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The Activity and Selectivity of Mn^{3+} and Mn^{4+} in Lanthanum Calcium Manganites for the Oxidation of Ammonia

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The series of oxides, $Ca_xLa_{1-x}MnO_3$, have a common perovskite structure and represent a simple system to study the effects of manganese valence and cation vacancies on catalytic properties. The samples were used as catalysts for the oxidation of ammonia to N_2, N_2O, and NO at 350–400°C. The results indicate that only two types of catalysts or sites are present which border at the region $x = 0.3$–0.4. When $0 \leq x \leq 0.3$, the catalysts produce large amounts of N_2O and N_2 whereas at $0.4 \leq x \leq 1.0$, appreciable amounts of NO are also formed. This difference may depend on whether oxygen is reacting in an atomic or molecular form. The results suggest that Mn^{3+} and Mn^{4+} do not act as individual surface ions but are part of a large group which acts as either an electron donor or acceptor. Cation vacancies in this system are unimportant.

I. INTRODUCTION

A current view of nonmetallic catalysts and one which is potentially very useful is to consider individual active ions as centers for coordination and reaction in analogy with homogeneous complexes. While this appears to be valid for low concentrations of active ions in an inert matrix, it has been found in many cases that neighboring ion interactions become important even at very low levels depending on the system. For example, Cimino and Pepe (*1*) have recently shown that for N_2O decomposition the specific activity of cobalt ions dispersed in MgO begins decreasing even at 0.1 atom % and this continues until pure CoO is reached. Similar effects have been reported for Cr^{3+} ions in $MgCr_xAl_{2-x}O_4$ (*2*), for Ni ions in $Ni_xMg_{1-x}Al_2O_4$ (*3*) for Mn^{3+}–Mn^{4+} in MgO (*4*) with N_2O decomposition and for Cr^{3+} in Cr_2O_3–Al_2O_3 (*5*) with dehydrogenation of isobutane. Furthermore, the concentration of an active ion in an inert matrix strongly effects its selectivity in certain reactions. This was demonstrated by Stone and Pepe (*6*) for the dehydrogenation vs dehydration of isopropanol over Cr_2O_3–Al_2O_3 solid solutions. The very dilute Cr^{3+} (0.1%) was almost exclusively a dehydrating catalyst, whereas higher concentrations tended toward dehydrogenation.

In catalysts with high concentrations of active ions it would appear that ions cannot be treated individually but involve neighboring ion effects or ion clusters. These longer range effects are difficult to characterize because very often concentrated systems involve different compounds and changes in coordination of the active ions. Many useful industrial catalysts require synergistic effects of two different ions performing different functions. One example is the work of Batist, Lippens, and Schuit (*7*) on bismuth molydate for butene oxydehydrogenation in which many bismuth molydate compounds are formed but some are much more selective than others. Another example is the cobalt molydate catalyst for oxidation of propylene (*8*). Depending on the Co/Mo ratio the major

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product can vary from carbon oxides to acetone to acrolein. Other oxidizable ions in place of Co^{3+} give different product distributions (*9*). Although these types of catalysts are obviously important, very little work has been done to clarify these neighboring group effects.

To investigate these group interactions requires two things; first, a simple model catalyst which would allow the isolation of the critical variables, and second, a test reaction to reflect changes in catalyst properties.

As a model catalyst system, the complete series of nearly isostructural perovskites, $Ca_xLa_{1-x}MnO_3$, first discovered by Jonker and Van Santen (*10*), seemed ideal. The fact that these materials have a single structure minimizes the geometric variables that might be associated with different compounds with different coordination. A part of the perovskite structure showing the coordination of the manganese ions is given in Fig. 1. The manganese ions are octahedrally surrounded by O^{2-} ions, whereas the Ca^{2+} or La^{3+} is surrounded by 12 O^{2-} ions. In one end member, $LaMnO_3$, the manganese valence is +3. Replacing La^{3+} by Ca^{2+} requires manganese to become +4 with small changes in lattice constant until the final member, $CaMnO_3$, which contains only Mn^{4+}.

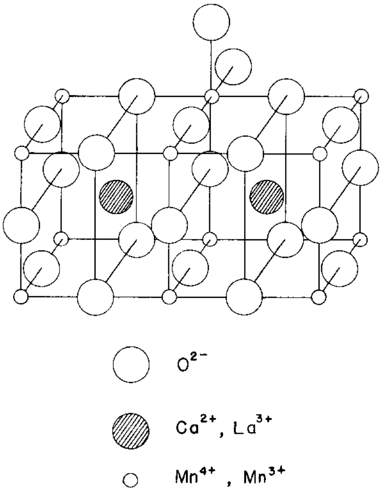

FIG. 1. Coordination of Mn ions at the surface of a perovskite lattice.

This system demonstrates the effect of three important variables in complex catalysts. The first is the effect of the valence of the active ion, in this case manganese. This would be shown by the end members, $LaMnO_3$ and $CaMnO_3$. A second variable is the effect of mixtures of ions with different valences, Mn^{3+} and Mn^{4+} as shown by the rest of the series $Ca_xLa_{1-x}MnO_3$. A third variable, the effect of excess lattice oxygen and cation vacancies, can also be shown in this system, since $LaMnO_3$ can be oxidized to the extent of 30% Mn^{4+} with only minor changes in structure by introducing cation vacancies.

