperature. The amount of oxygen transferred in an oxidation-reduction cycle can be calculated in two ways: by assuming (a) that the CO retained during the reduction half-cycle is oxidized during the

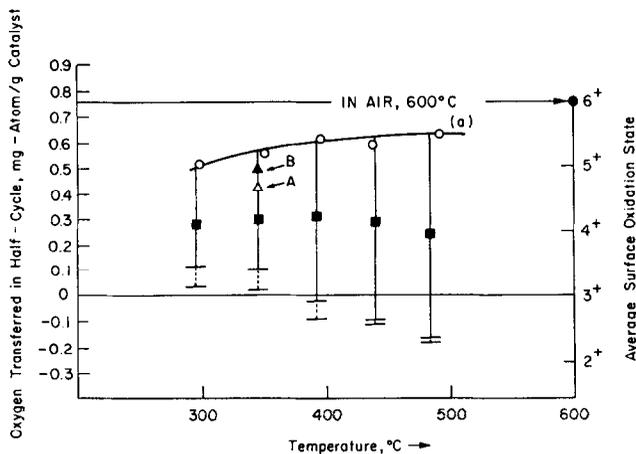


Fig. 8. Characterization of the surface state of catalyst A by oxidation-reduction cycles and iodometric titration in the oxidized state

TABLE 3
SUMMARY OF OXIDATION-REDUCTION CYCLES ON 46 g (80 cm³) OF CATALYST A

1	2	3	Reduction				Oxidation				12	13	14	
			Temp. (°C)	Cycle	CO conc. (% in gas)	CO uptake (mg-mole)	CO ₂ evolution (mg-mole)	NO conc. (% in gas)	NO uptake (mg-mole)	N ₂ evolution (mg-atom)				CO ₂ evolution (mg-mole)
295°	a	2.94	23.80	19.60	—	—	—	—	—	1.63	20.85	3.48	3.48	20.85
295°	b	2.56	20.56	16.49	11.03	10.69	3.28	3.28	1.96	1.96	10.72	1.01	4.29	21.41
345°	a	2.66	20.41	17.59	12.18	12.20	2.61	2.61	1.41	1.41	11.80	0.39	3.00	24.00
345°	b	2.78	23.78	22.61	—	—	—	—	1.54	1.54	26.29	3.44	3.44	26.29
345°	c	2.77	29.12	22.75	—	—	—	—	1.66	1.66	24.29	3.06	3.06	24.29
345°	d	2.97	25.92	21.53	12.24	12.53	2.40	2.40	1.87	1.87	12.84	1.36	3.76	25.37
392°	a	3.13	29.60	28.23	16.32	18.78	3.00	3.00	2.35	2.35	14.02	0.7	3.70	32.80
392°	b	3.34	32.79	28.22	—	—	—	—	2.16	2.16	31.40	3.28	3.28	31.40
440°	a	3.34	31.28	31.70	21.31	18.16	2.55	2.55	2.14	2.14	15.57	0.32	2.87	33.73
440°	b	3.11	31.97	30.47	—	—	—	—	2.18	2.18	32.52	3.00	3.00	32.52
484°	a	3.31	36.52	35.98	19.05	19.14	1.40	1.40	2.76	2.76	17.15	0.12	1.52	36.29
484°	b	3.57	35.70	32.91	—	—	—	—	2.36	2.36	38.48	2.16	2.16	38.48
345°	—	2.89	28.12	21.78	16.11	18.28	3.39	3.39	1.54	1.54	6.42	0.81	4.20	24.70
349° ^a	—	2.53	24.69	21.57	12.97 ^b	13.95 ^b	2.12	2.12	2.36	2.36	3.52	mil.	—	—

^a NO passage 22 hr.

^b In 40 min.

oxidation half-cycle and evolved as CO₂; or (b) that the CO retained has been chemisorbed on an oxidized site and exists as a carbonate-type surface complex until displaced as CO₂ in the oxidation half-cycle. In the case of (a) the amount of oxygen transferred in a cycle will be given either by the amount of CO₂ evolved in the reduction half-cycle or by the amount of oxygen taken up in the oxidation half-cycle from which the amount of CO₂ evolved in the same half-cycle has been subtracted. The averaged values calculated in this way have been drawn downwards as the solid bars on Fig. 8. In the case of (b) the oxygen transferred is given either by the amount of CO taken up or by the total amount of O₂ taken up. The averaged values of these measures exceed those of the case (a) by an extent equivalent to the retained CO. This is indicated as the dotted bar extensions of the solid bars in Fig. 8.

