

Activity of Mn^{3+} and Mn^{4+} Ions Dispersed in MgO for N_2O Decomposition

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The decomposition of N_2O was studied over MgO-MnO_x (MM) and over MgO-MnO_x-Li₂O (MML) catalysts. Pure α -Mn₂O₃ and Mg₉MnO₈ were also tested. The results show that Mn^{3+} ions are more active in N_2O decomposition than either Mn^{2+} ions or Mn^{4+} ions. Catalysts containing a mixture of Mn^{2+} and Mn^{4+} ions are also very active. Dilute catalysts having a given $[Mn^{3+}]/[Mn^{4+}]$ ratio were more active than concentrated catalysts having a similar $[Mn^{3+}]/[Mn^{4+}]$ ratio. A study of oxygen chemisorption on MML specimens was also carried out, and it showed that oxygen is less strongly held on Mn^{3+} -rich catalysts. A parallelism between activity for N_2O decomposition and strength of the oxygen-surface bond can thus be drawn. Reasons for these findings are discussed in terms of electronic configurations and interactions between transition metal ions.

INTRODUCTION

Oxides in which electronic and magnetic interactions between transition metal ions are systematically reduced by dispersion of the ions in an inert matrix have recently received attention as active solids for simple catalytic reactions. The dispersion principle allows the role of interactions between catalytically active ions to be evaluated and renders these systems specifically amenable to a discussion based on an electronically localized surface complex. Oxide solid solutions of nickel (1, 2, 3) and chromium (4) in MgO have been studied in this way both as catalysts for the decomposition of N_2O and as adsorbents in oxygen chemisorption. Transition metals which exhibit several valencies, such as manganese, introduce a further problem in catalysis, namely that of defining the most active valency state. In these cases, solid solution in a matrix such as MgO offers an advantage over the pure transition metal oxides in that the system is more stable with respect to bulk reduction or oxidation. Characterization of the physical properties of the solid solution, such as lattice param-

eters, magnetic susceptibility, and ESR behavior, enables the valency state to be defined. We report, in this paper, a study of the catalytic decomposition of N_2O by systems containing known amounts of Mn^{3+} and Mn^{4+} dispersed in MgO together with Li^+ ions. Oxygen adsorption has also been measured. The solid state chemistry of these oxides has been reported elsewhere (5).

II. EXPERIMENTAL METHODS

Catalyst Preparation and Chemical Analysis

Magnesium oxide from two sources has been employed: (i) "Specpure" MgO from Johnson and Matthey (London) was used for testing the activity of pure magnesium oxide and for preparing lightly doped specimens (0.2% atomic of Mn); (ii) MgO prepared by thermal decomposition (5 hr at 600°C) of reagent grade basic magnesium carbonate (Erba R.P.) was used for all other catalysts, as well as for a check of the 0.2% catalyst. Manganese sesquioxide (α -Mn₂O₃) was prepared by thermal de-

composition (5 hr), at 600 or 800°C, of reagent grade $MnCO_3$ (Erba R.P.). The carbonate was pretreated with acetic acid (6). The compound Mg_6MnO_8 was prepared according to Toussaint (7). For the preparation of solid solutions, a procedure based on impregnation of MgO with aqueous solutions of the nitrates of manganese (and of lithium was followed (5). The impregnated solids were fired at 1000°C in air, or in flowing hydrogen (containing about 1% of oxygen). Oxide specimens containing only magnesium and manganese and prepared in air are designated MM; specimens containing magnesium, manganese, and lithium are designated MML. The letter h (such as MMh) denotes preparation in hydrogen. The figure(s) after the letters give the nominal concentration(s) of manganese (and lithium) in atoms with respect to 100 magnesium atoms.

After samples were heated in air or in hydrogen, analyses of lithium and of manganese were performed for each sample. Details of the procedure used are reported elsewhere (5). For specimens fired in air, the analyses show that up to a $[Li]/[Mn]$ ratio of unity, practically all the lithium added remains in the solid. Some volatilization of lithium oxide occurs when the above ratio is comprised between one and two. A marked loss of lithium occurs only for $[Li]/[Mn]$ ratios higher than two. The analyses also distinguished between lithium which could be easily washed away by a water rinse and lithium which was retained in the solid residue. When referring to $[Li]/[Mn]$ ratios actually determined for a given specimen, the "solid residue" lithium is the quantity taken as $[Li]$. For $[Li]/[Mn]$ ratios not exceeding unity, the solid residue" lithium practically coincides with total lithium. Analyses of manganese included total manganese, as well as the number of equivalents of manganese oxidized to an oxidation number higher than two. For specimens heated in hydrogen, analyses of total manganese do not differ from those obtained for air-treated samples. Analysis of lithium, however, showed that almost the whole of the alkali had volatilized in hydrogen-treated specimens. Due to the

presence of a small oxygen pressure, some oxidized manganese was present in both MMh and MMLh, in amounts not greatly different in the two series. Table 1 contains the data concerning air-treated and hydrogen-treated specimens, as deduced from chemical, structural, and magnetic analyses.

Solid State Chemistry of the Catalysts

A summary of the main conclusions obtained from chemical, structural, and magnetic investigations (5) is given below, to make clear the nature of the solids used as catalysts.

1. With the exception of MM 0.2, specimens containing magnesium and manganese oxides only, and fired in air at 1000°C, consist of an MgO phase with a small amount of Mn^{2+} in solid solution, together with a second phase Mg_6MnO_8 . Most of the manganese is present in the latter phase. However, a calculation of the thickness of Mg_6MnO_8 layer, based on particle sizes deduced from surface area measurements, shows that a complete coverage of each MgO particle by a Mg_6MnO_8 shell is impossible below a Mn content of 1%. Moreover, due to the sharpness of the Mg_6MnO_8 X-ray pattern, it is also unlikely for higher Mn content that the Mg_6MnO_8 phase is present as a thin shell. The results of the calculation are:

MM 0.2 $R = 1250$, $\Delta R = 7$; MM 1 $R = 1070$, $\Delta R = 28$; MM 3 $R = 3100$, $\Delta R = 230$;
MM 4 $R = 2400$, $\Delta R = 160$; MM 5 $R = 3100$, $\Delta R = 408$;

where R (radius of the MgO particle) and ΔR (calculated thickness of the Mg_6MnO_8 phase, covering the MgO particle) are in Å. Catalyst MM 0.2 does not show the presence of Mg_6MnO_8 , in spite of careful prolonged X-ray analysis.

2. Specimens prepared in air, and containing lithia with a $[Li]/[Mn]$ ratio less than unity, contain Mn^{3+} in solid solution in MgO in amounts equivalent to the lithium content, while the excess manganese is present as Mg_6MnO_8 . A small amount of Mn^{2+} is still present in solid solution in MgO, in decreasing amounts as the lithium