The model reaction was the oxidation of ammonia. While the reaction is probably more complex than the commonly used CO oxidation or the N_2O decomposition, it has the distinct advantage that it demonstrates selectivity to three products, N_2, N_2O, and NO. Catalyst activity is known to be very sensitive to surface contamination, whereas selectivity should be sensitive to the quality of the surface sites and the type of oxygen adsorption even if some of the sites are blocked. This, of course, is true only at very low conversions where secondary reactions are not significant. A second reason for choosing this reaction was that no surface carbonates can form which are a real problem in hydrocarbon oxidations. Surface nitrates are generally less stable and more reactive. Finally, the ammonia oxidation proceeds at relatively low temperatures which reduces the likelihood of bulk reactions of the catalysts.

II. EXPERIMENTAL METHODS

a. Catalyst sample preparation. The catalyst samples were prepared by rapid precipitation of the carbonates from an aqueous solution of manganese, calcium, and lanthanum salts. This seemed preferable to the ceramic methods involving mixing of the oxides because the ions are more thoroughly mixed in the precipitate and the carbonates are a reactive form to insure a thorough distribution of the ions. The solution containing $Mn(OAc)_2 \cdot 4H_2O$, La_2O_3, and $CaCO_3$ in nitric acid was added rapidly with vigorous stirring to a solution of $(NH_4)_2CO_3$ and NH_4OH. The concentrations were chosen to give a nearly constant final pH and carbonate concentration for the different samples. The precipitate was filtered and then dried at 130°C overnight followed by 1 day at 250°C. The sample was ground thoroughly by mortar and pestle, heated to 700°C, reground, and pressed isostatically at 20,000 psig. The solid chunks were heated 15 hr at 1000°C, crushed to 20–40 mesh, heated at 1250°C for 3–5 hr in flowing nitrogen or air followed by cooling in the same atmosphere in the furnace. The nitrogen was first passed over a copper catalyst to remove all traces of oxygen. The crucibles for the high temperature treatments were 99% alumina to minimize contamination with silica.

b. Catalyst analysis. The analysis for calcium and manganese in the samples was determined by atomic absorption spectroscopy. The lanthanum was separated from calcium by precipitation as the hydroxide and from the manganese by precipitation as the oxalate. It was weighed as the oxide. The concentration of Mn^{3+} vs Mn^{4+} was determined iodometrically after dissolution in dilute hydrochloric acid under a nitrogen atmosphere. The total manganese in this solution was then determined by atomic absorption spectroscopy.

The structure of the catalysts were determined by X-ray of the powders with Fe-$K\alpha$ radiation. Samples with distorted perovskite structures were further examined on a Guinier focusing camera using Cu-$K\alpha$ radiation.

Surface areas were obtained by krypton absorption.

c. Ammonia oxidation analysis. The reaction was studied in a flow system with analysis by mass spectroscopy. The catalyst particles were mixed with 2 g of Alcoa T-71 high purity fused alumina to separate the active particles and reduce local heating. This bed formed a cylinder 13 mm o.d. by 30 mm long with a concentric thermocouple tube 6 mm o.d. Four thermocouples in this well indicated a temperature gradient along the bed of less than 5°C at 400°C and less than this at 350°C. Above and below the bed was packed with 8–14 mesh Alcoa T61 high purity fused alumina.

A gas cylinder was filled to 90 psig with a mixture of Ar and NH_3 in the mole ratio 5.8:1. The ratio was determined by measuring the volume flow of Ar with NH_3 removed and then titrating the NH_3 by bubbling this same mixture through 0.1 *N* H_2SO_4. This mixture was brought into the system and mixed with O_2 from a calibrated rotameter. The pressure above the reactor was maintained at 32 Torr by a valve after the reactor and the pressure drop across the reactor was less than 2 Torr. The product gases were passed through Ascarite and Drierite traps which removed water and ammonia, and a fraction of the resulting stream was analyzed on a Consolidated Electrodynamics Corp. 21-620 mass spectrometer.

The following procedure was used: first, Ar + NH_3 was used to purge the system and establish the N_2 ($m/e = 28$) background on the spectrometer. The argon and oxygen flows were measured and then mixed and analyzed on the mass spectrometer to give a feed analysis, in particular the ratio of the 32/20 peaks in the feed. The sample catalyst was heated up to 400°C in this feed and after 2 hr a product analysis was taken. Next, the temperature was lowered to 350°C where several points were taken at various amounts of bypass of the feed. Although at 350°C the activity remained constant throughout these experiments, at 400°C the activity tended to drop off in the first hour and gradually approached a constant value.

