JOURNAL OF CATALYSIS 31, 377–383 (1973)

The Surface Interaction of O_2 and NO with Manganous Oxide

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Received June 29, 1973

Surface interactions occurring during the contact of O_2 and NO with supported and unsupported MnO were studied by volumetric and gravimetric methods and electron paramagnetic resonance. At 25°C the interaction between oxygen and MnO is confined to the surface at complete coverage. The attainment of the monolayer coverage is very fast. The oxygen chemisorbs dissociatively and for every molecule adsorbed four Mn^{2+} spin centers are annihilated by oxidation to Mn^{3+}. At 400°C the Mn^{3+} ions disproportionate to Mn^{2+} and Mn^{4+} ions. At -78°C similar processes take place only on a part of the exposed surface. At >70°C the incorporation of oxygen into the bulk takes place.

The interaction of NO with the surface of MnO at 25°C leads to the oxidation of the manganous ions to Mn^{3+} and the simultaneous chemisorption of NO on the resulting Mn_2O_3 surface. The oxidation of MnO is not confined to the surface but takes place much slower than the surface interaction with O_2. The NO adsorbed on Mn_2O_3 can be desorbed as such. The gaseous product of the MnO oxidation is largely N_2O with small amounts of N_2. In contrast the chemisorption of NO on MnO_2 surfaces is very small.

INTRODUCTION

This work is a continuation of the studies being carried out in this laboratory on the chemisorption of NO on supported and nonsupported transition metal oxides and metals. This cycle has thus far included the adsorption of NO on chromium oxides (*1*), iron oxides (*2*), nickel oxide (*3*), copper oxides (*4*) and platinum (*5*).

Recently, the potential use of deep-sea manganese nodules has been discussed for the oxidation of CO and hydrocarbons (*6*) and for the reduction of NO by NH_3 (*7*). Ternary oxides incorporating manganese with a perovskite structure have been undergoing evaluation for similar purposes (*8*). In this context it was appropriate to investigate the chemisorption of nitric oxide on manganese oxide.

This investigation differs from the previous studies of NO chemisorption (*1–4*) in that the major emphasis is given to the interaction of the adsorbate with the oxide surface and to the changes occurring at the surface during the interaction.

For comparison, the interaction of the manganese oxide with molecular oxygen was also investigated. The adsorption of oxygen was followed by the volumetric method. Since the adsorption of oxygen on MnO is associated with the change in the oxidation state of the surface manganese ions and the Mn^{2+} ions has a well-defined EPR signal, it was possible to obtain additional information by following the changes in the paramagnetic resonance upon oxygen adsorption.

The adsorption of NO on MnO was followed gravimetrically, in some instances in conjunction with the mass-spectrometric analysis of the gas phase. The changes in the EPR signal resulting from the contact of supported MnO with gaseous nitric oxide were also investigated.

The solid bulk oxides of manganese have been characterized by Moore, Ellis and

Selwood (*9*). Depending on the conditions of the sample preparation and exposure to oxygen, stoichiometric MnO can be oxidized at room temperature up to $MnO_{1.58}$ (*10*). The incorporation of excess oxygen up to $MnO_{1.13}$ takes place without changes in the X-ray pattern (*9*). It can be assumed that the degree of MnO oxidation upon its contact with oxygen is strongly dependent on the surface-to-volume ratio of a given sample. Indeed, as will be shown below, conditions can be established where the interaction of oxygen and nitric oxide with MnO can be confined to the surface.

Experimental Methods

Two unsupported samples and one supported sample of manganese oxide were employed as the adsorbents. One unsupported sample (SM1) was made by precipitating MnO_2 by the interaction of stoichiometric amounts of $KMnO_4$ and oxalic acid, followed by the reduction of the precipitate with H_2 at 400°C to MnO. The BET surface area of SM1 (as measured by Kr adsorption at −195°C) was 3.05 m^2/g. The second unsupported sample (SM2) was made by the decomposition of $MnCO_3$ at 500°C *in vacuo*, followed by reduction with H_2 at 400°C. The BET area of SM2 (as measured by Kr adsorption at −195°C) was between 8.1 and 10.1 m^2/g, for two separate preparations. The supported sample (SM3) was made by thoroughly mixing a solution of 7.55 g of $Mn(NO_3)_2$ in 15 ml water with 200 ml of colloidal alumina suspension containing 40 g of γ-Al_2O_3 (Dispal, Continental Oil Co.) followed by addition of 50 ml of saturated solution of $(NH_4)_2CO_3$. The precipitate was centrifuged, washed with water and acetone, filtered and dried at 150°C. The solid was evacuated at 500°C to 10^{-6} Torr and reduced with H_2 at 400°C. The SM3 sample contained 3.8% by weight of Mn. The total BET surface area was 160 m^2/g. Cylinder grade oxygen of 99.6% min purity from Matheson Co. and NO purified by the previously published (*2*) procedure were used.