The distinction between the two schemes consists essentially in the assumption of reversible chemisorption of CO in case (a) and an irreversible chemisorption as carbonate ion in case (b). The examination of the pertinent references (13, 14) indicates that >70°, the irreversible mode predominates on chromia. The adoption of the scheme (b) extends the average oxidation state of the surface after the CO treatment at 300°C down to ~3⁺, which is plausible. Therefore, in the determination of the surface change the second alternative is adopted in this paper, while realizing that the actual state of affairs may lie somewhere in between, i.e., that both reversible and irreversible chemisorption of CO is possible, as discussed subsequently.

The square points on Fig. 8 indicate the partially oxidized state after treatment in the He-NO mixtures: these were determined by marking vertically upwards, from the lower horizontal bars, the amount of NO taken up in the NO oxidation of a reduced surface. Point A on Fig. 8 represents the effect of a tenfold increase of the NO partial pressure in the He-NO mixture, the data being given in the next to last line of Table 3. The increase of the NO partial pressure increases the fraction of the surface oxidized

by NO. The total amount of oxygen taken up by the sample is the same as in the other runs at the same temperature.

The prolonging of the time of the NO passage over the reduced surface also increases the extent of the surface oxidation. This is given by the last line of Table 3. The amount of O₂ picked up by the partially oxidized surface after a 22-hr passage of NO has been substantially diminished. The extent of NO oxidation of the surface after the prolonged passage is shown in Fig. 8 by point B. This slow oxidation of the surface by the NO is difficult to follow experimentally.

Above 300° there was no appreciable formation of N₂O during the passage of NO on a reduced surface. The *m/e* peak at 44 was accompanied by an *m/e* peak at 22 which accounted entirely for the primary peak as being due to CO₂. The absence of N₂O formation is evident also from the close correspondence of the NO taken up and the N₂ evolved.

Bearing in mind that in the CO-NO reaction the N₂O formation was observed at 250°, a special run was performed in which the catalyst reduced at 350° was oxidized by NO at 250°. Considerable amounts of N₂O were observed in the outlet. The estimated mole ratio of the integrated amounts of N₂O and N₂ at the exit was ~0.7. Significantly, the N₂ predominates at the beginning of the passage while the N₂O emerges from the catalyst bed towards the end which tends to indicate that the N₂O formed in the front part of the bed is reduced further by the catalyst surface downstream, to N₂, and that the N₂O formed in the parts of the bed downstream emerges as such in the outlet.

A series of oxidation-reduction runs was made using the unsupported sample C at 350°, the results being summarized in Table 4. Similarly to the supported sample there is no full oxidation of the surface by NO. The oxidation by NO proceeds to an extent higher than that for chromia supported on alumina: 70-75% of the oxygen in the oxidation half-cycle is taken up during the NO passage, as compared to ~50% at the same temperature on the supported catalyst. The averaged value of the CO uptake in the

TABLE 4
SUMMARY OF OXIDATION-REDUCTION CYCLES ON 18 g OF PURE CHROMIA (CATALYST C) AT 350°

Cycle	Reduction			Oxidation				
	CO conc. in gas (%)	CO uptake (mg-mole)	CO ₂ evolution (mg-mole)	NO conc. in gas (%)	NO uptake (mg-mole)	O ₂ conc. in gas (%)	O uptake (mg-atom)	Total O uptake (mg-atom)
a	4.60	7.41	7.02	1.85	5.05	2.15	1.60	6.65
b	4.83	6.50	6.45	—	—	2.82	6.69	6.69
c	5.00	7.49	7.19	—	—	2.52	6.62	6.62
d	4.52	6.81	6.46	8.38	5.28	2.57	1.26	6.54
e	3.78	6.16	5.87	6.77	4.40	2.76	2.19	6.59
f	4.62	6.79	5.96	—	—	8.42	6.22	6.22

reduction half-cycle and of the O uptake in the oxidation half-cycle is 6.71 mg-atoms O, which is equivalent to $(6.71 \times 6.023 \times 10^{20}) / (18 \times 25.2) = 8.91 \times 10^{18}$ atoms O/m².