Argon was used as an internal standard for all other gases. N_2O, N_2, and O_2 were calibrated versus argon and determined (μmoles/min) in the product. Nitric oxide never reached the mass spectrometer but dropped out as NH_4NO_2 which was identified as a solid by ir and by analysis of the aqueous solution as nitrite ion. Nitric oxide was calculated from the oxygen balance, i.e., from the difference between total oxygen converted and that used to form N_2 and N_2O according to the following equations:

TABLE 1
Composition and Properties of the Lanthanum Calcium Manganites

Sample no.	T (°C)	Atmosphere	(La + Ca)/ Mn ×100%	La/Mn ×100%	Ca/Mn ×100%	% Mn^{4+}	Surface area (m^2/g)	Structure	Parameters (Å)
0-N[a]	1250	N_2	103.0	103.0	0	2.8	0.51	O[b]	$a = 5.54$, $b = 5.73$, $c = 7.70$
0′-N	1250	N_2	101.1	101.1	0	0.6	0.35		
0-N	1100	N_2	103.0	103.0	0	5.7	0.52		
0-NA	1100	N_2 + air	103.0	103.0	0	9.3	0.39	O	$a = 5.53$, $b = 5.61$, $c = 7.73$
0-A	1250	Air	103.0	103.0	0	28.5	0.26	R[b]	$a = 7.78$, $a_{hex} = 11.05$, $c_{hex} = 13.33$, $\alpha = 90.58$
12.5N	1250	N_2	102.8	90.1	12.7	14.6	0.45	O	$a = 5.52$, $b = 5.57$, $c = 7.73$
12.5A	1250	Air	102.8	90.1	12.7	23.7	0.38	C[b]	$a = 7.76$
25-N	1250	N_2	103.4	77.3	26.1	26.3	0.49	C	$a = 7.74$
25-A	1250	Air	103.4	77.3	26.1	28.9	0.56	C	$a = 7.74$
40′-N	1250	N_2	99.7	60.8	38.9	35.4	0.39		
50-N	1250	N_2	101.7	50.8	50.9	48.3	0.64	C	$a = 7.62$
50-A	1250	Air	101.7	50.8	50.9	48.5	0.78	C	$a = 7.62$
75-A	1250	Air	102.5	25.8	76.7	73.8	0.60	C	$a = 7.54$
88′-A	1250	Air	102.2	51.3	87.0	89.2	0.36		
100-A	1000	Air	102.7	0	102.7	98.1	0.48	C	$a = 7.46$A
100′-A	1000	Air	101.1	0	101.0	103.3	0.62		

[a] The symbols here include the nominal Ca conc + atmosphere (N = N_2; A = air). The prime indicates the second preparation.

[b] O = orthorhombic; R = rhomohedral; C = cubic.

$$2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O,$$

$$2NH_3 + \tfrac{3}{2}O_2 \rightarrow N_2 + 3H_2O,$$

$$2NH_3 + \tfrac{3}{2}O_2 \rightarrow NH_4NO_2 + H_2O,$$

$$[NO] = [NH_4NO_2] = (\Delta O_2 - 2[N_2O] - 1.5[N_2])/1.5.$$

III. RESULTS

a. Catalyst Properties

The properties of the various catalyst samples used in this work are summarized in Table 1. The samples are named according to the nominal number of Ca^{2+} ions/100 Mn ions and the atmosphere present in the high temperature calcination ($N = N_2$ and $A =$ air), e.g., 50-N designates a sample containing 50 ions of Ca^{2+} and 50 ions La^{3+}/100 Mn ions and treated in nitrogen. Catalyst samples were prepared in two series at separate times and the prime (′) designates the second batch.

In Table 1, columns 2 and 3 indicate the temperature and ambient gases present during the final calcination. In samples containing up to 25% Ca^{2+}, the percentage of Mn^{4+} is very sensitive to the presence or absence of oxygen; in the region of 50% Ca^{2+}, air or nitrogen have no effect; and above 50% Ca^{2+}, calcination in pure nitrogen resulted in excessive reduction of the catalyst and complete change in the structure. The calcination temperature was generally 1250°C with the exception of 0-N and 0-NA (air/$N_2 \simeq 1{:}4$) for which 1100°C was used to control the degree of reduction and 100-A which was limited to 1000°C since there was appreciable loss of surface area above this temperature.

Columns 4–7 in Table 1 indicate the composition of the sample as determined by analysis. Expressed as atom % the ratio (Ca + La)/Mn should ideally be 100% for a true perovskite. However, a 2% excess of (Ca + La)/Mn was deliberately introduced to minimize the presence of manganese rich phases. The percentage of Mn^{4+} for samples containing $\leq 30\%$ Ca^{2+} matched closely the percentage of Ca^{2+} when these were pretreated in N_2 and thus calcium stabilized the presence of Mn^{4+}. These same samples calcined in air could be oxidized to reach a nearly common state with 24–29% Mn^{4+}.

TABLE 2
MANGANESE VALENCE BEFORE AND AFTER USE AS CATALYSTS

Sample no.	% Mn^{4+} Before use	% Mn^{4+} After use
0-N	2.5	2.8
0-A	28.5	30.0
75-A	73.8	83.8
100-A	106.0	108.9

The valences of certain sample catalysts were analyzed before and after use in the ammonia oxidation. The results are given in Table 2. The valence is unchanged within the accuracy of the analysis with the exception of 75-A which was oxidized during the reaction. X-Ray analysis also indicates a slight tendency for samples with $\leq 30\%$ Ca^{2+} to oxidize slightly. The fact that sample 100-A gives greater than 100% Mn^{4+} may be experimental error or, since Ca^{2+} is in excess, the presence of Mn^{5+} is not unreasonable. These results show that the bulk of the catalyst is stable throughout the reaction but says very little about the surface composition.

