Rare-Earth Manganites: Catalysts with Low Ammonia Yield in the Reduction of Nitrogen Oxides

Abstract. *Rare-earth manganites such as $La_{1-x}Pb_xMnO_3$, with $0.3 < x < 0.6$, and their perovskite-like homologs are active catalysts for the reduction of nitric oxide to molecular nitrogen. At low temperatures, innocuous nitrous oxide rather than ammonia is the main side product. The activity of single crystalline catalysts and of ceramic catalysts of this type is substantially improved by etching with dilute acids.*

In laboratory tests we have found that rare-earth (RE) manganites are active catalysts for the reduction of NO in concentrated mixtures of NO, CO, H_2, and H_2O. Even though we believe that our results are relevant to the problem of auto exhausts, we stress that tests on automobiles are needed to provide proof of the usefulness of these manganites for that application.

In order that the exhaust emissions of automobiles for the model year 1976 meet federal standards (*1*) for CO, hydrocarbons, and NO and NO_2 (NO_x) concentrations, a complex system consisting of a device for the recirculation of exhaust gas and a two-stage catalytic converter (CAT I and CAT II) is envisaged (*2*). In CAT I, NO_x will be reduced by CO and H_2 derived from the exhaust gas (*3*). In CAT II, CO and hydrocarbons will be oxidized with air to CO_2 and H_2O. Perovskites, exemplified by $La_{1-x}Pb_xMnO_3$ and $PrCoO_3$, have been considered as catalysts in CAT II because (i) in the oxidation of CO they show activities and lifetimes similar to those of Pt (*4*), (ii) they can be prepared at lower cost than Pt catalysts (*5*), and (iii) they are characterized by chemical and thermal stability. The major problem, however, in the new system concerns the catalyst to be used in CAT I, since the NO_x is predominantly reduced to NH_3 on presently known catalysts such as Cu-Ni and Pt-Ni alloys and various mixtures of Cu, Cr, Co, and Mn oxides, especially at lower temperatures (*3, 6, 7*). The subsequent oxidation of NH_3 in CAT II produces unacceptable NO_x concentrations in the treated exhaust.

We have tested the catalytic activity of the manganites $La_{1-x}Pb_xMnO_3$, with $0.3 < x < 0.6$, and homologs in which Pr, Nd, Ca, Sr, or Ba replaces part or all of the La and Pb. Before discussing the results of these tests, we present in the next three paragraphs the preparative procedures for the catalysts.

Single crystals of $RE_{1-x}Pb_xMnO_3$ (catalysts A, B, C, K, M, and N in Tables 1 to 3) were grown from a lead borate flux. In a typical preparation 13.04 g of La_2O_3, 9.48 g of Mn_2O_3, 12.00 g of B_2O_3, and 160.00 g of PbO were weighed into a 100-cm^3 Pt crucible with cover. The homogeneous melt obtained after the mixture had been heated in air for 4 hours at 1250°C was cooled to below 500°C at a rate of 3°C per hour or less. At room temperature, the $La_{1-x}Pb_xMnO_3$ crystals were removed from the flux with aqueous acetic acid (CH_3COOH) (1 : 8) and rinsed with hot distilled water. Crystals of $Pr_{1-x}Pb_xMnO_3$ or $Nd_{1-x}Pb_xMnO_3$ were prepared similarly. Chemical analysis showed that $x \approx 0.3$ (*8*). The ground crystals were etched for 2 to 5 minutes in hot (> 80°C) 20 percent HNO_3. The rate of dissolution of the catalyst in acid was slow, but it increased in the order $CH_3COOH < HNO_3 < HCl$. During etching, brown colloidal $MnO_{1.88}$ was sometimes precipitated but was carefully removed by rinsing.

It was possible to prepare $La_{0.5}Pb_{0.5}MnO_3$ with high surface area and a well-developed single-phase perovskite pattern by rapidly precipitating the hydroxides from an aqueous solution of the nitrates or acetates with an organic base, and then drying the precipitate and firing it in air or O_2 to 590°C (catalyst F). Catalysts D and E, fired at 400° and 500°C, respectively, still contain some unreacted material. Catalyst Q was similar to catalyst D, except that catalyst Q was etched for 10 minutes in 5 percent HNO_3 at 50°C. Catalysts G, L, and P, with surface areas S of 1 to 3 m^2/g, were prepared by decomposing intimate mixtures of acetates or carbonates, firing up to 1000°C with occasional remixing, and etching in 5 percent HNO_3 at 65°C for 5 minutes. X-ray diffraction measurements of these catalysts showed only one perovskite phase, with faint lines of impurities, presumably unreacted oxides.