E. Estimation of the Average Surface Oxidation State

For the subsequent characterization of the average surface state of oxidation of the chromium catalyst during the catalytic reaction we assume that the chromia surface in air at 600° is fully oxidized to the Cr⁶⁺ state. This assumption may seem arbitrary, but we feel that it is not far removed from the real situation. The ESR studies by Van Reijen *et al.* (15) have established that in samples of supported chromia, after treatment in air at 500°, the surface consists of 85% Cr⁶⁺ and 15% Cr⁵⁺, which gives an average surface oxidation state of 5.85. The average surface oxidation state should not be confused with the mean oxidation state as used by Deren *et al.* (16), or Matsunaga (17), where it pertains to both bulk and surface.

The excess oxygen of catalyst A after treatment with air at 600°, determined iodometrically, amounts to 0.76 mg atom O/g catalyst. This value was chosen as a fixed point for defining the Cr⁶⁺. Figure 8 shows, that based on this assumption the surface of the catalyst after oxidation in He-O₂ mixtures of 1.5–2.5% O₂ at 500°C has an average oxidation state of 5.65 which, taking into account the differences in O₂ pressure, is in fairly good agreement with Van Reijen *et al.* (15).

The mean oxidation state corresponding to

bulk and surface is calculated as follows: If at 600°C after treatment with air there are three excess charges over state Cr³⁺ present for each surface Cr, then the amount of chromium per gram of catalyst in the surface is $(0.76/3) \text{ Cr} \times 2 = 0.51 \text{ mg atom}$. The total amount of atoms in a sample containing 10% Cr corresponds to $\sim 2.0 \text{ mg-atoms Cr/g catalyst}$. Hence, one in four atoms is exposed on the surface and the mean oxidation state corresponding to bulk plus surface is $0.25 \times 6 + 0.75 \times 3 = 3.75$. This is, again, in fair agreement with the data of Eischens and Selwood (18), who have established an average thickness of three layers in a sample containing 6.0% Cr on Al₂O₃, and also with the data of Matsunaga (17), who found a mean oxidation number of ~ 3.8 for a sample containing 12.5% Cr on Al₂O₃ after calcination in air at 500°. Further, we have a means to compare our assignment of the oxidation state by using a very dilute catalyst B where every atom should be exposed on the surface (16). This catalyst contains 0.55% Cr or 0.1058 mg atoms total Cr/g catalyst. We note from Fig. 8 that at 486° the oxidation-reduction cycling under the conditions of Table 3, results in a change of the oxidation state of 3.2. For catalyst B, this would correspond to a transfer of $0.1058 \times 3.2 \cong 0.34 \text{ mg equivalent of charge/g catalyst}$ or to 0.17 mg-atom O/g catalyst. The actual figure measured on catalyst B under the same conditions is 0.156 mg-atom O/g catalyst, which is a very satisfactory agreement. If we adopt after Eischens and Selwood (18), that 1 g of chromia spread in a monolayer occupies an area of 813 m², then the 0.146 g of chromia

present in 1 g of sample A would occupy ~ 120 m². At an average thickness of four layers, the area that can be attributed to the chromia surface is 30 m²/g of catalyst.

We can test the plausibility of this estimation by comparing the amount of oxygen transferred in the oxidation-reduction cycle at 345° per unit of the assumed chromia area to that estimated above for pure chromia. The averaged transferred amount from Table 3, at 345°, is $(24.99 \times 6.023 \times 10^{20}) / (46 \times 30) = 1.09 \times 10^{19}$ O atoms/m² chromia, which is within 20% of that mentioned above for pure chromia (0.891×10^{19} O atoms/m² chromia).