TABLE 1
 CATALYSTS AND THEIR PROPERTIES

Sample	(Atoms per 100 Mg atoms)							Surface area (m ² /g)	E_a (kcal/mole)
	Mn _{tot}	Mn ³⁺	Mn ⁴⁺	Mn ⁺²	Li _{tot}	Li _{sol}	Li _{lith}		
MgO	—	—	—	—	—	—	—	23.0	31.7
Mn ₂ O ₃ 600	—	—	—	—	—	—	—	2.5	28.2
Mn ₂ O ₃ 800	—	—	—	—	—	—	—	1.8	22.3
MM 0.2	0.204	—	—	—	—	—	—	6.7	29
MM 0.2	0.204	—	0.01	0.19	—	—	—	6.7	31
MML 0.2:0.3	0.19	—	—	—	0.18	0.12	0.05	11.8	31.6
MML 0.2:0.6	0.20	—	—	—	0.37	0.27	0.14	3.3	30.6
MML 0.2:1.0	0.19	—	—	—	0.57	0.35	0.13	3.2	31.8
MM 1	1.15	0.0	0.84	0.31	—	—	—	7.8	14.9
MMLh 1:1	1.10	0.11	0.0	1.00	—	—	—	3.3	—
MML 1:2	1.13	1.05	0.08	0.0	1.1	1.1	0.0	6.5	16.4
MML 1:3	1.18	0.53	0.65	—	2.4	2.4	0.0	8.3	21.8
MM 3	2.95	0.0	2.71	0.24	—	—	—	2.7	20.1
MML 3:6	3.37	2.43	0.94	0.0	5.0	4.69	0.42	5.6	19.3
MML 3:15	2.90	0.49	2.41	0.0	8.2	5.35	2.54	2.0	25.0
MM 4	4.48	0.0	4.17	0.31	—	—	—	3.5	18.9
MMh 4	3.94	0.0	0.35	3.59	—	—	—	26.6	21.7
MM 5	5.40	0.0	4.91	0.49	—	—	—	2.7	18.7
MML 5:5	5.00	4.60	0.40	0.0	4.6	4.65	0.11	7.1	17.0
MML 5:10	5.00	1.69	3.10	0.0	8.2	7.70	0.70	6.0	22.7
MML 5:15	4.88	1.07	3.81	0.0	9.9	9.0	0.80	2.3	26.6
Mh ₆ MnO ₈	—	—	—	—	—	—	—	19.8	18.2

content increases. The concentrations of Mn³⁺ reach 100% at [Li]/[Mn] = 1. The magnetic moment in that case is equal to that expected for Mn³⁺ (4.9 BM), and the measured oxidation equivalents also correspond to Mn³⁺. No ESR spectrum of Mn²⁺ is seen, thus excluding the presence of equal amounts of Mn²⁺ and Mn⁴⁺. Also, the lattice parameter of a specimen having [Li]/[Mn] = 1 can be exactly matched with the one calculated for MgO containing equal amounts of Mn³⁺ and Li⁺¹.

3. For specimens prepared in air and having a [Li]/[Mn] ratio in the range between 1 and 2, both Mn³⁺ and Mn⁴⁺ are present and both are in solid solution in the MgO structure. When the above ratio reaches the value of 2, manganese is totally in the oxidation state +4. In contrast to MM samples, where Mn⁴⁺ ions are concentrated in the Mg₆MnO₈ phase, the Mn⁴⁺ ions in the present case are dispersed throughout the solid solution.

4. Specimens MMh, prepared in hydro-

gen without lithia, consist of MgO + MnO solid solution, plus a small amount of Mh₆MnO₈. Catalysts MMLh do not show the presence of Mg₆MnO₈.

Thus, in an oxidizing atmosphere, such as air at 1000°C, the specimens containing lithium and manganese in the ratio 1:1 form a stable solid solution of Mn³⁺ in MgO, instead of forming the phase Mg₆MnO₈, as observed in the absence of lithium. By increasing the [Li]/[Mn] ratio, it is possible to oxidize a controlled amount of the manganese in solid solution from Mn³⁺ to Mn⁴⁺, their ratio being not appreciably affected by the oxidizing atmosphere. Hence it is possible to make catalysts having different degrees of dilution (by varying the total manganese content) and different valency composition (by varying the [Li]/[Mn] ratio).

Experimental Procedure

A circulating system was used for the N₂O decomposition studies. The catalytic

reactor was made of fused silica (441 cm³), and the gas was forced (at about 100 cm³/min) through the catalyst (60 to 120 mg), spread over some silica wool. The tip of the thermocouple well, thin walled, was embedded in the catalyst. Thermoregulation $\pm 1^\circ\text{C}$ was achieved by a commercial device. The catalyst was protected from mercury vapor by two dry ice traps at the inlet and outlet tubes. A sample of 5.3 cm³ was withdrawn at regular intervals (usually about 5 min) and the N₂O was condensed in a liquid nitrogen trap. The residual gas pressure was read on a Pirani gauge (LKB Autovac). Occasional analyses by a mass spectrometer were carried out, to check that complete condensation of N₂O had concurred in the procedure adopted and also to determine the N₂/O₂ ratio in the uncondensed gas. The total decomposition was in general kept below 1%. The influence of the mass of the catalyst and of the gas circulation velocity was explored, but the absolute velocity constants (see below) were independent from the above parameters in the adopted range. All kinetic constants are reported as absolute velocity constants (cm min⁻¹) (1). Due to oxygen adsorption during the first N₂O decomposition experiment, the apparent velocity constants, as measured from the pressure increase as a function of time, was lower than the velocity constant measured in successive runs. For this reason the velocity constants reported below refer to a catalyst which has undergone more than one experiment. Surface areas were determined by krypton adsorption ($P_0 = 2.72$ Torr, $\sigma = 19.4 \text{ \AA}^2$). Cylinder N₂O was purified by double distillation. Other details of the procedure were as described earlier (1). A vacuum pretreatment of 4 hr at 480°C was applied to each fresh sample. Between runs, a 30-min vacuum conditioning at 480°C was adopted, except when stated.

Oxygen chemisorption studies were carried out in a Pyrex apparatus, of 244 cm³ total volume. The catalyst was contained in a small silica bulb and was protected from mercury vapor by a U-tube kept in liquid nitrogen. Oxygen pressures of about around 0.3 Torr were used. Pressure readings were

made with a McLeod gauge. The chemisorption was considered complete when three successive readings, at 20-min intervals did not differ by more than 0.002 Torr. A monolayer of oxygen was taken to correspond to 0.204 cm³ m⁻² (dissociative adsorption). The fresh specimen was given a vacuum treatment at 480°C for 4 hr; successive adsorptions were preceded by a 30-min vacuum treatment at 480°C, except when a measurement of more loosely bound oxygen was taken. In such a case, a 30-min evacuation at the adsorption temperature was used, and the amount successively chemisorbed at the same temperature gave a measure of the amount of oxygen which could be easily desorbed (hereafter called "reversible oxygen," as distinct from the "total oxygen").

III. RESULTS

N₂O Decomposition

The results obtained on the various catalysts are reported according to the composition of the solid. Reference to Table 1, reporting the composition of the solid, is made throughout the following pages.

Pure magnesium oxide. Pure magnesium oxide was studied at first as a reference. The comparison between different investigations on MgO is shown in Fig. 1. A very good reproducibility was obtained for the absolute activities previously found with a static system (1). The absolute activity also agrees very well with the one reported by Dell *et al.* (8).

Pure manganese sesquioxide, α -Mn₂O₃. Pure α -Mn₂O₃ was investigated for a comparison with previous work by different authors in an attempt to define the reproducibility of the activity of a manganese oxide surface. Results are shown in Fig. 1. Two samples prepared at different temperatures, 600°C and 800°C, gave different apparent activation energies (E_a), 28.2 and 22 kcal/mole, respectively. The activity of the two samples was equal at about 315°C. If α -Mn₂O₃ (600), after evacuation for 0.5 hr at 480°C, was treated with N₂O for 20 min before each experiment, the catalytic activity was reduced, becoming closer to