The volumetric adsorption apparatus was equipped with a capacitance gage as the pressure sensing element. The Cahn RG vacuum electrobalance was used for the gravimetric measurements. The mass-spectrometric analysis of the gas phase was carried out with a CEC-614 mass-spectrometer equipped with a batch-inlet system and operating at a pressure of 0.1 Torr at the high-pressure side of the gold leak into the analyzer section. The electron paramagnetic resonance spectra were taken with the Varian E-3 spectrometer, equipped with the E-4531 multipurpose cavity operating at 9.5 GHz.

Results and Discussion

Volumetric Measurement of O_2 Uptake on MnO

Figure 1 shows the specific uptake (per m^2 of BET area) of oxygen at an O_2 pressure of 1–3 Torr as a function of time and constant temperatures in the −23 to 148°C range. At 25°C about 95% of the uptake occurs within 1 min. Because of the very fast initial rates these could not be measured with sufficient accuracy to permit the determination of the activation energy of the chemisorption. After 30 min of contact the rate of the uptake at room temperature decreases to practically zero

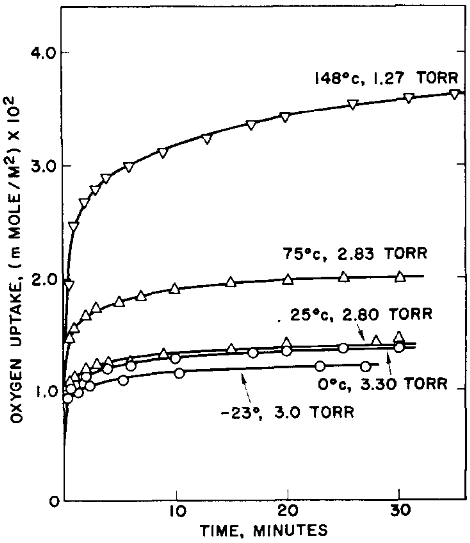

Fig. 1. Oxygen uptake on unsupported MnO (SM1).

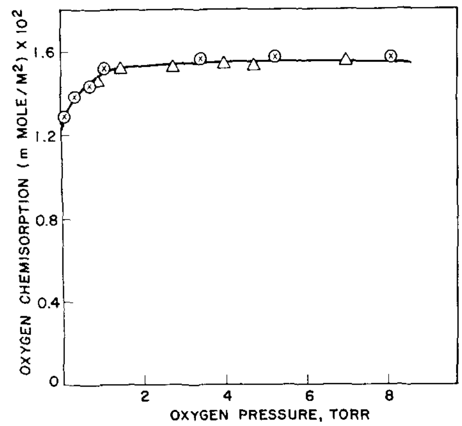

FIG. 2. Oxygen chemisorption isotherm on unsupported MnO at 25°C; (▽) SM1; (○) SM2.

TABLE 1
OXYGEN UPTAKE AT 25°C AND HYDROGEN USED IN REDUCTION AT 400°C

Sample	O_2 Uptake at 25°C (mmoles × $10^{-2}/m^2$)	H_2 Consumed in reduction at 400°C (mmoles × $10^{-2}/m^2$)	Ratio H_2/O_2
SM1	1.46	3.10	2.12
SM2	1.39	2.72	1.96
SM2	1.63	3.11	1.91
SM3	1.50	3.17	2.11
SM3	1.50	3.07	2.05

($<10^{-9}$ moles/m² hr). In the isotherm at 25°C given in Fig. 2 each point represents the uptake after 40 min of contact. The specific uptake for both SM1 and SM2 are well represented by a single isotherm. The uptake is practically pressure independent above ~2 Torr of O_2 and in the limit amounts to 1.55×10^{-2} mmoles O_2/m^2. If it is assumed that a monolayer coverage has been reached at room temperature the area occupied by one O_2 molecule is 11.3 Å². The area associated with one Mn^{2+} ion in MnO, calculated from the average for three low index crystal faces, is very close to this value, 10.8 Å².