The reduction of the sample results, at temperatures $>350^\circ\text{C}$, in the average surface oxidation number going below 3.0. At $\sim 500^\circ$ the reduction in CO brings the majority of the surface atoms to the chromous state. This is again in agreement with the observation of Van Reijen *et al.* (15) and Weller and Voltz (7) concerning the reduction of supported chromia surfaces in dry hydrogen at 500°C. The equilibrium $\text{Cr}_2^{3+}\text{O}_n + \text{CO} \rightleftharpoons \text{Cr}_2^{2+}\text{O}_{n-1} + \text{CO}_2$ lies far to the left similarly to the corresponding equilibrium with H₂/H₂O (15). The CO contained 1440 ppm CO₂ which apparently was enough to prevent the average surface state from being totally reduced in the lower end of the temperature range.

F. CO Chemisorption

If the retention of CO on the reduced surface, given in column 13 of Table 3, which appears as CO₂ evolved during the oxidation half-cycle, is construed as CO chemisorption, a comparison can be made with the data given by Van Reijen *et al.* (15) for a sample containing 2.24% Cr on silica gel. In Table 5, there are given the values of column 13 of Table 3 recalculated in terms of coverage (θ) of the surface Cr atoms. Since the dispersity of the chromium in sample A is 25%, full coverage ($\theta = 1$) is achieved when one CO molecule is sorbed on every fourth Cr atom of the total amount of Cr atoms.

Notwithstanding a higher CO pressure used in the work of ref. (15) the θ 's of Van Reijen *et al.* are lower by a factor of ~ 2 at a given temperature than those in this paper.

TABLE 5
CO CHEMISORPTION ON CATALYST A

Temp. (°C)	θ
295°	0.158
	0.193
345°	0.155
	0.156
	0.138
	0.169
	0.190
392°	0.169
	0.148
440°	0.129
	0.136
484°	0.069
	0.098

This difference may be associated in some degree to different dispersity [70% in (15) as recalculated by us], different support, etc., but mainly with the different initial oxidation state. The chemisorption in the work of ref. (15) takes place on a surface reduced totally to the chromous state and can be considered as being reversible. In our case the CO is passed initially over an oxidized surface and the chemisorption, at temperatures $<500^\circ$ when the surface is not yet entirely reduced to the chromous state, may take place in both the irreversible and reversible forms. As pointed out before, the major proportion is thought to take place in the irreversible form of carbonate surface groups.

G. Oxidation State of the Surface and Chemisorption during the In Situ Reaction

The average oxidation state of the catalyst bed in the integral reactor can be expected to be a function of the gas composition and therefore of the position along the catalyst bed axis in the direction of flow. To minimize the change in gas composition during passage through the bed, the amount of catalyst in the reaction was diminished to 17 g (30 cc), which increased the space velocity at the flow of 1400 cc/min to 2800 hr⁻¹. After the reaction had reached a steady state at a given temperature the reactor was blown out by He, a He-O₂ mixture of an O₂ concentration in the 1.5–2.5% range was led

TABLE 6
CHARACTERIZATION OF THE SURFACE STATE *In Situ* DURING THE CO-NO, CO-O₂, CO-NO-O₂
REACTIONS ON CATALYST A UNDER OVERALL OXIDIZING CONDITIONS

Reaction conditions ^a				State of the surface as determined by subsequent oxidation			
Temp. (°C)	Inlet gas composition (%)	CO conversion (%)	N ₂ /N ₂ O ratio in outlet	O uptake ^b (mg-atom/g catalyst)	CO chemisorption, θ	NO chemisorption, θ	Average surface oxidation state
309	CO 1.35 NO 2.66	91.4	1.00	0.236	0.067	~0.01	4.1
301	CO 1.33 O ₂ 1.84	52.2	—	0.067	Negligible	—	4.75
301	CO 1.32 NO 1.25 O ₂ 1.08	71.5	NO does not react	0.026	Negligible	Negligible	4.9
277	CO 1.45 NO 2.83	88.3	0.45	0.274	0.115	~0.01	3.9
273	CO 1.52 O ₂ 1.93	28.9	—	0.036	~0.04	—	4.85
273	CO 1.78 NO 1.55 O ₂ 0.96	65.2	NO does not react	0.048	~0.02	Traces	4.8

^a 17 g (30 cm³) catalyst; space velocity 2800 hr⁻¹.