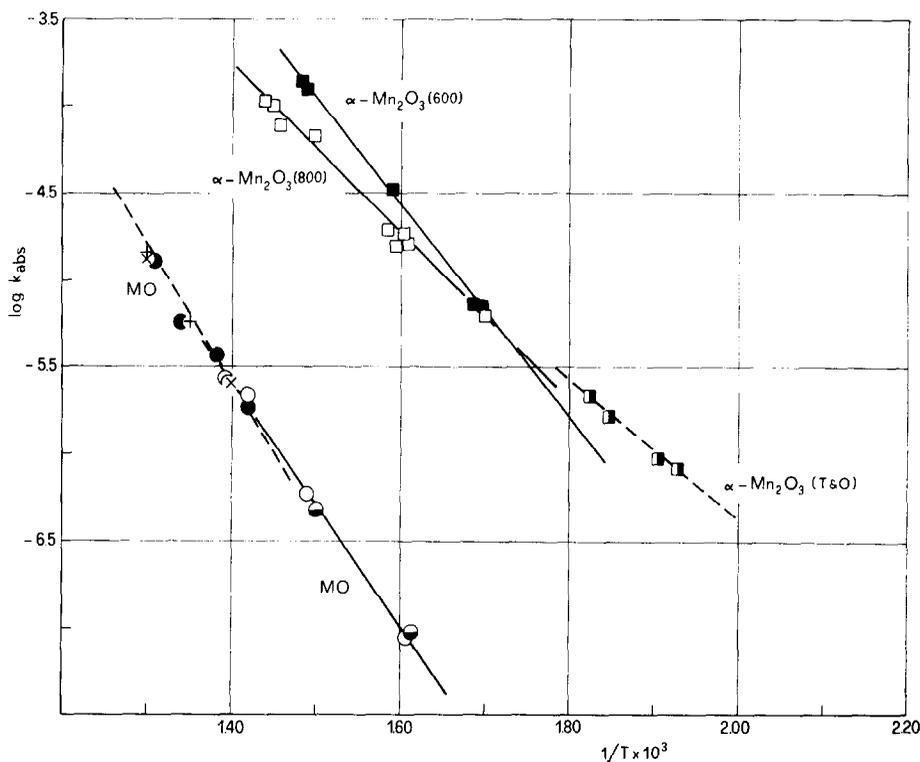


FIG. 1. A plot of $\log k_{\text{obs}}$ vs. $1/T$. Pure MgO (MO): \circ , \bullet , this work (two specimens), circulating system; \bullet , Ref. (1), static system; $+$, \times , Ref. (8), circulating system. Pure $\alpha\text{-Mn}_2\text{O}_3$: \blacksquare , prepared at 600°C ; \square , prepared at 800°C ; \blacksquare , from Tanaka and Ozaki (9), prepared at 700°C .

the one observed for $\alpha\text{-Mn}_2\text{O}_3$ (800), and the E_a value was also reduced to about 25 kcal/mole. The absolute activity is, therefore, very sensitive to the surface pretreatment.

Our results can now be compared with those of earlier investigators. Tanaka and Ozaki (9) have investigated the same reaction on a sample of $\alpha\text{-Mn}_2\text{O}_3$ prepared at 700°C , a temperature intermediate between our chosen temperatures. The pretreatment was somewhat different (evacuation at 420°C , N_2O pretreatment at reaction temperature, followed by evacuation for a few minutes at reaction temperature). The E_a value found by Tanaka and Ozaki (17 kcal/mole) is lower than our values. The absolute activity, however is not widely different, being only about 30% higher than that expected for N_2O -pretreated $\alpha\text{-Mn}_2\text{O}_3$ (600) reported above, if the activity of the latter is extrapolated to

the lower temperature range investigated by the Japanese authors. It is interesting to note that the absolute activity of their catalyst at 300°C is practically equal to the activity shown by our three catalysts $\alpha\text{-Mn}_2\text{O}_3$ (600), $\alpha\text{-Mn}_2\text{O}_3$ (600) N_2O pretreated, and $\alpha\text{-Mn}_2\text{O}_3$ (800).

A detailed kinetic study of N_2O decomposition on $\alpha\text{-Mn}_2\text{O}_3$ was carried out by Rheume and Parravano (10). These authors chose a different surface conditioning before each run, namely N_2O treatment at reaction temperature followed by 6-min evacuation with the oil rotary pump at reaction temperature. They derived a markedly higher activation energy value (35 kcal/mole) on the basis of their kinetic analysis. In order to compare their results with ours, a kinetic treatment based on initial velocities should be made. If a simple first-order law is assumed at the beginning of the reaction, their data yield a E_a value

of 18.1 kcal/mole (equal to $35 - 16.9$, the latter value being the enthalpy of N_2O adsorption). The E_a value would thus correspond to the one found by Tanaki and Ozaki, who gave their catalyst a similar N_2O pretreatment. The E_a values found by us, though higher, are shown to be sensitive to the pretreatment and to decrease when the catalyst is N_2O -treated. The absolute velocities which can be calculated from Rheume and Parravano's data at $340^\circ C$ are higher than ours by a factor of 4, which is not a large discrepancy, since it should be noted that their velocities, based on their complete kinetic equation, are not subject to the retarding effect of oxygen in the way that our initial velocities are. If the oxygen effect is included in their equation, lower values would be obtained, leading to a better agreement.

Pure Mg_6MnO_8 . The catalytic activity of Mg_6MnO_8 is lower than that found for $\alpha-Mn_2O_3$. The E_a value is 18.2 kcal/mole.

It should however be remembered that only a fraction of the cations exposed are transition metal ions. For a given number of anions, which can be assumed in close-packed structure to determine the number of surface cation sites available, the occupancy by Mn^{3+} in Mn_2O_3 is 66.7%, and by Mn^{4+} in Mg_6MnO_8 is 12.5%. The manganese cations in Mg_6MnO_8 are therefore more "dilute" by a factor of about 5. If the comparison between catalytic activities of the two phases, $\alpha-Mn_2O_3$ and Mg_6MnO_8 , takes this factor into account, the two phases would show similar catalytic activity in reference to each manganese ion. The comparison cannot be a rigorous one especially in view of the nonequality between the apparent activation energies, which implies that different energies of the oxygen-surface complexes are involved in the process and that differences between $\alpha-Mn_2O_3$ and Mg_6MnO_8 are not due solely to frequency factors. However, the results show that it

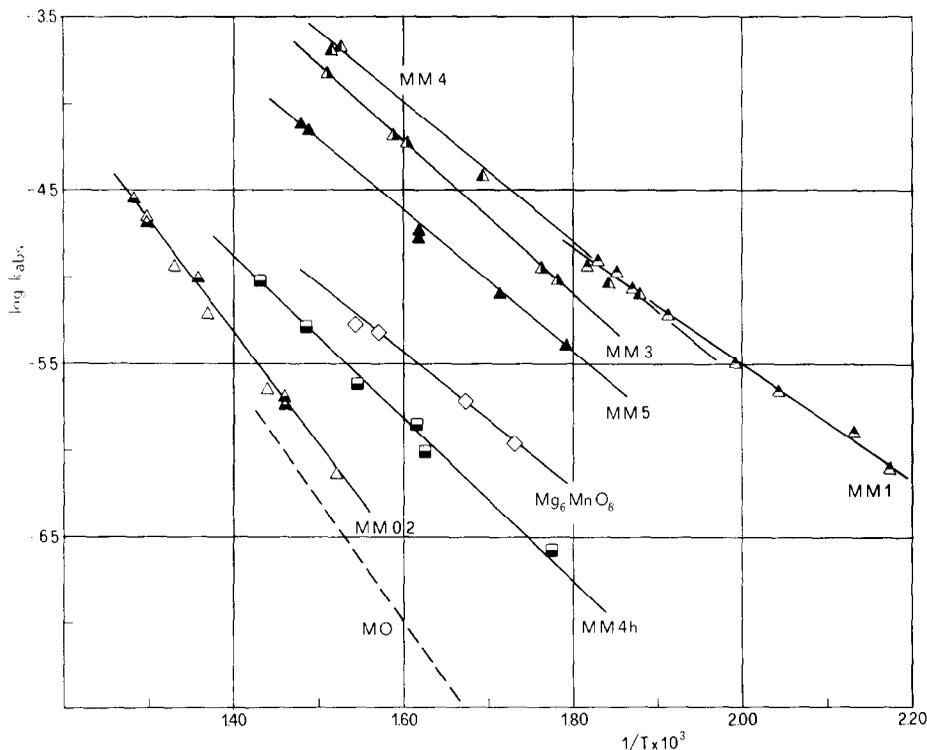


FIG. 2. A plot of $\log k_{abs}$ vs. $1/T$ for Mg_6MnO_8 , and for $MgO-MnO_x$ catalysts (MM). Two catalysts MM 0.2, having MgO ex-different sources were tested: Δ - MgO "Specpure" (Johnson & Matthey); \blacktriangle , - MgO ex-carbonate (for chemical purities, see text).

is not unreasonable to think that with α - Mn_2O_3 we are dealing not with the activity of Mn^{3+} ions, but with oxidized Mn^{4+} sites which result from the first contact with N_2O . The activity of Mn^{3+} ions cannot, therefore, be deduced from a study of Mn_2O_3 . It can only be stated that the activity of Mn_2O_3 is larger when a fresh surface is exposed, as previously remarked, and as also recorded by Tanaka and Ozaki. It would seem, therefore, that Mn^{3+} ions are more active than Mn^{4+} ions, but in the absence of information regarding the exact nature of the ions, the above conclusion is a tentative one. As shown below, more definite conclusions can be drawn from an examination of the activity of solid solutions.