We obtained supported $La_{0.5}Pb_{0.5}MnO_3$ by preparing the perovskite

Table 1. Reduction of NO with CO and H_2 over oxide and Ru catalysts.

Test No.	Catalyst*	S† (m^2/g)	Weight of catalyst (g)	Inlet gas mixture; NO-CO-H_2-He (ml/min)	Temperature (°C)	Conversion of NO (%)	Distribution of inlet nitrogen over products (%)		
							N_2	N_2O	NH_3
				Single crystals					
1	$La_{1-x}Pb_xMnO_3$ (A)	1.0	3.0	17-0-40-0	375	100	66	34	
2	$La_{1-x}Pb_xMnO_3$ (A)	1.0	3.0	9-8-22-0	375	100	100		
3	$La_{1-x}Pb_xMnO_3$ (B)	1.0	3.6	8-8-18-0	375	100	98		2
4	$Nd_{1-x}Pb_xMnO_3$ (C)	~1.0	3.7	8-8-18-100	360	100	54	46	
				Sintered oxides					
5	$La_{0.5}Pb_{0.5}MnO_3$ (D)	8.6	0.87	8-8-18-0	265	80	75		~5
6	$La_{0.5}Pb_{0.5}MnO_3$ (E)	7.0	1.16	8-8-18-0	250	72	2	70	
7	$La_{0.5}Pb_{0.5}MnO_3$ (F)	18	1.05	8-8-18-0	300	100	80	15	~5
8	$La_{0.5}Pb_{0.5}MnO_3$ (F)	18	1.05	8-8-18-0	350	100	67		33
9	$La_{0.7}Sr_{0.3}MnO_3$ (G)	2.5	0.65	8-8-18-0	375	100	88		12
10	$La_{0.7}Sr_{0.3}MnO_3$ (G)	2.5	0.65	8-8-18-0	450	100	74		26
				Ruthenium sponge‡					
11	Ru (H)	~0.5	1.34	8-8-18-0	230	100	52	13	35
12	Ru (H)	~0.5	1.34	8-8-18-0	300	100	50	2	48
13	Ru (H)	~0.5	1.34	8-8-18-0	375	100	50		50

* The atomic fraction x in the crushed single crystal catalysts may vary between 0.3 and 0.6. It is close to 0.3 in the examples presented here. Capital letters in parentheses indicate the various preparations (see text). † The specific surface area was determined with a Shell/Perkin-Elmer Sorptionmeter. For the single crystal catalysts a geometric surface area of 0.03 m^2/g was calculated. ‡ Included for comparison. The metal was mixed with quartz powder.

Table 2. Reduction of NO with CO over oxide catalysts.

Test No.	Catalyst*	S† (m^2/g)	Weight of catalyst (g)	Inlet gas mixture; NO-CO-He-H_2O (ml/min)	Temperature (°C)	Conversion of NO (%)	Distribution of inlet nitrogen over products (%)		
							N_2	N_2O	NH_3
				Single crystals					
14	$La_{1-x}Pb_xMnO_3$ (A)	1.0	3.0	17-17-0-0	260	81	4	77	
15	$La_{1-x}Pb_xMnO_3$ (A)	1.0	3.0	17-17-0-0	300	100	20	80	
16	$La_{1-x}Pb_xMnO_3$ (A)	1.0	3.0	17-17-0-0	350	100	66	34	
17	$La_{1-x}Pb_xMnO_3$ (B)	~1.0	3.6	17-17-0-0	280	83	12	71	
18	$La_{1-x}Pb_xMnO_3$ (K)	~1.0	3.8	17-17-0-0	375	78	21	57	
19	$La_{1-x}Pb_xMnO_3$ (K)	~1.0	3.8	17-17-34-1	375	90	48	42	‡
20	$Nd_{1-x}Pb_xMnO_3$ (C)	~1.0	3.7	8-8-120-0	375	72	28	44	
21	$Nd_{1-x}Pb_xMnO_3$ (C)	~1.0	3.7	8-8-120-3	375	90	65	25	‡
				Sintered oxides					
22	$La_{0.5}Pb_{0.5}MnO_3$ (D)	8.6	0.87	17-17-0-0	250	100	100		
23	$La_{0.7}Ba_{0.3}MnO_3$ (L)	2.2	0.77	17-17-100-0	375	87	65	22	
24	$La_{0.7}Sr_{0.3}MnO_3$ (G)	2.5	0.65	17-17-0-0	200	100	78	22	