The X-ray analysis (Table 1) indicates

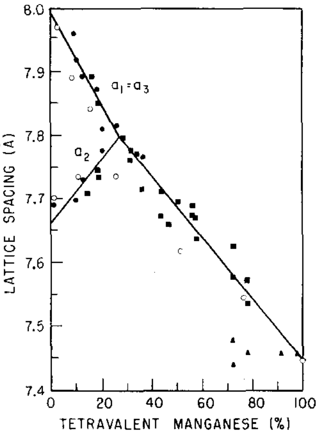

FIG. 2. Room temperature lattice constants for $Ca_xLa_{1-x}MnO_3$ as a function of percentage of Mn^{4+} from X-ray measurements by Yakel (*11*) [$LaMnO_3$ (●), solid solutions (■), and $CaMnO_3$ (▲)] and the present work (○).

TABLE 3

RATES AND SELECTIVITY OF AMMONIA OXIDATION ON LANTHANUM CALCIUM MANGANITES AT 400°C

Sample no.	Mn^{4+}/Mn total (%)	Surface area		μmoles/min		Conversion (%)		Selectivities (%)			Rates (μmoles/m^2/min)
		m^2/g	m^2	ΔNH_3	ΔO_2	NH_3	O_2	N_2O	N_2	NO	
0-N	2.8	0.51	0.099	281	262	28.5	21.6	48.1	43.5	8.4	2840
0-N	2.8	0.51	0.099	273	249	28.2	21.2	50.9	44.4	4.7	2760
0′-N	0.6	0.35	0.07	173	159	17.8	12.9	43.8	48.2	7.9	2470
12.5-N	14.6	0.45	0.137	269	249	27.0	20.3	50.1	43.5	6.4	1960
25-N	26.3	0.49	0.197	231	216	23.4	18.0	54.1	38.8	7.0	1170
40′-N	35.4	0.39	0.078	262	259	26.7	20.9	28.6	49.2	22.2	3360
50-N	48.3	0.64	0.064	235	238	23.7	19.6	17.2	53.4	29.4	3670
75-A	73.8	0.74	0.060	281	284	28.2	23.4	15.6	54.5	29.9	4680
75-A	73.8	0.74	0.060	265	270	26.8	21.8	15.2	53.7	31.1	4420
75-A	73.8	0.60	0.070	340	331	34.5	27.8	17.9	58.2	23.9	4860
88′-A	89.2	0.36	0.076	413	412	42.3	34.8	20.2	53.8	26.0	5430
88′-A	89.2	0.72	0.079	401	426	41.3	34.7	20.8	51.3	27.9	5080
100-A	98.1	0.48	0.102	343	342	34.4	28.1	15.9	56.4	27.8	3360
100′-A	103.3	0.62	0.124	478	482	49.3	39.0	17.1	54.1	28.8	3850
100′-A	103.3	0.62	0.076	347	351	35.3	29.8	16.1	54.6	29.4	4570

TABLE 4

Rates and Selectivities of Ammonia Oxidation on Lanthanum Calcium Manganites at 350°C

Sample no.	Mn^{4+}/Mn total (%)	Surface area		μmoles/min)		Conversion (%)		Selectivities (%)			Rates (μmoles/m^2/min)
		m^2/g	m^2	ΔNH_3	ΔO_2	NH_3	O_2	N_2O	N_2	NO	
0-N	2.8	0.51	0.099	118	107	11.9	8.8	40.0	51.8	8.2	1190
0′-N	0.6	0.35	0.070	62	55	6.4	4.5	37.4	56.3	6.3	890
12.5-N	14.6	0.45	0.137	92	81	9.2	6.6	43.3	53.9	2.8	670
25-N	26.3	0.49	0.197	86	81	8.7	6.7	48.5	41.6	10.0	440
40′-N	35.4	0.39	0.078	88	87	9.0	7.0	32.3	47.0	20.7	1130
50-N	48.3	0.64	0.064	72	74	7.2	6.0	20.4	49.7	29.9	1130
75-A	73.8	0.74	0.060	84	84	8.4	6.0	20.7	52.6	26.6	1400
75-A	73.8	0.74	0.060	81	86	8.2	7.0	17.5	47.7	35.1	1350
75-A	73.8	0.60	0.070	111	106	11.2	8.9	21.5	58.3	20.2	1590
88′-A	89.2	0.36	0.076	158	159	16.1	13.5	23.9	49.6	26.5	2080
88′-A	89.2	0.72	0.079	151	153	15.5	13.0	24.7	48.3	27.0	1910
88′-A	89.2	0.72	0.145	224	225	22.7	18.0	27.9	47.9	24.3	1540
100-A	98.1	0.48	0.102	134	135	13.5	11.1	17.8	54.2	28.0	1310
100′-A	103.3	0.62	0.124	218	222	22.5	18.0	20.4	50.4	29.2	1760
100′-A	103.3	0.62	0.076	151	155	15.3	13.2	18.3	50.8	31.0	2000

that below 25% Mn^{4+} there are small distortions from the true cubic perovskite structure and the parameters for orthorhombic and rhombohedral structures are included. This means that the coordination of O^{2-} ions around a manganese ion is a slightly distorted octahedron. Figure 2 shows published results by Yakel (*11*) as well as results from this work and they are essentially in agreement. A particularly interesting point is that the structure in the range 0–30% Mn^{4+} is a function only of Mn^{4+} and is independent of whether this is introduced by the presence of Ca^{2+} or by an excess of oxygen in the lattice.

b. Ammonia Oxidation

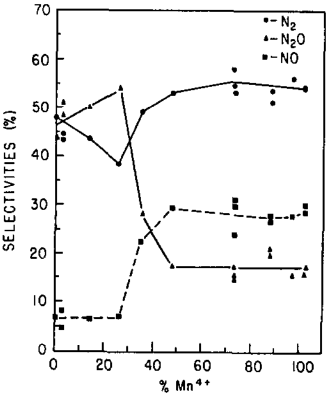

FIG. 4. Product selectivities for ammonia oxidation at 400°C vs percentage of Mn^{4+}.

