

THE REDUCTION OF ALKALI SUBSTITUTED LaMnO_3

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ABSTRACT

In order to determine the stability of some potential NO_x reduction catalysts ($\text{La}_{0.8}\text{M}_{0.2}\text{MnO}_3$, $\text{M} = \text{Na}, \text{K}, \text{Rb}$) the accelerated reduction of these catalysts in H_2 , N_2 atmospheres was studied. $\text{La}_{0.8}\text{K}_{0.2}\text{MnO}_3$ goes through a reversible oxygen loss at about 350°C corresponding to the reduction of the available Mn^{4+} to Mn^{3+} in H_2 , N_2 atmospheres. By reduction at higher temperatures a previously unreported phase La_2MnO_4 is formed. The most reducing conditions (10% H_2 in N_2 , $>940^\circ\text{C}$) formed only La_2O_3 and MnO . Between 700 and 880°C in 10% H_2 in N_2 potassium was eliminated from the sample by reduction to the metal and evaporation. Analogous results were found for Na and Rb substituted LaMnO_3 except that the intermediate phase La_2MnO_4 was not observed in the reduction of $\text{La}_{0.8}\text{Rb}_{0.2}\text{MnO}_3$.

INTRODUCTION

In the past few years considerable attention has been given to a variety of compounds in the perovskite system ABO_3 , particularly $\text{La}_{1-x}\text{M}_x\text{MnO}_3$ where M is a large cation such as Pb, Sr, Ba, K, etc., as potential catalysts for automobile emission control^{1,2}. This family of catalysts has been shown to enhance the activity for both oxidation and reduction. While oxide catalysts are generally quite stable in oxidizing atmospheres, many are sufficiently easily reduced as to be unsuitable for use as reduction catalysts.

Previous work^{3,4} on the stability of LaCoO_3 and some substituted rare earth manganites in reducing atmospheres (H_2 in N_2) has shown the manganites (typified by $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$) to be more stable than the cobaltates while alkaline earth substituted lanthanum manganites were even more stable. Recently, alkali substituted lanthanum manganites have been shown to be of particular interest as reduction catalysts for NO_x control⁵.

The purpose of this study was to force the reduction of alkali substituted lanthanum manganites by using relatively strongly-reducing atmospheres. The reduction was studied by thermogravimetry (TG) and X-ray diffraction.

EXPERIMENTAL

Samples of $\text{La}_{0.8}\text{K}_{0.2}\text{MnO}_3$ have been prepared by milling K_2CO_3 , La_2O_3 , and Mn_2O_3 in ethyl alcohol using high alumina ceramic mill and balls, drying the mixture, and firing at 1100°C . The surface area was found to be $2.6 \text{ m}^2 \text{ g}^{-1}$ from nitrogen adsorption (BET) measurements. Thermogravimetric (TG) traces were obtained using a Dupont 950 thermogravimetric analyzer. The weight of the starting samples was approximately 25 mg. Three conditions were used in the TG experiments:

<i>Heating rate</i>	<i>Gas composition</i>
(1) $20^\circ\text{C min}^{-1}$	10% H_2 , 90% N_2
(2) 5°C min^{-1}	1% H_2 , 99% N_2
(3) 5°C min^{-1}	10% H_2 , 90% N_2

In order to determine changes in the original perovskite structure during reduction, samples were analyzed by X-ray diffraction (G. E. Model XRD-3 diffractometer and Cr K_α radiation with a V filter using Si as an external standard) at several stages of the weight loss*. The TG reduction runs were interrupted at appropriate degrees of weight loss and the samples quenched by removal of the balance arm from the furnace. After quenching, no appreciable weight change was noticed. For a semi-quantitative chemical analysis the energy dispersive X-ray fluorescence analyzer on a scanning electron microscope was used.

RESULTS AND DISCUSSION

A typical weight loss curve for the nominal composition $\text{La}_{0.8}\text{K}_{0.2}\text{MnO}_3$ is shown in Fig. 1 for condition (1). The X-ray diffraction results from the quenched specimens show the weight loss to be broken into three broad categories. These are:

Part I. Up to 3 wt. % loss where only the perovskite phase is seen in the quenched specimens.

Part II. From 3.5 to 8.5 wt. % loss where the perovskite phase evolves an intermediate phase which, with further weight losses, is partly replaced by MnO and La_2O_3 .

Part III. Greater than 8.5 wt. % loss where the only phases detectable are MnO and La_2O_3 .