* The atomic fraction x in the crushed single crystal catalysts may vary between 0.3 and 0.6. It is close to 0.3 in the examples presented here. Capital letters in parentheses indicate the various preparations (see text). † The specific surface area was determined with a Shell/Perkin-Elmer Sorptionmeter. For the single crystal catalysts a geometric surface area of 0.03 m^2/g was calculated. ‡ The amount of NH_3 formed was too small to analyze.

powder at 575°C and applying it as a slurry to a ceramic honeycomb (*9*), drying and firing at 550°C for several hours (catalyst R). We prepared catalyst S by the same procedure, using a reaction temperature of 1000°C and a firing temperature of 800°C and then etching in 5 percent HNO_3 for 5 minutes at 65°C. The Ru sponge catalyst (catalyst H) was used as received (*10*).

We used a continuous flow system with catalyst charges of approximately 2 cm^3 (*4*). The effluents were analyzed by gas chromatography. We determined NH_3 concentrations from an analysis of the N_2, N_2O, and NO concentrations in the measured inlet and exit flows and, concurrently, by collecting NH_3 as solid $(NH_4)_2CO_3$.

Crushed single crystals or ceramic preparations of the manganites were active for the reduction of NO to N_2 (Tables 1 and 2). Tests in which the gas feed included H_2 or H_2O provided data on the formation of NH_3. An essentially complete reduction of NO to innocuous N_2 and N_2O was obtained. Between 200° and 375°C less than 10 percent of the converted NO yielded NH_3 on most of these catalysts, and even at 450°C only about 25 percent of the NO was reduced to NH_3. This result compares favorably with the reduction of NO on Ru (Table 1) (*7, 11*). We found that the manganites are considerably more active for the reduction of NO than $PrCoO_3$, $PrFeO_3$, and $SmCrO_3$.

The reduction of NO in auto exhaust may occur by reaction with CO or H_2 (*3*). On $La_{1-x}Pb_xMnO_3$, NO is reduced by CO and H_2 (see test 1 in Table 1 and test 16 in Table 2); H_2 and especially mixtures of CO and H_2 are more effective, yielding close to complete conversion of NO to N_2 (tests 2 and 3 in Table 1). In a mixture with CO and H_2, most of the NO is reduced by CO on these catalysts; for example, in test 2 (Table 1) more than 75 percent of the NO was reduced by CO. We observed that the manganites are not very active in the water gas shift reaction. At lower temperatures, N_2O rather than NH_3 is a side product in the NO reduction for all NO conversions. We tentatively conclude that NH_3 is not an intermediate product in the NO reduction over these catalysts. This means that the selectivity toward N_2 and N_2O is an intrinsic property of the perovskites in the temperature range studied. Crushed and etched single crystals were particularly selective. Catalysts prepared by ceramic techniques yielded more NH_3 than crushed and etched single crystals, especially at higher temperatures (tests 8 and 10 in Table 1).

The effect of H_2O on the reaction between CO and NO is to enhance the reaction rate (compare tests 18 and 19 or 20 and 21 in Table 2). With H_2O present, there is also a shift from N_2O to N_2, and some NH_3 was detected. The N_2O produced is not expected to be a problem in exhaust treatment; N_2O is not included in the federal NO_x standards. Indeed, it is a nontoxic and rather common component of the atmosphere (*12*) and decomposes much more readily than NO. Above 400°C, N_2O decomposes into N_2 and O_2 on a $La_{1-x}Pb_x$-MnO_3 catalyst, even in the presence of an excess of O_2. These conditions are easily met in CAT II.

We tested the stability of several catalysts in a reducing mixture consisting of 10 percent H_2, 10 percent CO_2, and 80 percent N_2 by thermogravimetry. At a heating rate of 10°C per minute, $LaCoO_3$ had lost 25 percent of its oxygen after reaching a temperature of 575°C. The manganites are more stable,

Table 3. Activity of etched oxidation catalysts for the test reaction $CO + \frac{1}{2} O_2 \rightarrow CO_2$. Flow rate: 33 ml/min of a stoichiometric mixture at normal temperature and pressure.