1. Activity vs composition. The activities of the catalysts were measured by the rates of reaction of a constant feed of ammonia and oxygen in argon. The results at 400 and 350°C are given in Tables 3 and 4, respectively. The amount of catalyst was chosen to obtain around 25% conversion of ammonia and oxygen at 400°C although this varied between 17–49%. The changes in ammonia and oxygen (μmoles per unit time), ΔNH_3 and ΔO_2, are very similar to one another so neither one is limiting the reaction rate. Specific surface areas in column 3 are very small so diffusion limitations should be absent. Total surface areas are given in column 4 and if one assumes that the distribution of crystal faces is similar for all samples, this area is proportional to the number of Mn ions on the surface. The specific rate of change of ammonia based on a unit surface area is thus a useful measurement of the activity of the manganese ions in their respective environments.

Figure 3 indicates the specific rate of reaction of ammonia vs percentage of Mn^{4+} in the catalyst and includes points from different preparations of certain samples to indicate the range of uncertainty for each sample. The specific activities of $LaMnO_3$ and $CaMnO_3$ differ by around 50%. Addition of up to 25% Mn^{4+} reduces the specific activity of $LaMnO_3$; further addition increases it up to a maximum at 88% Mn^{4+}. These differences, while significant, are certainly not as large as one might expect upon proceeding from Mn^{3+} to Mn^{4+}, the total range being a factor of around 5. Also,

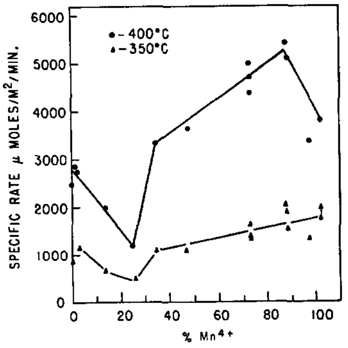

FIG. 3. Specific rates for ammonia oxidation vs percentage of Mn^{4+}.

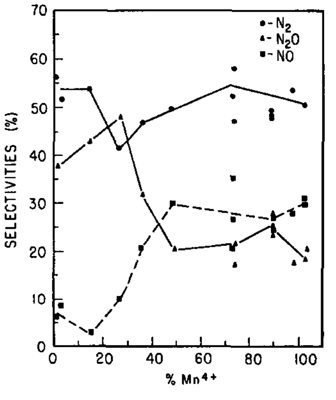

FIG. 5. Product selectivities for ammonia oxidation at 350°C vs percentage of Mn^{4+}.

TABLE 5

THE EFFECT OF EXCESS LATTICE OXYGEN ON SPECIFIC RATES

Sample no.	Mn^{4+}/ total Mn	Surface area (m^2/hr)	Wt (g)	(μmoles/min)		Conversions (%)		Selectivities (%)			Rates (μmole/ m^2/min)
				ΔNH_2	ΔO_2	NH_3	O_2	N_2O	N_2	NO	
400°C											
0-N	2.8	0.51	0.099	281	262	28.5	21.6	48.1	43.5	8.4	2840
0-N	2.8	0.51	0.099	273	249	28.2	21.2	50.9	44.4	4.7	2760
0′-N	0.6	0.35	0.070	173	179	17.9	12.9	43.8	48.2	7.9	2470
0-NA	9.3	0.39	0.101	333	304	33.4	24.9	50.5	44.7	4.8	3300
0-NA	28.5	0.26	0.092	228	209	22.9	17.1	47.3	46.3	6.4	2480
12.5-N	14.6	0.45	0.137	269	249	27.0	20.3	50.1	43.5	6.4	1960
12.5-A	23.7	0.38	0.099	238	220	23.8	17.9	52.3	42.0	5.6	2400
25-N	26.3	0.49	0.197	231	216	23.4	18.0	54.1	38.8	7.0	1170
25-A	28.9	0.59	0.196	312	292	31.5	24.0	33.3	39.8	6.9	1590
350°C											
0-N	2.8	0.51	0.099	118	107	11.9	8.8	40.0	51.8	8.2	1190
0′-N	0.6	0.35	0.070	62	55	6.4	4.5	37.4	56.3	6.3	890
0-NA	9.3	0.39	0.101	134	115	13.4	9.4	42.4	56.8	0.8	1330
0-A	28.5	0.26	0.092	99	84	9.9	6.9	37.7	61.7	0.6	1080
12.5-N	14.6	0.45	0.137	92	81	9.2	6.6	43.3	53.9	2.8	670
12.5-A	23.7	0.38	0.099	104	92	10.4	7.5	40.9	54.3	4.8	1050
25-N	26.3	0.49	0.197	86	81	8.7	6.7	48.5	41.6	10.0	400
25-A	28.9	0.56	0.196	135	122	13.6	10.0	41.7	52.1	6.2	690

there is no gradual uniform change as one proceeds from Mn^{3+} to Mn^{4+}.