From volumetric measurements it is impossible to deduce whether the oxygen adsorption is dissociative, and this is discussed below in conjunction with the EPR measurements. There is, however, an indication for the charge transfer taking place from the color change from green for the MnO to black after O_2 adsorption. This oxygen cannot be desorbed by pumping in vacuum up to 400°C, but is readily reduced by H_2 at this temperature. Table 1 indicates the 2:1 stoichiometric ratio between the oxygen taken up at 25°C and the hydrogen used up in the reduction at 400°C.

It is seen from Fig. 1, that at higher temperatures (148°C) the O_2 adsorption is not confined to the surface and at −23°C it is associated with a part of the surface only. The overall excess oxygen after 40 min of contact, corresponding to the curves of Fig. 1, is given by $MnO_{1.016}$ at −23°C, $MnO_{1.021}$ at 25°C, $MnO_{1.029}$ at 75°C and $Mn_{1.052}$ at 148°C. A sample with a greater surface area would contain more excess oxygen upon contact at room temperature. As observed by LeBlanc and Wehner (*10*) rapid addition of oxygen at relatively high pressures to finely divided MnO results in oxides with the overall formula of $MnO_{>1.2}$, even when the addition is performed at room temperature or below. In our opinion the rapid exothermic oxidation of the surface raises the surface temperature above that of the surroundings and as a result the oxygen incorporation into the bulk takes place.

The assumption of one monolayer coverage at 25°C gives the value of the exposed MnO surface area in the supported sample SM3 as 1.61 and 1.73 m²/g from two separate determinations. This corresponds to 33.0 and 35.4 m²/g of MnO in SM3. The 2:1 ratio between the hydrogen used in reduction at 400°C and oxygen adsorbed at 25°C holds for the supported SM3 sample as well, as given in Table 1. The average thickness of the MnO on the supported sample is ~25 layers, calculated using 2.22 Å as the layer thickness (½ the lattice constant of MnO).

EPR Signal Changes During Contact of MnO with O_2

Among the oxidation states of manganese ions only the Mn^{2+} is in the ground S-state without first-order crystal-field effects on the sixfold spin degeneracy or first-order spin–orbit coupling effects. In dilute solutions and in dilute solid crystals, a sharp 6-line EPR spectrum is obtained from Mn^{2+}, with $g \sim 2.00$ and a splitting of $\sim$100 G. In concentrated solutions or in amorphous solids a strong broad single line is obtained at room temperature. Other oxidation states such as Mn^{3+} or Mn^{4+} have signals too weak and too broadened by spin–orbit interaction and large zero-field splitting to be observed in amorphous powder at room temperature. If the chemisorption of O_2 (and of NO) results in the change of the oxidation state of the Mn ions near or at the surface, the EPR is an ideal tool to observe this change.

The measurement of EPR signals were made *in situ* before, during and after the admission of O_2 (or NO) to the sample tube placed in the instrument cavity at 25 and −78°C. Care was taken to prevent signal saturation. The only sample suitable for the EPR measurements is the supported one, SM3, in which the MnO is spread into a relatively thin layer as mentioned before. The spectra obtained before and after contact with O_2 at 25 and −78°C are shown in Fig. 3.

The intensity of the signal was measured by taking the first moment of the derivative signal, such as in Fig. 3, by the analogue gravimetric method of Burgess (*11*). Although the error in the absolute spin concentration measurements is expected to be as high as ±20%, the error in relative concentrations measured from signals of similar line shapes is closer to ±2% (*12*). In the present case where the signals derive from the same sample, the relative error can be expected to be even smaller. Where the sample tube had to be taken out of the cavity for heat treatment, the error can be expected to be larger due to the problem of exact repositioning of the tube in the cavity.