Magnesium oxide–manganese oxide specimens without lithia (MM). As previously observed, the Mg_6MnO_8 phase is likely to be present in discrete patches over the MgO particles. A difference in the activity is found according to the manganese content, as illustrated in Fig. 2.

If only 0.2% (atomic) manganese is added, no Mg_6MnO_8 is detectable and the activity rises to a limited extent only. A close agreement was found between preparations based on "Spec-pure" MgO and MgO ex-carbonate (Fig. 2). The small increase of activity of MM 0.2 with respect to pure MgO is to be contrasted with the behavior presented by more heavily doped specimens known to contain the Mg_6MnO_8 phase. The catalytic activity of MM 1 is over a hundred times as large as that observed for MM 0.2 and also markedly more active (roughly 20 times) than pure Mg_6MnO_8 . Catalysts MM 3 and MM 5 are also more active than Mg_6MnO_8 , although the increase in activity is becoming less. It is obvious that the catalytic activity of MM specimens cannot be justified only by the presence of Mg_6MnO_8 over the surface of their particles. Even though a precise knowledge of the distribution of the Mg_6MnO_8 phase is lacking, the activity pattern deducible from the catalytic results is the exact opposite of what could be expected if the surface of the Mg_6MnO_8 phase were the only active surface. If a uniform

thickness is assumed, one would expect that the patches of Mg_6MnO_8 must be present in the following order of increasing area: MM 1, MM 4, MM 3, MM 5. This is precisely the order in which the catalytic activity decreases. We conclude that the major role in catalysis is played, not by the surface of Mg_6MnO_8 , but rather by the region at the boundary between Mg_6MnO_8 and MgO , a region which contains both Mn^{4+} and Mn^{2+} (the last species present in solid solution in MgO). Attention is then focused on the possibility of formation of Mn^{3+} , by an electron transfer from Mn^{2+} to Mn^{4+} . This transfer is easy in the boundary region between Mg_6MnO_8 and MgO , and the high activity of MM specimens can thus be understood. Furthermore, the large discrepancy in activity found between MM 0.2 and MM 1 can be explained by the absence of Mn^{4+} ions in the former catalyst, which did not show the presence of the Mg_6MnO_8 phase. Differences between the various catalysts can be ascribed to a different morphology of the Mg_6MnO_8 patches, affecting the extent of the intermediate boundary region, and/or to the influence of additional factors, such as the ability of creating special defects (e.g., anion vacancies) in the intermediate region. When the surface becomes increasingly covered by Mg_6MnO_8 , the boundary region between Mg_6MnO_8 and MgO becomes more and more restricted, and the activity decreases with increasing Mg_6MnO_8 content towards the value of pure Mg_6MnO_8 itself.

Specimens with lithia (MML) and the activity of Mn^{3+} and Mn^{4+} ions. Only specimens having a $[\text{Li}]/[\text{Mn}]$ ratio equal to or higher than unity are considered, that is, those which contain Mn^{3+} and Mn^{4+} ions dispersed in solid solution. Figure 3 shows the Arrhenius plots for catalysts of different manganese content and different $[\text{Li}]/[\text{Mn}]$ ratio. Comparison between specimens having the same Mn content and a different $[\text{Li}]/[\text{Mn}]$ ratio is facilitated by the use of symbols of the same shape for each Mn content. As shown, specimens having a high $[\text{Li}]/[\text{Mn}]$ ratio, hence a high Mn^{4+} content, are always less active than the corresponding specimens having a $[\text{Li}]/[\text{Mn}]$

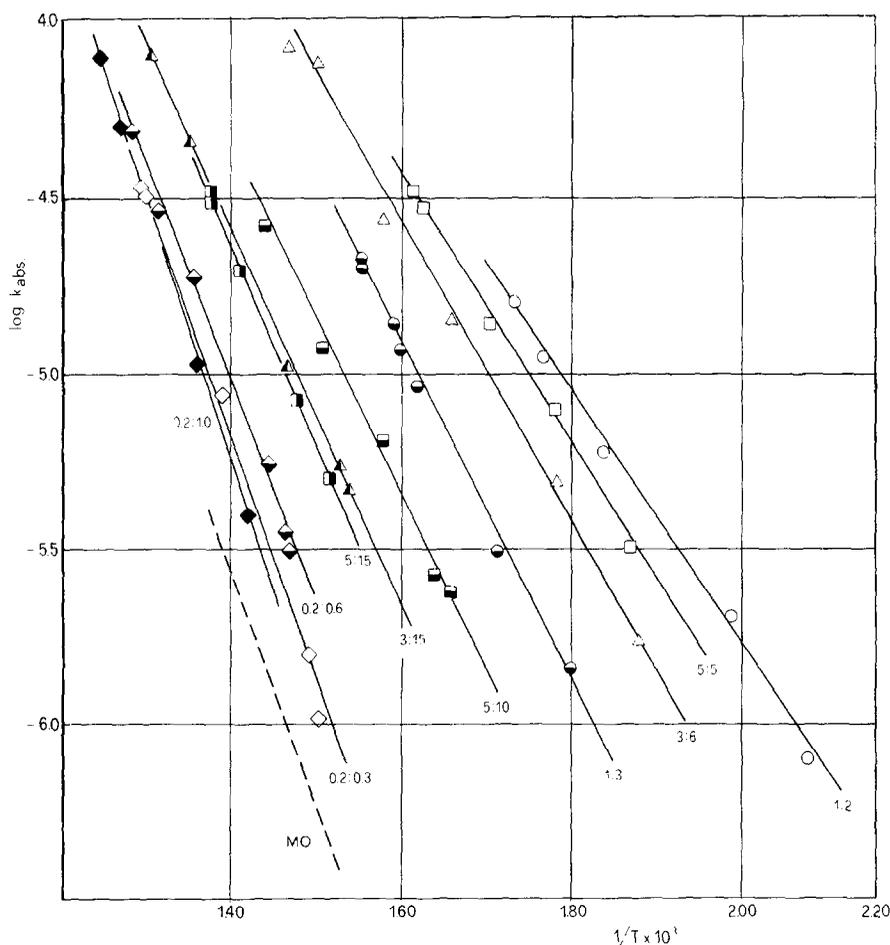


FIG. 3. A plot of $\log k_{\text{obs}}$ vs. $1/T$ for $\text{MgO-MnO}_x\text{-Li}_2\text{O}$ catalysts (MML). Values specify the nominal ratio $\text{Mn}:\text{Li}$ (in atoms, referred to 100 Mg atoms).

ratio close to unity, hence a high Mn^{3+} content. In addition to a variation of activity, a change of the apparent activation energy E_a is observed: the higher the Mn^{4+} content, the higher is the E_a value. A graph can thus be derived, Fig. 4, where the E_a value is reported as a function of the percentage of Mn^{4+} .