2. Selectivity vs composition. The selectivities to N_2, NO, and N_2O, defined as moles of ammonia converted to a particular product over the total converted ammonia, are also given in Tables 3 and 4 and are plotted in Figs. 4 and 5 at 400 and 350°C, respectively. Again there is no gradual change in going from 0–100% Mn^{4+}. Rather, the catalysts are divided into only two types with a small transition region in between. On the La^{3+} rich side of the series (0–25% Mn^{4+}) N_2O is the major product (50–55%), N_2 is slightly less (39–48%), and NO is much smaller (5–8%). On the Ca^{2+} rich side (50–100% Mn^{4+}) N_2 is still a major product (51–58%), NO is now second (24–31%), and N_2O is much less than before (15–21%). The point at 40% Mn^{4+} is merely intermediate between these two extremes. While there is some scatter in the data, particularly at 350°C where conversions are lower, the data indicate very little change throughout these two regions. It should again be noted that what is designated as NO was not detected as such but was calculated as NH_4NO_2 from the oxygen balance. It was readily apparent, however, that NH_4NO_2 coated the product lines only when Ca^{2+} rich catalysts were used. The low value of NO on the La^{3+} rich side is almost within the experimental uncertainty. This marked difference in product distribution shows that two completely different sites are present in the two regions which do not correlate simply with either Mn^{3+} or Mn^{4+}.

3. Effect of excess lattice oxygen. Up to 29% Mn^{4+} can be introduced into stoichiometric $LaMnO_3$ with very little structural change simply by adding oxygen to the lattice at high temperatures and this must be accompanied by cation vacancies. This property makes possible a comparison in catalytic activity between catalysts with the same concentration of Mn^{4+} but having either Ca^{2+} or cation vacancies as compensation. As Table 5 shows, selectivities in this range are typical of the 0–30% Mn^{4+} region, i.e., high N_2O and low NO selectivities. Thus, cation vacancies have no effect on selectivity. Specific activities do vary as shown in Fig. 6. Considering first the oxidized $LaMnO_3$, the presence of excess oxygen has only very little effect on activity although there is a slight maximum at 9–10% Mn^{4+}. Samples compensated with Ca^{2+} with no cation vacancies experience a steady but small drop in specific activity. Oxidation of these same samples brings the activity up towards that of the Ca^{2+} free samples although for 25 N this is not completely recovered. Thus Mn^{4+} compensated by Ca^{2+} is slightly less active than a similar level of Mn^{4+} compensated by cation vacancies but the effects are not very large.

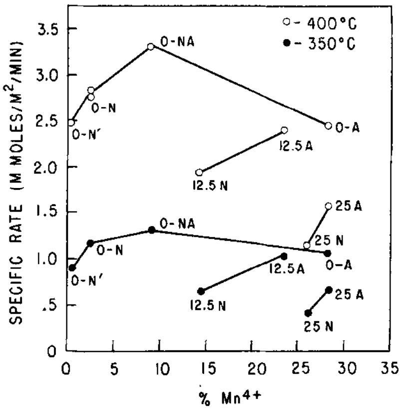

FIG. 6. Catalyst activity for ammonia oxidation as a function of percentage of Mn^{4+} compensated by Ca^{2+} or by excess oxygen.

4. Selectivity vs conversion. Although conditions were chosen to achieve a constant conversion level for all samples, results indicated that selectivity was nearly independent of conversion level. Table 6 contains two types of evidence. One of these involves decreasing the feed rate, i.e., increasing the residence time, to increase the conversion on a given sample. A second method was to vary the catalyst sample size. In this case even at 49.3% conversion the selectivities are not changed. Therefore, the small differences in conversion between points in Tables 3, 4 and 6 would not influence the selectivity. It has often been observed elsewhere that selectivity is sensitive to flow rates at high conversion levels and that secondary reactions are important (*12*).

TABLE 6
THE EFFECT OF CONVERSION ON SELECTIVITY

Sample no.	Relative residence times	Sample wt (g)	Conversion (%)		Selectivities (%)		
			NH_3	O_2	N_2O	N_2	NO
Varying residence times (350°C)							
0-N	1	0.195	11.2	7.8	43.2	56.3	.5
	1	0.195	11.9	8.8	40.0	51.8	8.2
	1.42	0.195	15.2	11.2	40.9	52.1	7.0
	2.16	0.195	19.5	14.2	42.6	52.4	5.0
100-A	1	0.212	13.4	10.9	18.1	54.4	27.5
	1	0.212	13.5	11.1	17.8	54.2	28.0
	1.42	0.212	17.9	14.6	18.8	54.0	27.2
	2.16	0.212	21.0	16.9	20.7	54.9	24.5
Varying sample size							
(400°C) 100-A′	1.0	0.122	35.3	29.8	16.1	54.1	29.4
100-A′	1.6	0.200	49.3	39.0	17.1	54.6	28.8
(350°C) 100-A′	1.0	0.122	15.3	13.2	18.3	50.8	31.0
100-A′	1.6	0.200	22.5	18.0	20.4	50.4	29.2

5. Effect of products. The additions of 6% N_2O to the normal feed over $LaMnO_3$ had no detectable effect on the catalyst and N_2O did not appear to react. The observed conversion of N_2O alone over the same catalyst at 400°C in the absence of O_2 and NH_3 was only 2.3%, so N_2O will appear as it is formed with almost no loss. A similar addition to $CaMnO_3$ caused an immediate and permanent deactivation of the catalyst. The amount of N_2O produced normally at 400°C over $CaMnO_3$ is only 10% of this level but it may account for the slow deactivation of $CaMnO_3$. Again, N_2O decomposes very little on $CaMnO_3$.