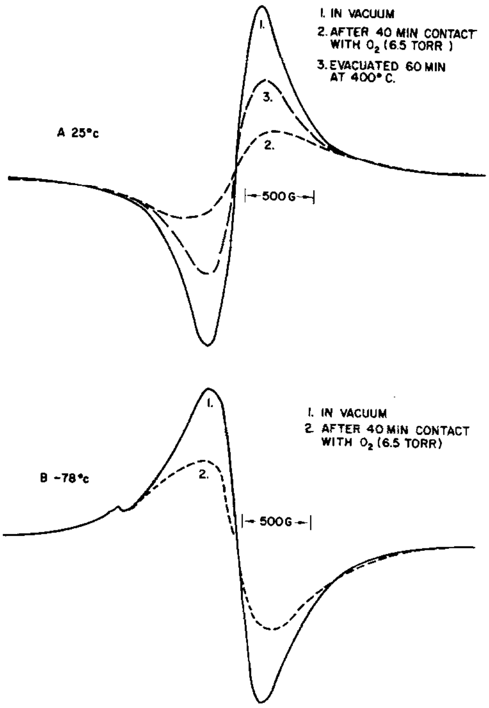

FIG. 3. EPR derivative spectra during contact of the supported SM3 sample with oxygen.

On Fig. 3A, Curve 1 gives the EPR signal in vacuum at 25°C; Curve 2 shows the decrease in signal intensity upon contact with oxygen (6.5 Torr) and Curve 3 gives the partial recovery of the signal upon heating to 400°C. Figure 3B gives the analogous 1 and 2 curves at −78°C.

The extent of spin loss upon contact of oxygen with the SM3 sample is tabulated in Table 2, along with the extent of recovery upon the heat treatment. It is possible

TABLE 2

CHANGE IN EPR SIGNAL INTENSITY ON CONTACT OF OXYGEN WITH SM3 SAMPLE

Temp (°C)	Treatment of sample	Relative signal intensity	Relative spin loss	No. of spins lost/O_2 molecule
25	Vacuum	1	—	—
25	O_2, 6.5 Torr	0.845	0.155	4.27
25	Pumping at 200°C 1 hr	0.845	0.155	4.27
25	Pumping at 400°C 1 hr	0.916	0.084	2.31
−78	Vacuum	1	—	—
−78	O_2, 6.5 Torr	0.914	0.086	3.6

from the observed spin loss and the amount of oxygen taken up at 25°C (as determined from the volumetric measurements) to establish the number of spins lost per one molecule of oxygen adsorbed. Thus 1 g of MnO in SM3 has 33 m^2 of area and 1 m^2 of MnO area adsorbs 1.55×10^{-5} mole O_2. Therefore the ratio of O_2 adsorbed to the total number of Mn in SM3 is $1.55 \times 10^{-5} \times 33 \times 71 = 0.0363$. The actual number of spins lost due to adsorption of one O_2 molecule is obtained by dividing the observed relative spin loss by 0.0363, and is given in the last column of Table 2. The ratio obtained at 25°C is very close to 4. It is plausible then to describe the charge-transfer process taking place on the surface by the equation

$$O_2 + 4Mn^{2+} \xrightarrow{25°C} 4Mn^{3+} + 2O^{2-}. \qquad (1)$$

This observation implies, of course, that the chemisorption of O_2 is dissociative and affects the four outer layers of the MnO lattice. Other nondissociative charge-transfer processes, such as

$$O_2 + Mn^{2+} \xrightarrow{25°C} Mn^{3+} + O_2^- \qquad (2)$$

may also cause spin loss and broaden the EPR signal via spin–spin coupling. Since the ratio of the chemisorbed O_2 molecules to spin loss in the above process is only unity, as opposed to the observed value of 4, it can be regarded as a minor (or a transitional) surface process.

At room temperature the process stops at the surface, but at higher temperatures there is gradual incorporation of the oxygen into the bulk.

The partial recovery of the EPR signal at 400°C must be explained by the disproportionation reaction

$$2Mn^{3+} \xrightarrow{400°C} Mn^{2+} + Mn^{4+} \qquad (3)$$

since no oxygen can be removed from the surface by pumping at this temperature as confirmed by subsequent reduction with H_2. The magnitude of this recovery, of about half of the observed spin loss, agrees well with the disproportionation.