A question can be raised about the role of lithia upon the observed variation of catalytic activity. Bickley and Stone (11) have shown that N_2O decomposition occurs on Li_2O with an apparent activation energy of about 16 kcal/mole. In our samples, the apparent activation energy *increases* with increasing lithia content, from about 16 to about 25 kcal/mole, whereas, if free lithia

were responsible for an appreciable part of the N_2O decomposition, the E_a value should be closer to 16 kcal/mole when measured on specimens with the highest lithia content. Secondly, the highest activity is recorded for samples containing least lithia, for instance, MML 1:2 is more active than MML 1:3, and MML 1:2 is much more active than MML 5:15, the latter two catalysts having a lithia content in the ratio 1:9. Thus, the participation of lithia can be excluded in the process recorded by the E_a value. However, it cannot be excluded in succeeding processes, such as oxygen diffusion, which take place after breaking of the N-O bond has occurred.

Activity of specimens reduced in hydro-

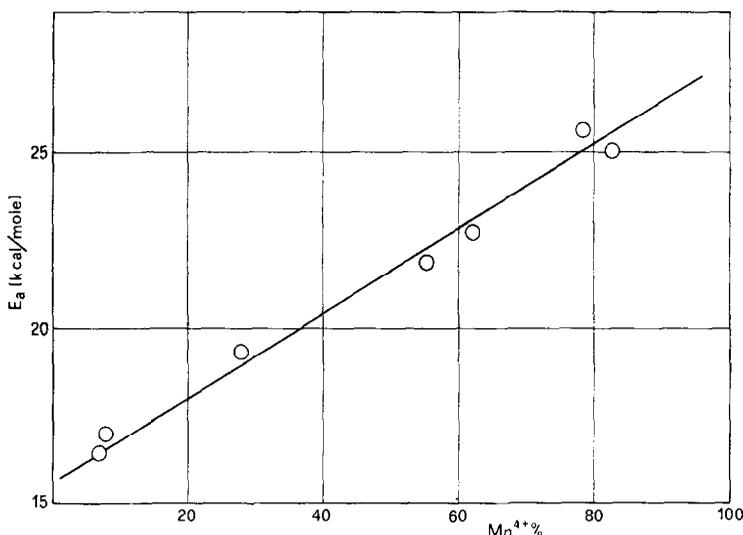


Fig. 4. A plot of the apparent activation energy E_a vs. percentage of Mn^{4+} .

gen. Two specimens were tested for catalytic activity, and a marked difference was observed with respect to oxidized specimens.

A specimen MM 4 h, having 3.9% Mn^{2+} and 0.35% Mn^{4+} (in atoms per 100 Mg atoms), showed a marked decrease (about 50 times) of catalytic activity in respect to the oxidized sample MM 4 ($Mn^{2+} = 0.31\%$; $Mn^{4+} = 4.17\%$). The E_a value also increased (from 18.9 for MM 4, to 21.7 for MM 4 h).

A specimen MML 1:1 h has been tested up to 435°C, but its catalytic activity was not measurable. Thus, a decrease of 100-fold activity, at least, must have been caused by the transformation of the majority of Mn^{3+} into Mn^{2+} , and in conditioning where Mg_6MnO_8 can no longer be present.

Comparison between catalysts with lithium (MML) and without lithium (MM). The MML sample containing 0.2% Mn is more active than the corresponding one with the same manganese content but without lithium. As already observed, the situation of MM 0.2 is a special one, because of the solubility of manganese in MgO as Mn^{2+} . Addition of lithia transforms it into Mn^{3+} . The small but significant increase of activity can be attributed to this transformation. The lithium-containing specimens with 1 and 3% Mn are less active than

MM 1 and MM 3. As noted earlier, MM 1 and MM 3 are remarkably active, not because of the presence of manganese in Mg_6MnO_8 , but because of the "mixed" region containing Mn^{4+} and Mn^{2+} . The addition of lithium not only transforms Mn^{4+} into Mn^{3+} , but also provokes diffusion of manganese ions into the bulk, diluting the surface. The decrease of the absolute activity on adding lithium is thus ascribed to the decrease of the number of exposed active sites (Mn^{2+} plus Mn^{4+}). Reversal of the trend occurs at 5% Mn. It is now the MM specimen (MM 5) which is less active than the corresponding specimen containing lithium and having a Li:Mn ratio of about unity. This can be understood, since MM 5 is comparable to Mg_6MnO_8 , with few "mixed" sites Mn^{2+} Mn^{4+} . The addition of lithia, while eliminating comparatively few active sites, provokes the formation of a large number of new ones, namely Mn^{3+} ions. The observed effect of lithia on MM specimens can thus be justified on the basis of the solid state chemistry of these systems. The comparison between MM and MML is, nevertheless, rendered somewhat uncertain by the complex situation of the active surface of MM catalysts.

Oxygen chemisorption during catalysis. It has already been mentioned that oxygen

chemisorption occurs during the catalysis of the N_2O decomposition. Knowledge of the number of N_2O molecules decomposed, the volume of the apparatus, the N_2/O_2 ratio, and the catalyst surface area enables calculation to be made of the deficit of oxygen molecules in the gas phase and hence of the oxygen surface coverage. The latter is calculated as the percentage ratio between the number of adsorbed oxygen atoms and the number of the cations in a surface of MgO equally composed of (100), (110), and (111) planes. The experimental results of the N_2/O_2 ratio and related quantities are reported in Table 2. Examination of the sequence MML 3:4 shows that the oxygen coverage decreases in successive experiments, but comparison of runs such as a5 and a8, made at the same temperature, is difficult because the amount of N_2O decomposed is not the same. It was indeed found impracticable to make a systematic investigation of the influence of temperature and catalyst composition on oxygen chemisorption, because of the impossibility of producing a fixed amount of oxygen in a given sequence. It can be stated, however,

that the oxygen produced in the first N_2O decomposition experiment (on a surface not subjected to previous catalysis experiments) is likely to be totally adsorbed by the surface up to high oxygen coverage (see MML 3:15). As shown, the oxygen coverage decreases in successive experiments, but it never goes much below 15%. Catalysts containing a large amount of lithium (MML 3:15) appear more apt to chemisorb large quantities of oxygen. It is not, however, possible to attribute this ability to the presence of lithia itself (Li_2O), since oxygen retentions, even in the assumption of a surface totally composed of lithia, are about 100 times larger than those found by Bickley and Stone (11) for a pure lithia specimen outgassed at $450^\circ C$ (10^{16} molecules/ m^2 in their case, vs. 10^{18} molecules/ m^2 in our case, in a similar oxygen pressure range).

Oxygen adsorption from molecular oxygen. The oxygen coverages attained during catalysis are especially interesting when compared with coverages obtained from adsorption of molecular oxygen. The adsorption experiments, reported below, were designed for correlation with the catalysis

TABLE 2
OXYGEN ADSORPTION DURING N_2O DECOMPOSITION

Catalyst ^a	Expt ^b	T (°C)	Decom- position (%)	O ₂		p _{O₂} ⁰ (Torr) ^c	O ₂ in deficit	θ (%) ^d
				produced (mole- cules/ $m^2 \times$ 10^{-18})	Observed N ₂ /O ₂ ratio in gas phase			
MML 3:4	a5	358	0.130	4.02	2.78	0.038	1.12	19.6
	a6	408	0.167	5.29	2.48	0.050	1.03	18.0
	a7	382	0.163	4.86	2.50	0.047	0.93	16.4
	a8	358	0.090	2.71	2.93	0.026	0.84	14.7
MML 3:6	b2	358	0.27	2.36	5.46	0.070	1.35	24.0
MML 5:5	c2	327	0.23	2.01	3.94	0.092	0.99	17.6
MML 5:6	b2	366	0.58	11.4	2.32	0.173	1.46	25.6
	b3	406	0.65	12.8	2.15	0.195	0.89	15.7
MML 3:15	b1	434	0.08	2.68	1000	0.024	2.68	(50)
MML 5:15	b6	406	0.06	1.88	3.60	0.018	0.84	14.6
	b5	460	0.32	10.1	2.65	0.096	2.48	43.5

^a See Table 1 for analyses.

^b The numeral refers to the sequence in which experiments were done with a given specimen. The letter refers to a given portion of the catalyst, taken from a single batch.