Test No.	Catalyst*	S† (m^2/g)	Weight of catalyst (g)	Temperature (°C) for CO conversion‡ of		
				5%	10%	20%
	Single crystals					
25	$La_{1-x}Pb_xMnO_3$ (B)	1.0	3.6	135	150	
26	$La_{1-x}Pb_xMnO_3$ (M)	~1.0	3.4	110	125	150
27	$Nd_{1-x}Pb_xMnO_3$ (N)	~1.0	3.8		130	
	Sintered oxides					
28	$La_{0.5}Pb_{0.5}MnO_3$ (P)	1.0	1.7	160	180	
29	$La_{0.5}Pb_{0.5}MnO_3$ (Q)	31	0.60	97		
30	$La_{0.7}Ba_{0.3}MnO_3$ (L)	2.2	0.77	118		
31	$La_{0.7}Sr_{0.3}MnO_3$ (G)	2.5	0.65	115	130	
	Catalyst supported on cordierite					
32	$La_{0.5}Pb_{0.5}MnO_3$ (R)§	2.4	3.4	125	150	190
33	$La_{0.5}Pb_{0.5}MnO_3$ (S)§	0.6	3.6		200	215

* The atomic fraction x in the crushed single crystal catalysts may vary between 0.3 and 0.6. It is close to 0.3 in the example presented here. Capital letters in parentheses indicate the various preparations (see text). † The specific surface area was determined with a Shell/Perkin-Elmer Sorptionmeter. For the single crystal catalysts a geometric surface area of 0.03 m^2/g was calculated. ‡ Normalized at a charge of 3.0 g of catalyst for the single crystal catalysts, but not normalized for the others. § The supported catalyst contained 19 percent active material.

with a 25 percent oxygen loss at 690°C for $La_{1-x}Pb_xMnO_3$ and at 740°C for $Nd_{1-x}Pb_xMnO_3$ (*13*). These compounds are expected to be rather stable under the appreciably less reducing exhaust conditions in CAT I.

In earlier tests we obtained data on the efficacy of crushed single crystals of RE manganites in the oxidation of CO (*4*). Their activity was substantially improved by etching with dilute acids (tests 25 through 27 in Table 3). Conversions of 10 percent CO were reached at temperatures at least 50°C lower than those reported for unetched catalysts (*4, 14*). The activities of crushed single crystals of $La_{1-x}Pb_xMnO_3$ and $Nd_{1-x}Pb_xMnO_3$ ($x \simeq 0.3$) were not affected by the addition of 2 percent H_2O in tests in which mixtures of 16 percent CO and 8 percent O_2 in He were reacted at a space velocity of 8000 cm^3 of gas per hour per cubic centimeter of catalyst volume. We have also prepared very active catalysts by ceramic methods amenable to large-scale production (tests 28 through 33 in Table 3).

The conditions of our tests differ substantially from auto exhaust conditions in both concentration and space velocities. Our tests constitute only a preliminary evaluation of these catalysts for application in auto exhaust systems. The results of these and of a variety of other tests have led us to submit test samples of $La_{1-x}Pb_xMnO_3$ to several automotive companies. We suggest that the RE manganites should be evaluated as promising catalysts for the reduction of nitrogen oxides in auto exhaust, on the basis of (i) their low yield of NH_3, (ii) their good activity in the reduction of NO at relatively low temperatures, (iii) their stability under reducing as well as oxidizing conditions, and (iv) the fact that they have some measure of tolerance to lead (*4*). In fact, it seems feasible to develop these catalysts for use in the reducing as well as the oxidizing stages of catalytic exhaust converters.