^b During subsequent oxidation

over the catalyst at 300°C, the O₂ uptake was determined and the average surface oxidation state established by means of Fig. 8. The results of these experiments are given, respectively, in Tables 6 and 7 for the overall oxidizing and reducing conditions.

The faster reaction between CO and NO as compared to CO and O₂ when conducted separately and the selectivity for oxygen in the competitive oxidation of NO are observed here as well as in the initial experi-

ments. The striking result is, that in the presence of oxygen irrespective of the excess of CO, the average surface oxidation state tends to the limiting value observed after the passage of He-O₂ mixtures at the same temperature. When NO is the only oxidizing agent in mixture with CO, the average surface oxidation state is considerably lower, and, again, irrespective of the excess of CO almost the same as achieved during the passage of the He-NO mixture at similar

TABLE 7
CHARACTERIZATION OF THE SURFACE STATE *In Situ* DURING THE CO-NO, CO-O₂, CO-NO-O₂
REACTIONS ON CATALYST A UNDER OVERALL REDUCING CONDITIONS

Reaction conditions ^a					State of the surface as determined by subsequent oxidation			
Temp. (°C)	Inlet gas composition (%)	O ₂ conversion (%)	NO conversion (%)	N ₂ /N ₂ O ratio in outlet	O uptake ^b (mg-atom/g catalyst)	CO chemisorption, θ	NO chemisorption, θ	Average surface oxidation state
222	CO 2.67 NO 1.58	—	50.6	0.37	0.272	0.127	~0.015	3.9
232	CO 2.70 O ₂ 0.9	7.0	—	—	0.032	0.015 -0.02	—	4.9
243	CO 2.83 NO 0.71 O ₂ 0.56	46.8	<1.0	—	0.028	0.01	Negligible	4.9

^a 17 g (30 cm³) catalyst; space velocity 2800 hr⁻¹.

^b During subsequent oxidation.

partial pressures (for not very long times) over the catalyst. These results can be adduced as direct proof that the presence of oxygen leads to a higher oxidation of the surface *in situ*, i.e., the oxygen acts as a poison of the active surface.

The CO chemisorption on the surface *in situ* is quite appreciable in the absence of oxygen and very small in its presence. The figures of NO chemisorption are deduced from the appearance of NO upon the passage of He-O₂ mixtures; these are very small but it is possible that the oxygen does not dislodge the chemisorbed NO from the surface so that the chemisorbed amounts could be larger.

DISCUSSION

Notwithstanding the higher negative free energy change in oxidations by NO as compared with O₂ ($\Delta F^\circ_{f,298\text{ K}}$ for NO is + 20.7 kcal/mole), there appears consistently in practice, whenever both oxidizing agents are present in a system, a selective participation of oxygen in the oxidation-reduction reactions. This is, in particular, prominent in the industrially important process of the catalytic oxidation of NH₃ by oxygen to NO. It was noted by Yakovlev (19) that the reaction NH₃ + NO must be associated with a higher activation barrier than NH₃ + O₂; were it not so, NO would not have been formed in the products, and these latter would contain only N₂, H₂O, and excess O₂.*

Other evidence on the competitive oxidation of other reducing agents by NO and O₂, although scant, also points in the same direction (2). Hence, the result that on all catalysts tested in this study, with the exception of Fe₂O₃ and Cr₂O₃, the CO-O₂ reaction was faster than the CO-NO reaction, is in line with this generalization. While the elucidation of this apparent selectivity on supported Fe₂O₃ was postponed, the results on chromia can be satisfactorily explained by the poisoning effects of oxygen on the active surface of

this catalyst. In the simultaneous presence of O₂ and NO in the system, under oxidizing or reducing conditions, there is a clear selectivity for the participation of O₂ in the oxidation of the CO. Again, the oxidation of the chromia surface by NO, at least with respect to the last fraction of the surface to be oxidized, is slower than by O₂. It is obvious that this is associated with kinetic hindrances, because the extension of the oxidation period of the chromia by NO or the increase of the NO partial pressure can measurably extend the proportion of the surface oxidized. Owing to the slow oxidation by NO of a certain fraction of the surface, the average oxidation state of the surface, during the *in situ* reaction between CO and NO in the absence of O₂, is relatively low and the corresponding active surface high.