^c Virtual oxygen pressure, i.e., the pressure which would have been built up by N_2O decomposition in the absence of chemisorption.

^d Calculated for dissociative adsorption of oxygen per total number of cations, as specified in the text.

TABLE 3
 VARIATION OF OXYGEN COVERAGES IN SUCCESSIVE ADSORPTION EXPERIMENTS
 Catalyst outgassed for 30 min at 480°C between adsorption experiments

Sample	T (°C)	p_{O_2} (torr) ^a	θ_1^b	θ_2	θ_3	θ_4	θ_5	θ_7	θ_8	θ_{10}
MML 3:6	346	0.40	42	6.3	—	5.4	—	—	—	—
3:15	350	0.33	—	8.7	—	—	—	5.2	—	—
	396	0.40	105	—	—	—	6.1	—	—	—
5:5	295	0.44	(21) ^c	10.7	—	6.7	5.2	—	4.6	—
5:15	298	0.35	54	15	10.3	—	—	—	5.5	5.3

^a p_{O_2} = average of initial pressure in different runs.

^b θ_n = Oxygen coverage (see text for definition) after the n th adsorption experiment.

^c All oxygen had been adsorbed, and the experiment was then interrupted.

study, and had the purpose of providing information on the following points: (i) estimation of the amount of oxygen chemisorbed more loosely on the surface, and its dependence on catalyst composition, and on temperature, (ii) comparison of the oxygen coverage reached from molecular oxygen adsorption with coverages attained during catalysis; and (iii) investigation of the influence of catalyst composition on oxygen uptake.

“Strong” and “weak” oxygen chemisorption. The uptake of oxygen on a freshly outgassed surface (4 hr, 480°C), not previously subjected to any adsorption experiment (first adsorption experiment), is very large, and it has not always been pursued to completion (as defined in Experimental Methods). A marked drop of oxygen uptake was observed in the second adsorption experiment, which succeeded the first experiment after a shorter (30 min) outgassing at 480°C. Successive adsorption runs showed a progressive, but less marked decay. The situation is illustrated by Table 3, where oxygen coverages θ_n in successive experiments are reported, the index n referring to the n th adsorption experiment. A blank space in Table 3 indicates either that adsorption was not pursued to completion, or that adsorption was not carried at the same temperature. Even though runs successive to the first one were preceded by a shorter outgassing (0.5 hr), most of the adsorbed oxygen that could be removed was evacuated at the beginning of the outgassing

treatment. Thus, the discrepancy between subsequent adsorbed quantities cannot be accounted for by the difference of outgassing time. The first adsorption experiment thus shows that the surface is potentially capable of adsorbing a large amount of oxygen. After the initial uptake, however, a large fraction of the surface is “blocked” towards the adsorption-desorption experiments. A large fraction of the oxygen initially adsorbed is, therefore, strongly held by the surface, and not released in successive experiments. The result suggests that at least two forms of oxygen are present, one more weakly bound, which will be called O_{ads}^w , and one more strongly bound, called O_{ads}^s . This notation does not necessarily imply an atomic form, but it simply refers to the energy of the bond. It is also possible to consider that a continuous spectrum of energies is involved, instead of two distinct forms. O_{ads}^w and O_{ads}^s would then correspond to two different distribution. It appears, more logical, however, to think in terms of different natures of the chemisorbed forms (see below). The reason for the difference between the first and successive adsorption experiments can be sought in two different and perhaps concomitant causes: (a) The original surface contains many —OH groups, and the first outgassing removes H_2O molecules, creating bare sites for oxygen adsorption. A large fraction of oxygen adsorbed in the first experiment occupies these sites, and it is strongly adsorbed. (b) The chemi-

sorbed oxygen initially present on a fresh sample is held, on the average, more weakly than the oxygen adsorbed after the surface has been cleaned in the first outgassing. This is because the equilibrium concentrations of the two forms depend on the temperature, and a larger fraction of the weak O_{ads}^w form is present at lower temperatures. The surface of a fresh specimen is closer to the proper thermodynamic equilibrium pertaining to room temperature, and as such it is richer in O_{ads}^w . When outgassed, a large fraction of surface oxygen is driven off. On the first adsorption experiment, many sites are then available for oxygen chemisorption. The fairly high temperatures, at which adsorption has been investigated, require that a large fraction of oxygen be present as O_{ads}^s . The adsorption may well proceed through the O_{ads}^w form, but, the final form is predominantly a strong one, and it will not be driven off in successive outgassing treatments; hence lower θ_n values will be observed. Also, the kinetics of the first adsorption are different

from the kinetics of the successive adsorption experiments, as illustrated for MML 5:5 in Fig. 5. A stronger adsorption taking place in the first run is suggested by the steeper uptake curve.

Comparison with oxygen adsorption during catalysis. Qualitatively, both quantities θ_{cat} (coverage attained in adsorption experiments) decrease in successive experiments. However, θ_{ads} shows a more marked drop, while θ_{cat} stays at higher levels ($\theta_{ads} \sim 5\%$; $\theta_{cat} \sim 15\%$). The observed difference can perhaps be explained if dissociative adsorption of oxygen is assumed. Then, while in the adsorption from molecular oxygen, the O_2 molecule must be broken and two sites must be available, in the N_2O decomposition an oxygen atom is directly produced, and only one adsorption site is required.

Catalyst composition and oxygen uptake. In view of the difficulty of defining the oxygen uptake by a fresh surface, it is impossible to compare initial capacities between catalysts of different composition.

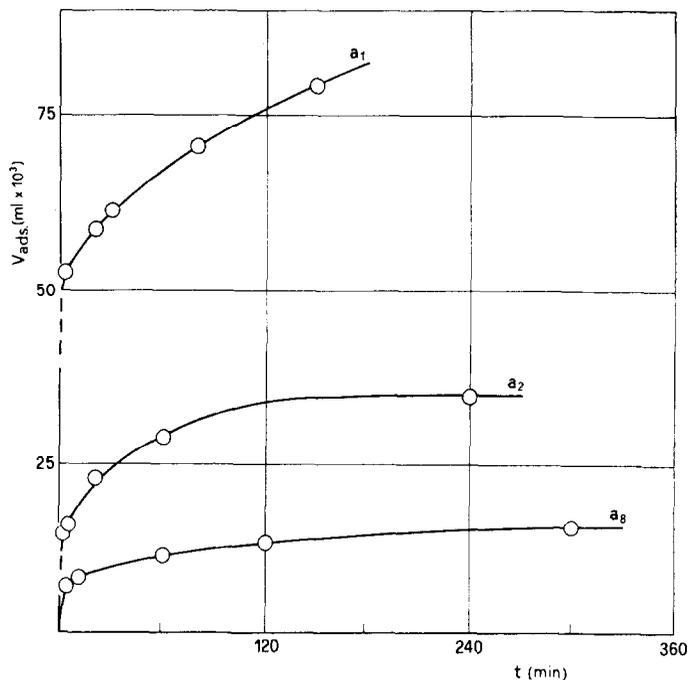


FIG. 5. The progress of chemisorption of oxygen with time on MML 5:5, on the first, second, and eighth chemisorption run.