Table 1 summarizes the phases present at each stage of weight loss for condition (1). The numbers are the X-ray diffraction intensities of the strongest peak for each phase normalized to 100 for the strongest peak on the pattern. These weight loss categories will be discussed separately.

*Some of the X-ray data were also taken with a Debye-Scherrer camera.

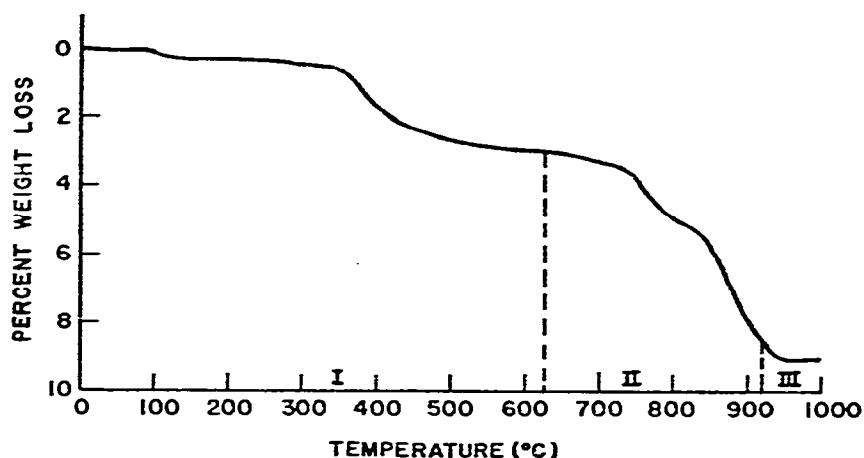


Fig. 1. Weight loss curve for $\text{La}_{0.8}\text{K}_{0.2}\text{MnO}_3$ at $20^\circ\text{C min}^{-1}$, 10% H_2 in N_2 .

TABLE I

INTENSITIES OF STRONGEST PEAKS OF PHASES PRESENT DURING REDUCTION OF $\text{La}_{0.8}\text{K}_{0.2}\text{MnO}_3$

Phase	Percent weight loss							
	3	3.5	4	5	6.5	7.2	8.5	9.2
Perovskite	100	100	100	67	57	47	25	
La_2MnO_4		29	58	100	100	71	34	
MnO			22	35	52	73	55	55
La_2O_3					55	100	100	100

Part I

In Fig. 1, for Part I where only the perovskite phase is detected, the rather abrupt weight loss at about 350°C is of particular interest. If a sample of $\text{La}_{0.8}\text{K}_{0.2}\text{MnO}_3$ is reduced and cooled to room temperature in the reducing atmosphere and then reheated in air, it will rapidly reoxidize at about 150°C as shown in Fig. 2. The dashed line in Fig. 2 shows the initial reduction in 10% H_2 , 90% N_2 while the solid line is for the reoxidation of the same sample in air. The small discontinuity at room temperature is due to the buoyancy difference of the two atmospheres. However, only on the initial reduction of a sample is the weight loss as abrupt as shown in Fig. 1.

This ease of reoxidation may be useful in catalytic devices for recovering from high-temperature, highly reducing conditions. The ability of these materials to lose and take up oxygen without irreversible structural change is also thought to be necessary for their catalytic activity.

From the X-ray diffraction experiments the original samples of $\text{La}_{0.8}\text{K}_{0.2}\text{MnO}_3$ have a rhombohedrally distorted perovskite structure⁶ with $a = 7.798 \text{ \AA}$ and $\alpha = 90.30^\circ$. After the 350°C reduction the structure was very nearly cubic with a cell

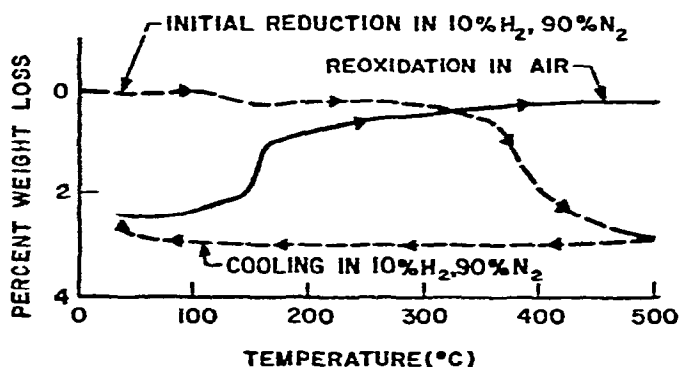


Fig. 2. Reduction and reoxidation curves of $\text{La}_{0.8}\text{K}_{0.2}\text{MnO}_3$.

edge of 7.862 Å. After reoxidation in air at 150°C the cell constants were $a = 7.816$ Å and $\alpha = 90.31^\circ$. The larger cell of the reduced material is probably due to a greater proportion of the larger Mn^{3+} . This cell expansion with reduction was also found for $(\text{La}, \text{Pb})\text{MnO}_3$ and LaMnO_{3+x} ⁹. The cell size upon reoxidation agrees well with the original material.