The catalytic reactions with oxygen as the oxidant have been the subject of numerous studies and a generalization of the vast experimental material (8, 9, 10) has shown that the activity sequence of transition metal oxides with respect to the reactions CO-O₂, H₂-O₂, oxidation of hydrocarbons, oxygen exchange, and N₂O decomposition follows a well-defined parallelism. It is assumed (9) that the catalytic oxidation-reduction reactions with the oxygen as oxidant proceed by a route which is essentially an oxygen transfer mechanism consisting of three major steps: (a) the reduction of the catalyst surface by the reducing agent, (b) the desorption of the oxidized product, and (c) re-oxidation of the catalyst surface by oxygen [steps (a) and (c) can be composed of a number of more elementary stages]. In the temperature region above 150-200°C, where step (b) is considered to be relatively fast, the activity of the transition metal oxides correlates well with several measures of the surface-oxygen bond strength, decreasing regularly as this bond strength increases. It is concluded (10) that the limiting stage of the process is associated with scission of the catalyst-oxygen bond [step(a)].

It is therefore relevant that the activity sequence Fe₂O₃ > CuCr₂O₄ > Cu₂O > Cr₂O₃ > NiO > Co₃O₄ > MnO > V₂O₅ noted here in the oxidation of CO by NO on the transition metal oxides does not follow the pattern ob-

* It should be mentioned however, that at low temperatures and high space velocities NH₃ is claimed to be the only selective reducing agent for NO in the presence of O₂, using a number of catalysts (20).

served in the oxidation reactions with the participation of oxygen. The hypothesis advanced here is that the limiting stage of the oxidation mechanism with the participation of NO differs from that with the participation of O₂. With O₂ as the oxidizing agent, the rate-limiting catalyst-oxygen bond scission occurs during the reduction of the catalyst [step (a)] or possibly, at low temperatures, during the desorption of the oxidized product [step (b)]. In the oxidation with the participation of NO the slow step may well be the reoxidation of an active site [step (c)]. This reoxidation must involve the accommodation of the nitrogen atom. Excluding the possibility of the chemisorption of the N atom on neighboring surface sites, the formation of the nitrogen-nitrogen bond has to be postulated, which for the formation of N₂ requires the presence of a pair of NO molecules situated in close proximity.

Relatively little is known about the mode of NO chemisorption; it is, however, pictured usually as a linear attachment to the metal ion through the nitrogen end of the molecule (21, 22, 23). In this case for the oxidation of the surface, besides the necessity of accommodating the nitrogen, there will be an additional requirement for a surface rearrangement which will bring the oxygen atom of the NO molecule into contact with the surface (22). The N₂O formation observed in the oxidation of the reduced chromia surface and in the oxidation of CO by NO, under steady state conditions, on chromia and on the majority of other metal oxide catalysts (5), lends support to the assumption that one of the steps in the catalytic oxidation of CO parallels the oxidation of a reduced surface site. The view has been advanced earlier (5) that the reduction of NO by CO can proceed in two stages, the first being a partial reduction to N₂O. In the catalytic reaction, this reduction occurs during the surface oxidation step and it is worthwhile to point out that the nitrogen-nitrogen bond formation to produce N₂O may come about by the abstraction of nitrogen from an NO molecule, chemisorbed on a reduced surface, by another NO molecule striking from the gas phase. The N₂O molecule thus formed can subsequently oxidize

another reduced site, being itself converted to N₂. If the reaction rate is low, or space velocity high, the N₂O is swept out of the reactor before it is converted to N₂ (5). More detailed studies are required to establish firmly the reaction path but the possibility of the N₂O intermediate cannot be discounted.