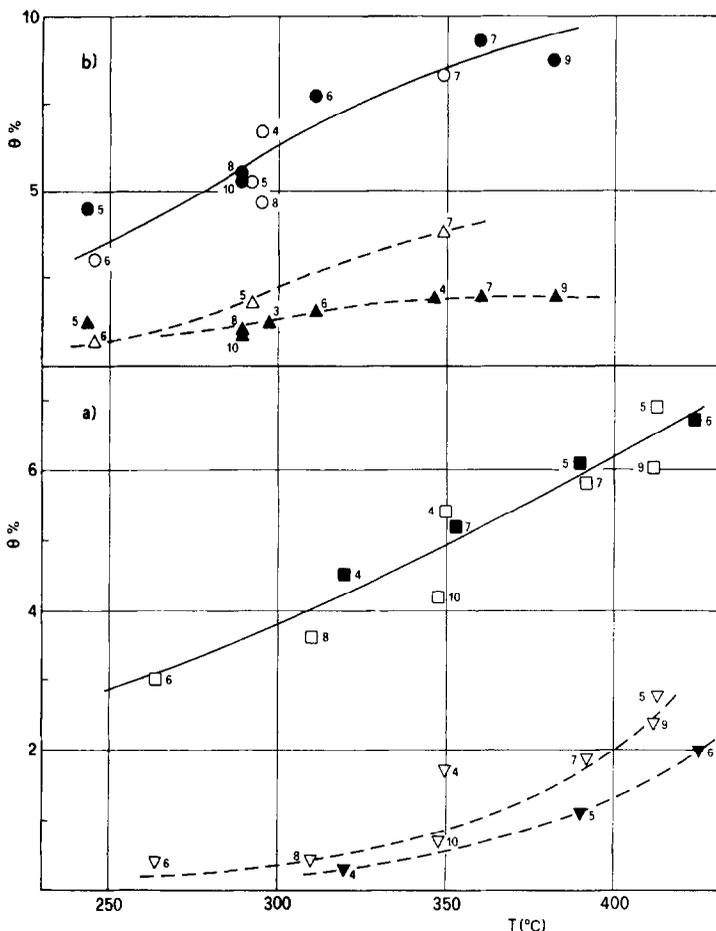


FIG. 6. Oxygen coverages, in percent, ($\theta\%$) at different temperatures: (a) total oxygen uptake, solid line: \square , MML 3:6 ($Mn^{3+} = 72\%$); \blacksquare , MML 3:15 ($Mn^{3+} = 17\%$); "reversible oxygen" uptake, broken line: ∇ , MML 3:6; \blacktriangledown , MML 3:15; (b) total oxygen uptake, solid line: \circ , MML 5:5 ($Mn^{3+} = 92\%$); \bullet , MML 5:15 ($Mn^{3+} = 22\%$); "reversible oxygen" uptake, broken line: \triangle , MML 5:5; \blacktriangle , MML 5:15. The value near the point refers to sequence in which the experiments were done.

It is possible, however, to make such a comparison on "adsorption conditioned," i.e., on surfaces previously subjected to at least three adsorption experiments, when the chemisorbed amounts do not vary much (see Table 3). Figure 6a shows the oxygen coverages reached at different temperatures on the adsorption conditioned surface of catalysts MML 3:6 ($Mn^{3+} = 72\%$; open squares) and MML 3:15 ($Mn^{3+} = 17\%$; black squares). The coverage is practically independent of Mn^{3+} content. Consider now the "reversible oxygen" (as defined in Experimental Procedure), represented as a broken line in Fig. 6a. There is a consistent

tendency to find a higher amount of more loosely bound oxygen on the specimen MML 3:6 (open triangles) having a higher Mn^{3+} content. The two catalysts MML 5:5 ($Mn^{3+} = 92\%$; open circles) and MML 5:15 ($Mn^{3+} = 22\%$; black circles) are compared in Fig. 6b. Similarly, the reversible oxygen is represented as broken lines.

In summary, the adsorption experiments have shown that a marked decrease of oxygen uptake occurs after the first adsorption experiment, and that no appreciable differences between Mn^{3+} -rich catalysts and Mn^{4+} -rich catalysts are found in respect of the total oxygen uptake. However, the oxy-

gen chemisorbed is more loosely held on the Mn^{3+} -rich catalysts than on the Mn^{4+} -rich catalysts.

IV. DISCUSSION

Activity of manganese ions in different valency states. The solid solution study gives a definite proof that Mn^{3+} ions are more active in N_2O decomposition than either Mn^{4+} ions or Mn^{2+} ions. The first part of the statement, which compares Mn^{3+} and Mn^{4+} , is demonstrated by a comparison of specimens with different $[Mn^{3+}]/[Mn^{4+}]$ ratio. It also gives an explanation for the differences found for fresh Mn_2O_3 surfaces with respect to aged ones. In spite of the necessary presence of lithium ions, it has been possible to exclude any serious interference from lithia in interpreting the activity of manganese ions. The very weak activity of Mn^{2+} ions is demonstrated by the reduced samples MMh and MMLh. It should be noted in this regard that the higher resistance of Mn^{2+} ions to oxidation when in solid solution brings out this difference in a much more clear way than can be achieved by comparison of the activities of pure oxides.

A high activity towards N_2O decomposition is not confined to catalysts initially containing the species Mn^{3+} .

Catalysts containing a mixture of Mn^{2+} and Mn^{4+} , even though in two different phases, are highly active. This behavior should be contrasted with the case of the activities of *isolated* phases containing Mn^{2+} or Mn^{4+} , which are low, and suggests that the Mn^{3+} center can be formed by mutual electron transfer: $Mn^{2+} + Mn^{4+} \rightarrow Mn^{3+} + Mn^{3+}$.

In addition to the presence of the Mn^{3+} centers, atomic defects can play a role in the subsequent oxygen transfer and oxygen desorption process, as briefly discussed below; the situation in a Mn^{3+} -containing solid solution on the one hand, and in a Mn^{2+} - Mn^{4+} two-phase system on the other, therefore, can be considerably different. However, it must be stressed that only when Mn^{3+} or potentially similar centers are present is a catalyst highly active.

Influence of dilution on the catalytic activity. In view of the influence of valency state on the activity, the effect of dilution can be studied only on catalysts having a similar $[Mn^{3+}]/[Mn^{4+}]$ ratio. This comparison is shown in Fig. 7, where the activities of three pairs of catalysts are confronted, each pair having a similar $[Mn^{3+}]/[Mn^{4+}]$ ratio but a different *total* manganese content. The comparison is made by reporting the Arrhenius plot for k_{abs}^{Mn} ,

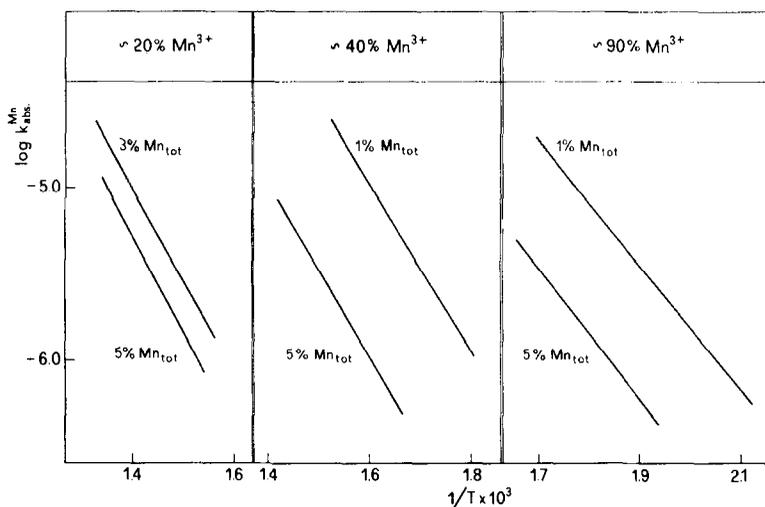


FIG. 7. Normalized activities ($\log k_{obs}^{Mn}$ vs. $1/T$) of three pairs of catalysts, each pair having a similar percentage of Mn^{3+} but different total manganese (Mn_{tot}) content. Catalysts at $\sim 20\%$ Mn^{3+} , MML 3:15 and MML 5:15; at $\sim 40\%$ Mn^{3+} , MML 1:3 and MML 5:10; at $\sim 90\%$ Mn^{3+} , MML 1:2 and MML 5:5.