By doing a crude experiment with a magnet on the thermobalance, it was found that the unreduced manganite is magnetic with a Curie temperature at about 90°C. After the 350°C reduction the material was essentially non-magnetic at room temperature but again became magnetic at room temperature if reoxidized. This also suggests a large proportion of Mn^{3+} in the reduced sample which depresses the Curie temperature of these magnetic phases below room temperature.

Discounting the weight losses at about 120°C probably due to water, the samples lose about 1.7 wt. % over the steep portion of the weight loss at 350°C. This is larger than the expected theoretical loss of 1.44 wt. % for a stoichiometric sample of $\text{La}_{0.8}\text{K}_{0.2}\text{MnO}_3$ being reduced to all Mn^{3+} and would indicate an oxygen excess in the as prepared structure or some reduction to Mn^{2+} .

The thermogravimetric, X-ray, and magnetic evidence thus shows this initial reduction to be a reversible loss of oxygen in the perovskite structure due to the reduction of the available Mn^{4+} . This part of the reduction does not precipitate any non-perovskite phases.

Part II

The range of weight loss of 3.5–8.5% is characterized by the breakup of the perovskite structure. This occurs by the precipitation of an intermediate phase which has been identified to be isostructural with La_2NiO_4 ^{8,9} and has not been reported previously. These compounds belong to a group having the tetragonal K_2MgF_4 structure¹⁰ with $a = 3.864$ Å and $c = 12.958$ Å. The cell volume is slightly larger than that reported for La_2NiO_4 . This is consistent with the relative sizes of divalent Mn and Ni. Brief X-ray data for this compound, La_2MnO_4 are presented in Table 2.

Table 1 shows that during Part II the amount of perovskite is decreasing. The

TABLE 2

OBSERVED AND CALCULATED d -SPACINGS FOR La_2MnO_4 Tetragonal cell constants are $a = 3.864 \pm 0.002$, $c = 12.958 \pm 0.009$.

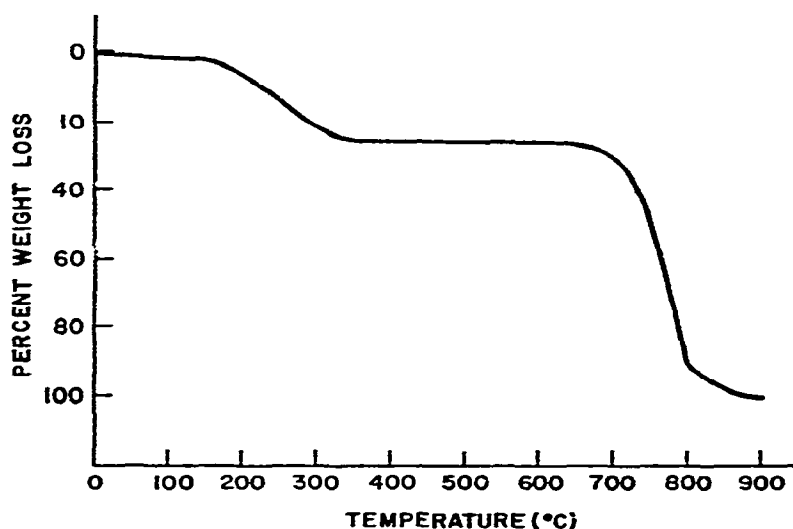
h	k	l	$d_{\text{calc.}}$	$d_{\text{obs.}}$	<i>Int.</i>
0	0	2	6.479	6.45	w
1	0	1	3.703	3.70	m
1	0	3	2.880	2.88	vs
1	1	0	2.732	2.73	s
1	1	2	2.517	2.52	vw
0	0	6	2.159	2.16	s
1	1	4	2.088	2.09	s
2	1	1	1.713	1.71	m
1	1	6	1.694	1.68	w-m

X-ray diffraction data of the quenched samples are not definitive in this range because of broad or weak diffraction peaks. However, as the perovskite is further reduced it does maintain a nearly cubic symmetry and goes through only minor lattice constant changes.