The essence of the hypothesis that has been advanced is, that on a supported chromia catalyst and also on the majority of other transition metal oxides, the reoxidation step by NO is conceivably an event of low probability and can be the limiting stage in the overall reaction sequence. Thus, the step associated with the scission of the catalyst-oxygen bond, while being the slowest in the oxidation by O₂, will not be the slowest in the oxidation by NO. The hypothesis explains the two most important observations of this work. Firstly, the preferential participation of oxygen in the catalytic oxidation-reduction reaction on most of the transition metal oxides, since step (c) will be carried out preferentially by O₂ rather than by NO, and secondly, the absence of the inverse correlation between the rate of CO oxidation by NO and the catalyst-oxygen bond strength. It is tempting to associate the extreme kinetic stability of the thermodynamically unstable NO molecule with the difficulty of forming an active surface complex involving the nitrogen-nitrogen bond. In order to ensure fast participation of the NO in the oxidation-reduction cycle a catalyst will have to chemisorb NO appreciably in the presence of oxygen [for the purpose of competing with O₂ in step (c)]. In spite of this difficult requirement, the conclusion should not be drawn that the search for a catalyst capable of selectively reducing NO in the presence of oxygen under overall oxidizing conditions is to be abandoned.

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REFERENCES

1. SHELEF, M., OTTO, K., AND GANDHI, H., *Atmospheric Environment*, to be published.

2. (a) ROTH, J. F., AND DOERR, R. C., *Ind. Eng. Chem.* **53**, 293 (1961); (b) BAKER, R. A., AND DOERR, R. C., *J. Air Pollution Control Assoc.* **14**, 409 (1964); (c) BAKER, R. A., AND DOERR, R. C., *Ind. Eng. Chem., Process Design Develop.* **4**, 188 (1965).
3. (a) AYEN, R. J., AND PETERS, M. S., *Ind. Eng. Chem., Process Design Develop.* **1**, 205 (1962); (b) AYEN, R. J., AND YU-SIM NG, *Air Water Pollution, Intern. J.* **10**, 1 (1966).
4. CHKHUBIANISHVILI, M. G., AND CHAGUNAVA, V. T., *Soobshch. Akad. Nauk Gruz. SSR* **41**, 591 (1966).
5. SHELEF, M., AND OTTO, K., *J. Catalysis* **10**, 408 (1968).
6. CHAPIN, D. S., AND JOHNSTON, H. L., *J. Am. Chem. Soc.* **79**, 2406 (1957).
7. WELLER, S. W., AND VOLTZ, S. E., *J. Am. Chem. Soc.* **76**, 4695, 4701 (1954).
8. GOLODETS, G. I., AND ROITER, V. A., *Ukr. Khim. Zh.* **29**, 667 (1963).
9. KLIER, K., *J. Catalysis* **8**, 14 (1967).
10. BORESKOV, G. K., *Kinetika i Kataliz* **8**, 1020 (1967).
11. KUBOTA, B., *J. Am. Ceram. Soc.* **44**, 239 (1961).
12. O'REILLY, D. E., AND MCIVER, D. C., *J. Phys. Chem.* **66**, 276 (1962).
13. GARNER, W. E., *J. Chem. Soc.*, p. 1239 (1947); DOWDEN, D. A., AND GARNER, W. E., *ibid.*, p. 893 (1939).
14. HAYWARD, D. O., AND TRAPNELL, B. M. W., "Chemisorption," 2nd ed., pp. 269-273. Butterworths, Washington, 1964.
15. VAN REIJEN, L. L., SACHTLER, W. M. H., COSSEE, P., AND BROUWER, D. M., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964* **2**, 829 (North-Holland Publ. Co., Amsterdam, 1965).
16. DEREN, J., HABER, J., AND SIECHOWSKI, J., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964* **2**, 994.
17. MATSUNAGA, Y., *Bull. Chem. Soc. Japan* **30**, 868, 984 (1957); **31**, 745 (1958).
18. EISCHENS, R. E., AND SELWOOD, P. W., *J. Am. Chem. Soc.* **69**, 1590 (1947).
19. YAKOVLEV, V. S., *Ukr. Khim. Zh.* **30**, 287 (1964).
20. ANDERSON, H. C., GREEN, W. J., AND STEELE, D. R., *Ind. Eng. Chem.* **53**, 201 (1961).
21. BLYHOLDER, G., AND ALLEN, M. C., *J. Phys. Chem.* **69**, 3998 (1965).
22. YATES, J. T., AND MADEY, T. E., *J. Chem. Phys.* **45**, 1673 (1966).
23. TEREININ, A., AND ROEV, L., *Actes Congr. Intern. Catalyse, 2nd, Paris, 1961* **2**, 2183 (see also numerous references therein, to the work by Terenin *et al.*).