The effect of NO on the catalyst was difficult to determine because it reacts rapidly with ammonia and oxygen to form N_2 even in the absence of catalyst. When 1% NO was added to a stream of NH_3 (12.5%), O_2 (15.5%) and Ar (71%) over a Vycor filled reactor at 120°C, the conversion of NO to N_2 was virtually quantitative with trace amounts of NH_4NO_2 dropping out on the walls. Nitric oxide also reacted with O_2 in the lines to the extent of 88% conversion in the absence of NH_3 to form NO_2. Thus, if NO were formed in a surface catalyzed reaction, it would react further with ammonia and oxygen in a post-catalyst zone to form some N_2 or drop out as NH_4NO_2 depending on the temperature profile of the reactor and the moisture level. Even though NH_4NO_2 seemed to drop out rather efficiently from a product stream, no doubt some of the N_2 was produced from these reactions and the yield of NO is not quantitative. This does not seriously impair the interpretation of results.

IV. DISCUSSION

a. Catalytic properties of Mn^{3+} and Mn^{4+}. A comparison of the catalysts $LaMnO_3$ and $CaMnO_3$ demonstrates the catalytic activities of Mn^{3+} and Mn^{4+} in concentrated form. The validity of this is based on the assumption that La^{3+} and Ca^{2+} are inert ions, which seems reasonable since La_2O_3 and CaO are not nearly as active oxidation catalysts as Mn_2O_3 or MnO_2. In these model catalysts, the manganese ions are situated as octahedral O^{2-} complexes which have very nearly the same dimensions and are present in compounds which are stable under the reaction conditions. The use of Mn_2O_3 or MnO_2 for such a comparison would not be desirable because these are readily oxidized or reduced and may produce a surface of completely different composition and structure. For example, results by Krauss and Neuhaus (*13*) indicate that both Mn_2O_3 and MnO_2 give around 60%

N_2O with the remainder N_2, very similar to the present results on $LaMnO_3$.

The results of this study indicate that Mn^{3+} is not very much different from Mn^{4+} in reactivity. This is different from the results of Cimino and Indovina (*4*) who found that highly diluted Mn^{3+} in MgO is more reactive than Mn^{4+} for N_2O decomposition. There is no reason to assume that at high concentration Mn^{3+} and Mn^{4+} would have this same relationship. However, $LaMnO_3$ does give a product distribution significantly different from that of $CaMnO_3$. This may very well be due to differences between Mn^{3+} and Mn^{4+} since the surface complexes of either O_2 or NH_3 would be energetically different for the two ions.

b. Catalytic properties of mixtures of Mn^{3+} and Mn^{4+}. In the system $Ca_xLa_{1-x}MnO_3$ it is possible within narrow limits to obtain all mixtures of Mn^{3+} and Mn^{4+} in nearly identical environments. If certain activities were associated with Mn^{3+} and Mn^{4+} as individual complexes, one might expect a smooth change in catalytic behavior as Mn^{3+} decreases and Mn^{4+} increases. The results show that this is obviously not the case. The addition of as much as 30% Mn^{4+} to $LaMnO_3$ either by oxidation or by introducing Ca^{2+} produced little or no change in activity and no detectable change in selectivity. Likewise, addition of even 50% Mn^{3+} into $CaMnO_3$ gives very little if any change in the activity or selectivity. The conclusion must be that the essential nature of the surface does not change within these regions.

c. $[Ca^{2+}]$ vs cation vacancies as catalyst promoters. It was surprising to observe that the excess oxygen taken up by $LaMnO_3$ causes no increase in activity. Such a process might be represented by the following equation (*14*)

$$\tfrac{3}{2}(O_2)_g \rightarrow 3O_O + V_{Mn}''' + V_{La}''' + 6h,$$

$$Mn_{Mn}{}^{4+} \equiv h \equiv 6(V_{Mn}''') \equiv 6(V_{La}'''),$$

where

V_{La}''' = a La^{3+} vacancy and V_{Mn}''' = a Mn^{3+} vacancy.

The oxygen associated with these vacancies might be expected to be more active than normal lattice oxygen. Krauss and Neuhaus (*13, 15*) have clearly shown that for oxides such as MnO, NiO, and CoO which rapidly pick up excess oxygen from the feed, the selectivity to N_2O is directly proportional to this excess lattice oxygen. In the case of $LaMnO_3$, this excess oxygen is incorporated only at high temperatures and not from the feed at 400°C to any degree. This oxygen is not very reactive. The proposed vacancies at the 0–4% level do not affect the surface processes. When Ca^{2+} is present, the activity is slightly reduced from that of a similar catalyst without Ca^{2+} at the same level of Mn^{4+} and the activity increases with oxidation. These differences may have to do with the distribution of Ca^{2+} or Mn^{4+} ions on the surface.

d. Ammonia oxidation. The oxidation of ammonia was chosen primarily to indicate catalytic behavior of the model catalysts. It is obviously a complicated reaction and it was not the purpose of this study to probe this reaction. However, the reaction has been studied rather extensively on a variety of catalysts, and the mechanism may give some indication of the nature of the two types of surface. Most of the literature before 1950 was reviewed in a paper by Zawadski (*12*) in which he proposed the mechanism shown below involving the formation of absorbed imide ions.