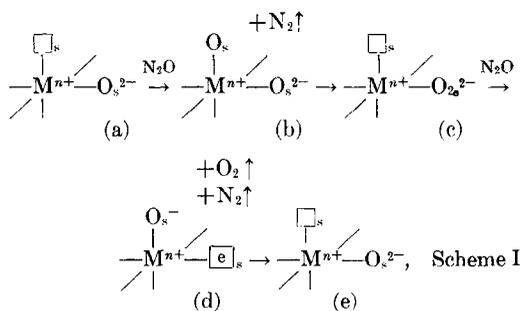
where $k_{\text{abs}}^{\text{Mn}} = k_{\text{abs}}/x_{\text{Mn}}$, x_{Mn} being the manganese molar concentration. In this way the quantity $k_{\text{abs}}^{\text{Mn}}$ is normalized with respect to manganese concentration. As shown, in each case the most dilute specimen is the most active. Thus catalysts having a greater proportion of isolated Mn^{3+} ions are intrinsically more efficient in sustaining the N_2O decomposition than those where Mn^{3+} ions are less isolated.

Adsorption of oxygen and catalytic activity. A correlation between catalytic activity for the N_2O decomposition and oxygen chemisorption has also been brought out by the experiments. A higher lability of chemisorbed oxygen parallels a higher catalytic activity. It follows from this and from the preceding paragraphs that the +3 valency of manganese must be associated with a lower average strength of the oxygen-surface bond. It may be recalled that different rates of homomolecular exchange as well as of surface exchange of oxygen have been recorded by Boreskov (12) for three specimens having a different average manganese valency. A specimen of composition $\text{MnO}_{1.83}$, consisting of $\text{MnO}_2 + \alpha\text{-Mn}_2\text{O}_3$ showed a lower (factor 10) rate for both reactions in comparison with a specimen $\text{MnO}_{1.55}$, consisting of $\alpha\text{-Mn}_2\text{O}_3$ only. This isotopic study, therefore, supports the conclusion of weaker oxygen-surface bonds on the Mn^{3+} ions. Finally, reversing the argument, the very low catalytic activity of Mn^{2+} ions points to a higher strength of the bond in the oxygen-surface complex in that case. An indication in support of this hypothesis can be found in the calorimetric measurements of the heats of adsorption of oxygen on manganese oxides made by Garner and Ward (13). The authors showed that the heats of adsorption on a specimen consisting of $\alpha\text{-Mn}_2\text{O}_3$ were lower than those recorded on a reduced specimen, containing both Mn_2O_3 and Mn_3O_4 ($\text{Mn}^{2+}\text{Mn}_2^{3+}\text{O}_4$). The Mn^{3+} ions, therefore, appear as the most favorable ones for the formation of a more labile oxygen-surface complex.

It is unwarranted to consider the formation of only one type of surface complex.

The study of the oxygen adsorption has given clear evidence of the existence of at least two forms of chemisorbed oxygen, one of which is more weakly adsorbed, $\text{O}_{\text{ads}}^{\text{w}}$, and the other more strongly held $\text{O}_{\text{ads}}^{\text{s}}$. The two forms do not necessarily correspond to atomic forms, and in fact molecular forms such as O_2^- or O_2^{2-} may constitute the weak form. Also as noted a continuous change of the bond strength can be envisaged, the two forms being extreme cases. Irrespective of their nature, however, production of the weak form tends to be sustained during catalysis. In fact, during catalysis, the amount of oxygen which can be chemisorbed and desorbed (as followed by the N_2/O_2 ratio), is larger than the amount of oxygen chemisorbed and desorbed in molecular oxygen adsorption experiments, even though initial chemisorbed quantities are comparable. The catalytic process can then be correlated with the oxygen chemisorption, and the nature and the strength of the oxygen-surface complex will be responsible for the catalytic activity.

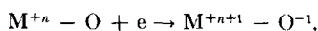
The dissociation of N_2O leaves an oxygen atom chemisorbed on the center responsible for dissociation. If this center is called M, the step is represented by $\text{N}_2\text{O} + \text{M} \rightarrow \text{N}_2 + \text{O-M}$. Following this, the O-M bond must be broken. The release of oxygen can occur through the migration of the oxygen atom, such as in the scheme below



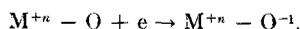
where \square is an oxygen vacancy, e is an electron, n is the valency of the cation, and the subscript s refers to surface position. Bonds left unspecified lead to bulk or to other surface atoms. The oxygen release is, therefore facilitated by factors favoring

the formation of the peroxide ion. In this respect, the presence of lithium can exert a positive action, but it should be remembered that MgO is also known to form a peroxide. It may be noted that this "peroxide mode" has been postulated by Dowden (14) and by Bickley and Stone (11). Desorption of oxygen can in fact take place after migration of the peroxide surface ion on the surface, until a suitable electron trap is met. On a freshly outgassed surface, rich in anion vacancies and trapped electrons, the chemisorbed oxygen would tend to fill in the vacancies. The absence of empty electron traps, and the adverse condition for the formation of the peroxide ions (since oxygen vacancies are present to capture oxygen atoms) lead to a strong oxygen-surface bond.

On the other hand, the weak chemisorbed oxygen can be transformed into a strongly held species, by an electron transfer process, either by electron transfer from the M center,



or by electron transfer from donors in the bulk



All charges are formal ones, and a -2 charge instead of a -1 , together with -1 charge instead of a zero charge, can be written on the anions in the last two equations. The important point is that an electron donation can strengthen the M-O bond, and block that center for future catalytic action.

The overall situation can, therefore, be described as follows. A catalyst containing Mn^{3+} centers is more active because the oxygen is held less strongly on the Mn^{3+} ions. A transformation into a ionic bond by electron transfer renders the oxygen-surface bond so strong that it can be disregarded for successive catalytic steps. Dilution in the insulating matrix of MgO favors the permanence of bonds less ionic in character by suppressing the electron transfer from the interior. Covalent character and Mn^{3+} centers are to be associated

with a high activity. A possible explanation for this conclusion is outlined below.

Electron configuration and oxygen bond strength. The influence of the electron configuration of a given ion can be taken into account in the process of breaking the metal-oxygen bond. Dowden and Wells (15) were the first to discuss the problem from this point of view, and it has subsequently been elaborated by other authors. Crystal-field stabilization energy is only a small fraction of the total energy of a given ionic grouping. However, on a surface a whole range of bond energies is involved, of which the very strong and the very weak bonds are not catalytically significant. A small variation in energy for the energetically important fraction of chemisorbed molecules or atoms can then be important. This may be the case for the more covalently-held oxygen. The d^4 configuration of Mn^{3+} is known to provoke the formation of two weaker bonds on the ligands of octahedral coordination complexes. The situation of a Mn^{3+} ion on a surface will differ from that encountered for a free coordination complex because some of the ligands, oxygen ions, are anchored to the rest of the crystal, i.e., geometrical restriction are imposed. The d^4 complex will therefore lose its optimum symmetry, but the bond projecting from the surface of a 100 plane will still be weaker than those in the plane. It may be recalled that the d^4 configuration, together with the d^0 configuration, shows the most favorable contribution for a dissociation mechanism when examined from the standpoint of the Crystal field stabilization energy (16). The concept of a weak manganese-oxygen bond being present when a d^4 configuration is involved is the result needed to explain the high activity of Mn^{3+} (d^4) in N_2O decomposition as compared with Mn^{2+} (d^5) or Mn^{4+} (d^3).

It is reasonable to predict that oxidation reactions will also be favored by the presence of Mn^{3+} ions as catalysts for the same reason. Along these lines, the findings by Brooks (17, 18) about the higher ability of slightly reduced MnO_2 towards

hydrogen oxidation can be interpreted as due to the presence of Mn^{3+} sites in non-stoichiometric dioxide, rather than being caused by "disorder." The presence of disorder could assist the subsequent surface diffusion, as noted above, but it would be of help only if taken together with an initial ability of the oxide to adsorb oxygen less strongly on appropriate sites. A further deduction which can be made from the present work is that oxidation reaction should be assisted by conditions which tend to preserve the +3 valency state of manganese. Work to examine this hypothesis is in progress in our laboratory.

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