R. J. H. VOORHOEVE
J. P. REMEIKA, D. W. JOHNSON, JR.
Bell Laboratories,
Murray Hill, New Jersey 07974

References and Notes

1. Clean Air Amendments of 1970, Public Law 91-604, section 6.
2. Committee on Motor Vehicle Emissions of the National Academy of Sciences, Semiannual Report to the Environmental Protection Agency (1 January 1972).
3. In the water gas shift reaction, H_2 is formed from H_2O and CO. See: J. H. Jones, J. T. Kummer, K. Otto, M. Shelef, E. E. Weaver, *Environ. Sci. Technol.* **5**, 790 (1971); R. L. Klimisch and G. J. Barnes, *ibid.* **6**, 543 (1972).
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5. D. B. Meadowcraft, *Nature* **226**, 847 (1970).
6. R. A. Baker and R. C. Doerr, *Ind. Eng. Chem. Process Des. Develop.* **4**, 188 (1965); M. Shelef and H. S. Gandhi, *Ind. Eng. Chem. Prod. Res. Develop.* **11**, 2 (1972).
7. R. L. Klimisch, paper presented at the 22nd Canadian Chemical Engineering Conference, Toronto, 17–20 September 1972.
8. This analysis was conducted by Ledoux and Co., Teaneck, N.J.
9. These honeycombs were corrugated structures (2.5 cm in diameter, 7.6 cm long) manufactured by the American Lava Corp.
10. The metal (99.999 percent pure) was obtained from United Mineral and Chemical Corp.
11. The results for Ru in Table 1 are similar to those obtained by Klimisch [see (*7*)] and by Shelef and Gandhi [M. Shelef and H. S. Gandhi, *Ind. Eng. Chem. Prod. Res. Develop.* **11**, 393 (1972), figure 2] for much more dilute mixtures of CO, NO, and H_2 at 230° to 375°C. If real exhaust is used, the results for Ru catalysts are generally much better; Ru is presently a favorite choice for CAT I, even its lifetime is reported to be limited [for example, see (*7*)]. We have no data that permit a comparison of Ru and the RE manganites under exhaust conditions.
12. Y. Henderson and H. W. Haggard, *Noxious Gases and the Principles of Respiration Influencing Their Action* (Reinhold, New York, 1943), pp. 99, 135, 149; M. Nicolet, in *Physics of the Upper Atmosphere*, J. A. Ratcliff, Ed. (Academic Press, New York, 1960), p. 27.
13. The extent to which these perovskite-like compounds can be reduced before they will decompose to form CoO, MnO, La_2O_3, and so on, is not known.
14. The possibility of etching these catalysts for the purpose of activating them is of interest also because such etching would remove lead deposits from a catalyst that had been used in an auto exhaust converter.
15. We thank L. E. Trimble for carrying out most of the tests reported here; P. K. Gallagher for discussions and for providing several precipitated oxides; M. Robbins for samples of $La_{0.8}Pb_{0.2}MnO_3$ with high surface area; Mrs. A. S. Cooper for x-ray analysis of several products; T. Y. Kometani for chemical analyses; F. Schrey for measuring the specific surface areas of the catalysts; and P. E. Freeland, D. J. Nitti, and J. J. Darold for assistance in the preparation and testing of catalysts. We also thank B. T. Matthias for supplying the initial impetus for this project and for his continuing interest and encouragement.

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Crystallographic Orientation of Clinoenstatite Produced by Deformation of Orthoenstatite

Abstract. *Uniaxial compression at 800°C and 5 kilobars confining pressure of a specimen cored from a single crystal of orthoenstatite [(Mg,Fe)SiO_3] produced fine lamellae 100 to 1000 angstroms thick of untwinned clinoenstatite. The two phases are joined along (100) planes and have* b *and* c *axes in common. The orientation of the clinoenstatite* a *axis contradicts several previously suggested transformation mechanisms and reduces the set of possible mechanisms by a factor of 2.*

The transformation of enstatite ($MgSiO_3$) from the orthorhombic to the monoclinic polymorph is dramatically promoted by shear stress on (100) planes parallel to the [001] direction (*1*, *2*) but is only slightly promoted by hydrostatic pressure (*3*). A thermodynamic explanation of this effect has been given by Coe (*4*); it involves the assumption that the transition is macroscopically characterized by a reversible transformation strain of finite simple shear on (100) parallel to [001] through a well-defined angle. The actual displacement of atoms need not conform to simple shear in order to achieve the macroscopic deformation, but the movements of atoms must be coherent and long-range diffusion must be slow compared to the time required to accomplish the transformation. Metallurgists call such trans-

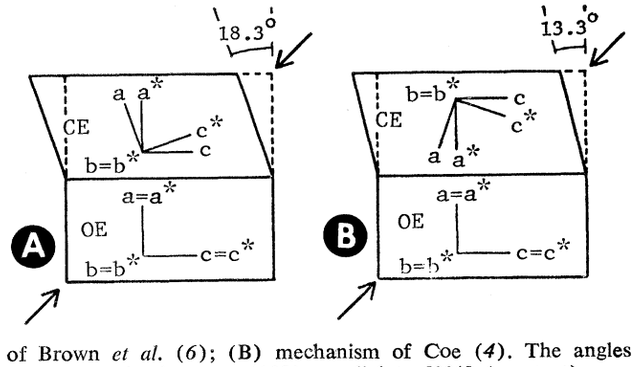

Fig. 1. Geometries for two mechanisms proposed for the transformation of part of a macroscopic piece of orthoenstatite (OE) to clinoenstatite (CE), showing the relation between the compression direction (arrows) and the direct (*a, b, c*) or reciprocal (*a*, b*, c**) crystallographic axes. (A) Mechanism of Brown *et al.* (*6*); (B) mechanism of Coe (*4*). The angles shown are the angles of macroscopic shear on (100) parallel to [001] (see text).