Initial reaction step:

$$NH_3 + O \rightarrow NH + H_2O. \tag{1}$$

Reactions leading to N_2O:

$$NH + O \rightarrow HNO, \tag{2}$$

$$2HNO \rightarrow N_2O + H_2O. \tag{3}$$

Reactions leading to NO:

$$NH + O_2 \rightarrow HNO_2, \tag{4}$$

$$HNO_2 \rightarrow NO + OH, \tag{5}$$

$$2OH \rightarrow H_2O + O. \tag{6}$$

Reactions leading to N_2:

$$NH + NH \rightarrow N_2 + H_2, \tag{7}$$

$$NH + NH_3 \rightarrow N_2H_4 \rightarrow \text{decomp}, \tag{8}$$

$$NH + HNO \rightarrow N_2 + H_2O, \tag{9}$$

$$NH_3 + HNO_2 \rightarrow N_2 + 2H_2O. \tag{10}$$

Although certain features such as the presence of NH as an intermediate are controversial, there seems to be good agreement that N_2O results from an atomic form of adsorbed oxygen. By "atomic" oxygen is meant adsorbed or lattice oxygen atoms which very likely are partially charged but are nevertheless very reactive. Examples of this are the work of Krauss and Neuhaus cited above on excess oxygen in MnO and also their observation that ammonia reacts directly with MnO_2 to give the same products as NH_3 and gaseous O_2 in the presence of MnO_2. If the atomic oxygen is sufficiently concentrated, almost 100% yields of N_2O can be obtained; at lower levels the NH can react further to form N_2 as well.

Nitric oxide results from a molecular form of oxygen, either adsorbed or gaseous, although the evidence for this is not direct. Oxygen atoms generated from its formation can contribute to N_2O formation, and of course N_2 is a possible product.

From this mechanism one can conclude that the lanthanum rich region of catalysts have a high concentration of atomic oxygen on their surfaces and this concentration is fairly constant throughout the region. This can be visualized either as adsorption of oxygen atoms on Mn^{3+} ions or capture of free electrons by oxygen; however, the sites for this adsorption are not limited to surface Mn^{3+} but involve oxidation of bulk Mn^{3+} as well.

In the calcium rich region the surface may act as an electron acceptor rather than donor. This means that oxygen would not be adsorbed as atoms and that the lattice oxygen associated with Mn^{4+} is not reactive. Under these conditions ammonia would absorb as a donor which would weaken the N–H bond and allow it to react with molecular oxygen, either gaseous or adsorbed, to generate NO. According to the mechanism, NO will produce atomic oxygen (step 6) to account for the observed N_2O. The selectivities in this region are similar to those reported by Zawadski (*12*) on Pt gauze at the same temperature and flows. Results by Krauss and Neuhaus (*13*) show that 15% K_2O added to MnO_2 changed the selectivity at 350°C from 60% N_2O for the pure MnO_2 to 60% NO. The effect of K_2O in this case is similar to that of Ca^{2+}, namely converting the labile oxygen of MnO_2 to the more stable oxygen present in a potassium manganite.

The possibility exists that certain ions are favored on the surface by the treatment at high temperatures. For example, Mn^{4+} and Ca^{2+} might be preferred on the surface by an oxidizing atmosphere and Mn^{3+} and La^{3+} might be preferred by a reducing or neutral atmosphere. While this cannot be completely ruled out, it is true that the high temperatures used would favor a random distribution. Experimentally, the evidence is that sample 50-N treated in nitrogen gave the same products as 75-A and 100-A treated in air, and likewise samples with 0–30 Ca^{3+} calcined in air or in nitrogen gave the sample products.

It is of interest to note that electrical conductivity and magnetic susceptibility, which are also sensitive to Mn^{3+}–Mn^{4+} interaction, also divide this series into two parts (*10, 16*). From 0 to 50% Mn^{4+} the series is ferromagnetic with a maximum saturation magnetization at around 30% Mn^{4+} and electrical conductivity reaches a maximum also at around 30% Mn^{4+}. From 50 to 100% Mn^{4+} the system is antiferromagnetic and the conductivity is constant and low. Although this does not directly correlate with catalytic properties, the similarity is striking and there may be a real relationship. It would be particularly useful to know the conductivity type in the two regions.

SUMMARY

In the system $Ca_xLa_{1-x}MnO_3$, Mn^{3+} and Mn^{4+} do not behave as isolated sites for catalysis in the oxidation of ammonia. Although coordination on an atomic scale may occur, electronic properties of the whole group of ions define the nature of the adsorbed species. Thus, this series is divided into only two types of catalyst rather than a whole series of gradually changing catalysts. It is therefore not meaningful to consider the activity of Mn^{3+} vs Mn^{4+} but rather one must consider the properties of Mn^{3+} rich or Mn^{4+} rich mate-

rial. Mixed perovskites of many other transition metals exist and may be useful for examining more complex interactions of transition metal ions in a well-characterized form.

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