The intermediate phase, La_2MnO_4 , predominates in the 5–6.5% wt. loss range but at higher temperatures also reduces to La_2O_3 and MnO .

Part III

This part is characterized by an overall weight loss of 9.2% and the existence of the phases La_2O_3 and MnO which are apparently the equilibrium phases at the highest temperatures used with a 10% H_2 , 90% N_2 atmosphere.

Fig. 3. Reduction curve for KOH in 10% H_2 in N_2 .

The final reaction products were initially assumed to be consistent with the following decomposition scheme:



However, after reduction, no X-ray diffraction evidence for potassium was found. Also the 9.2% wt. loss is considerably greater than 5.05% expected for the above reaction.

By using the energy dispersive X-ray fluorescence analyzer on a scanning electron microscope it was evident that the potassium began to disappear for samples heated above about 700°C and were not detected for samples heated to 880°C or above using the TG condition (1). A TG experiment (Fig. 3) with KOH under condition (1) confirmed the volatilization of potassium in this temperature range.

In the TG experiment no effort was made to control the H₂/H₂O ratio but only reasonably dry gases were used. At the boiling point of potassium (774°C) K₂O will be reduced to metallic potassium unless the H₂:H₂O ratio is less than 100:1 (ref. 11). Since the ratio was greater in these experiments, the potassium in the samples was reduced to the metal and evaporated. This is again confirmed in Fig. 3 for the reduction of KOH where there is a broad flat plateau of presumably K₂O (up to about 630°C) which then reduces and volatilizes.

If then the reaction for the reduction of La_{0.8}K_{0.2}MnO₃ is:



the weight loss would be 9.29% which is in excellent agreement with the observed 9.2%.

The phenomena described up to now have been for heating in atmosphere (1). For condition (3) the results were nearly identical except that the slower heating rate tended to lower the observed temperatures of the reactions by 40–70°C. For the mildly reducing condition (2) the perovskite was not completely decomposed at the maximum temperature of ~970°C (7.25% wt. loss) and the intermediate phase La₂MnO₄ was less pronounced.

While the reduction of the perovskite has been demonstrated in H₂ containing atmospheres, no appreciable weight loss is seen if the samples are heated in pure N₂ even at temperatures up to 950°C. Also residual gas analyses of the samples heated in vacuum (~10⁻⁷ torr) show little oxygen release up to 1000°C.

Similar studies were done on La_{0.8}Na_{0.2}MnO₃ and La_{0.8}Rb_{0.2}MnO₃. The sodium substituted perovskite went through steps of decomposition analogous to the potassium substituted material with identical end products. However, the low-temperature reversible oxygen loss was spread out over a wider temperature range for both Na and Rb. The rubidium substituted perovskite produced only La₂O₃ and MnO upon extensive reduction and did not form the intermediate phase La₂MnO₄. For both the Na and Rb substituted cases the final weight loss at 970°C for condition (1) was consistent with complete volatilization of the alkali.

CONCLUSIONS

1. Thermogravimetric, X-ray diffraction and magnetic evidence show $\text{La}_{0.8}\text{K}_{0.2}\text{MnO}_3$ to undergo a reversible oxygen loss in H_2 , N_2 atmospheres at about 350°C corresponding to the reduction of the available Mn^{4+} to Mn^{3+} .

2. Reductions beyond about 3 wt. % loss precipitate the previously unreported phase La_2MnO_4 .

3. At even higher temperatures in H_2 , N_2 atmospheres, La_2MnO_4 and the perovskite phase decompose to La_2O_3 and MnO , the apparent equilibrium phases at 950°C and 10% H_2 in N_2 .

4. The potassium in the original perovskite is reduced to the metal and evaporated from the sample between 700 and 880°C .

5. Varying the heating rate for a given atmosphere affected only the apparent temperatures of the decompositions. Lowering the H_2 from 10 to 1% caused a lesser degree of reduction and a smaller amount of the intermediate phase La_2MnO_4 .

6. Analogous experiments with $\text{La}_{0.8}\text{Na}_{0.2}\text{MnO}_3$ and $\text{La}_{0.8}\text{Rb}_{0.2}\text{MnO}_3$ showed similar results except that for the Rb substitution the La_2MnO_4 phase was not detected.

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