At −78°C, the coverage is smaller (see the trend in Fig. 1), or about ⅔ of that observed at 25°C. But the number of spins quenched by one O_2 molecule is again close to 4, indicating that the process described by Eq. (1) is taking place.

Gravimetric Measurements of NO Adsorption on MnO

The investigation of the NO chemisorption by solid oxides of manganese presents considerable difficulties. These are associated with the fact that the adsorption of No on oxidized samples of MnO_2 is very slow, of the order of 0.023 mg/m^2/hr at 26°C, while the adsorption of NO by MnO is inevitably accompanied by the chemical interaction leading to the oxidation of the surface of the solid and therefore also a partial reduction of the adsorbent-NO.

The oxidation of MnO by NO is immediately observable by the color change from green to black upon exposure at room temperature.

The NO uptake curves are given in Fig. 4. These are less steep initially than those observed for oxygen, but on the other hand, are not of the Langmuirian-type, with continuing slow weight increase even at 25°C. The monolayer coverage which corresponds to one NO molecule per 10.3 Å is equivalent to 0.45 mg NO/m^2. This value is exceeded

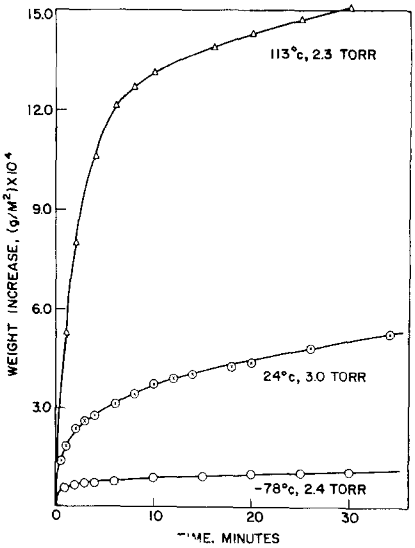

FIG. 4. Weight increase of unsupported MnO (SM1) in contact with NO as a function of time.

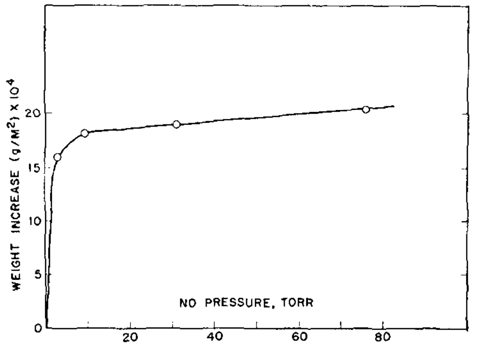

FIG. 5. Weight increase of unsupported MnO (SM1) in contact with NO as a function of pressure.

at 25°C indicating again oxidation of the surface. In fact, the slow weight increase is indicative of the oxidation of the bulk. Thus, the pseudo-isotherm of Fig. 5 was constructed from values obtained at a given pressure, where the rate of uptake has decreased to less than 0.02% of the amount already taken up. This is generally reached at times longer than 10 hr. As seen from Fig. 5 the weight increase exceeds severalfold that corresponding to NO monolayer coverage.

The mass-spectrometric analysis of the gas in contact with the MnO was carried out after contacting 0.825 g of MnO, having a total surface area of 2.55 m², prereduced with H_2 at 400°C, with 180 Torr of NO in a 16 ml glass vessel. The results of this analysis are presented in Table 3. After 2000 min all the initial amount of 0.17 moles NO had disappeared. No molecular nitrogen was noted in the gas phase. At room temperature the only product of NO reduction by MnO is N_2O. It has to be assumed that the oxygen atoms in the amount corresponding to the N_2O formed, have been incorporated into the lattice, presumably with the concomitant formation of Mn^{3+} ions. The surface Mn_2O_3 does adsorb NO. In fact, the amount of NO adsorbed, as calculated by the difference in the last column of Table 3, is about twice that expected from monolayer coverage on MnO or about 3.2 mmole NO × 10^{-2}/m².

The NO adsorbed on the surface was then pumped off, first at room temperature and then at 100 and 200°C. The bulk of the gas disengaged at room temperature, >95%, was NO; the remainder was N_2O with traces of N_2. At higher temperatures the bulk was N_2O with some N_2 and practically no NO. It was not possible to estimate exactly the proportions disengaged at room temperature and elevated temper-

TABLE 3
CHANGES IN GAS COMPOSITION OF NO IN CONTACT WITH MnO AT 25°C[a]

Times (min)	NO (mmoles in gas)	N_2O (mmoles in gas)	NO[b] (mmoles adsorbed)
0	0.17	0	0
25	0.1602	0.0012	0.0076
80	0.1413	0.0039	0.0209
150	0.1287	0.0095	0.0223
1400	0.017	0.039	0.055
2600	—	0.043	0.084

[a] Sample SM1, 0.825 g.
[b] By difference.

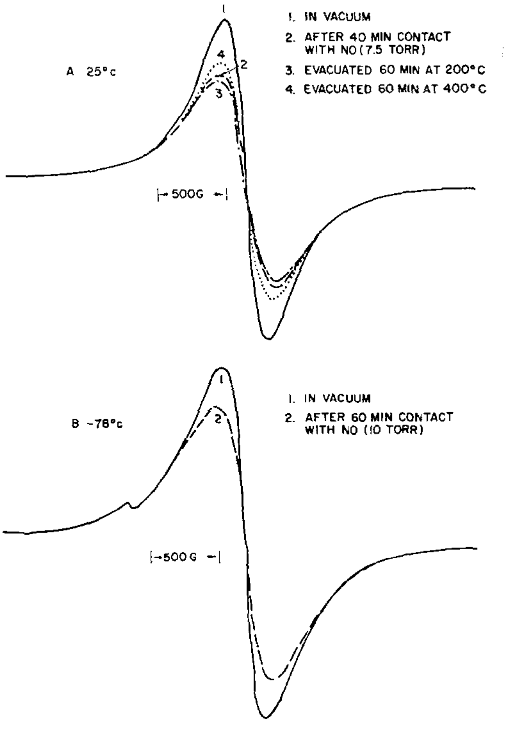

FIG. 6. EPR derivative spectra during contact of the supported SM3 sample with NO.

atures but it can be stated that most of the adsorbate was disengaged as NO.

EPR Signal Changes During Contact of MnO with NO

The EPR spectra obtained in the interaction of NO with SM3 at 25 and −78°C are presented in Fig. 6. These are very similar to the spectra of Fig. 3 observed in the contact of the same supported MnO sample with oxygen. The loss of signal upon contact with NO is smaller than that observed in contact with oxygen, as given in Table 4. This is in agreement with the adsorption behavior which showed an almost instantaneous interaction of the whole MnO surface with the oxygen, while the oxidation of the MnO by NO takes place relatively slowly. The increase in the spin loss of the NO covered sample upon pumping at 200°C, as opposed to the oxygen covered sample, is consistent with the formation of N_2 and N_2O during the desorption at this temperature, as the oxygen released in the act of desorption can further oxidize Mn^{2+}, causing additional spin loss. Evacuation at 400°C restores part of the signal by the disproportionation reaction (*3*).

The number of spins lost in relation to the oxygen incorporated into the MnO lattice is, of course, the same irrespective of the source of oxygen, as seen in Tables 2 and 4.

TABLE 4
CHANGE IN EPR SIGNAL INTENSITY ON CONTACT OF NO WITH SM3 SAMPLE

Temp (°C)	Treatment of sample	Relative signal intensity	Relative spin loss	No. of spins[a] lost/O_2 molecule
25	Vacuum	1	—	—
25	NO, 7.5 Torr	0.946	0.054	4.1
25	Pumping at 200°C, 1 hr	0.943	0.057	4.4
25	Pumping at 400°C, 1 hr	0.966	0.034	2.8
−78	Vacuum	1	—	—
−78	NO, 10 Torr	0.962	0.038	3.4

[a] The oxygen incorporated after contact was measured by reduction with H_2 at 400°C and estimated assuming 2:1 H:O ratio. To be consistent with Table 2, the spin loss per one O_2 molecule is reported here as well.

ACKNOWLEDGMENT

We thank Dr. Klaus Otto for the mass-spectrometric analyses.

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