

Oxygen non-stoichiometry and reducibility of B-site substituted lanthanum manganites

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Abstract

LaMn_{0.8}B'_{0.2}O_{3+δ} (B'=Ni, Zn, Cu) and LaMn_{0.5}Cu_{0.5}O_{3+δ} perovskites were studied by temperature programmed reduction (TPR). Oxygen non-stoichiometry of the perovskite samples calcined in air ($P_{O_2}=0.21$ bar) at 750°C decreased upon Zn²⁺ ($\delta=0.03$), Cu²⁺ ($\delta=0.04$) and Ni³⁺ ($\delta=0.08$) substitution as compared to LaMnO_{3.16}. LaMn_{0.5}Cu_{0.5}O_{3+δ} had reductive non-stoichiometry and contained low amounts of La₂CuO₄ and CuO. The reducibility at low and mean temperatures ($t<500^\circ\text{C}$) increased in the sequence (Mn, Ni) \approx (Mn, Zn) $<$ Mn $<$ (Mn, Cu). © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Copper-substituted lanthanum manganites LaMn_{1-x}Cu_xO_{3+δ} exhibit high catalytic activity for CO oxidation [1–4] and NO–CO reaction [2]. The rates of these reactions have been found to correlate well with the reducibility and CO adsorption capacity of the catalyst [2,3] but also with the oxygen availability measured by temperature programmed desorption (TPD) [4]. The pronounced synergetic effect that arises upon copper substitution was ascribed in [2,3] to the combined high CO adsorption capacity of copper sites and the high reactivity of oxygen bonded to manganese. The increased mobility of lattice oxygen in copper-substituted lanthanum manganites and the change to a high activity state by surface reduction in the reactive environment have been

proposed by Chan et al. [4] as reasons for the enhanced activity.

In spite of these promising results with copper-substituted lanthanum manganites, less is known about manganese substitution with other transition metals [3]. The aim of this paper is to compare the effects of Ni, Cu and Zn substitution on the oxidative non-stoichiometry, the Mn⁴⁺/(Mn⁴⁺+Mn³⁺) ratio and reducibility of lanthanum manganite, by means of the temperature programmed reduction (TPR) technique. Nickel, though divalent in most of its oxides, was found to adopt the trivalent state in the perovskite LaNiO₃ [5]. Copper was found by X-ray photoelectron spectroscopy (XPS) to adopt the divalent state in substituted lanthanum manganite [3]. As for zinc, it is known as a divalent cation. It is therefore expected that substitution of Cu²⁺ and Zn²⁺ for Mn³⁺ should lead to a decrease in the oxidative non-stoichiometry and/or an increase of the Mn⁴⁺ content. In order to facilitate the assignment of the TPR peaks, reduction runs with NiO, CuO and ZnO were also carried out.

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2. Experimental

The perovskites have been prepared by decomposition of metal nitrates $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Fluka), $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Fluka), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Fluka), $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Fluka), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Riedel de Haen), after the method given in [6,7]. Calculated amounts of dried nitrates were dissolved in distilled water and glucose was added to enhance the surface area of the catalysts. The solution was evaporated to dryness and the solid material was calcined at 750°C in air for 6 h. The simple oxides have been prepared by decomposition of the corresponding metal nitrates in air at 600°C (NiO), 500°C (CuO), except for ZnO which was of Merck quality.

Cu K α X-ray analysis were performed on a HZ G4 diffractometer for all samples. TPR experiments were carried out by using a flow device equipped with a thermal conductivity detector [8]. The gas flow (30 ml/min NTP with 10% H_2 in N_2) passed over about 50 mg of sample in a quartz reactor, then through a cold trap prior to the detector. The temperature was raised at a linear rate of 10 K/min from 20 to 950°C , then it was kept at 950°C for 20 min. To calibrate the TPR curves, hydrogen pulses of known volumes were injected into a nitrogen flow. The hydrogen consumption was calculated from the peak area and expressed as an equivalent amount of oxygen removed from the sample. The calibration method was checked up by reducing a sample of copper oxide (CuO) in the same device. A hydrogen consumption equivalent to 0.98 mol O/mol CuO was found.

3. Results and discussion

The XRD-patterns of $\text{LaMn}_{0.8}\text{B}'_{0.2}\text{O}_{3+\delta}$ ($\text{B}'=\text{Ni}$, Zn, Cu) samples revealed only features of the perovskite phase. For $\text{LaMn}_{0.5}\text{Cu}_{0.5}\text{O}_{3+\delta}$, additional lines of La_2CuO_4 and CuO were found, though the total amount of these phases (estimated from the ratios of the most intense XRD lines) did not exceed 10%.

The TPR profiles of the simple NiO, CuO, Mn_2O_3 and ZnO oxides are given in Fig. 1. Those of La_2O_3 and MnO_2 were discussed in a previous work [9]. Essentially, La_2O_3 was not reducible and the manga-

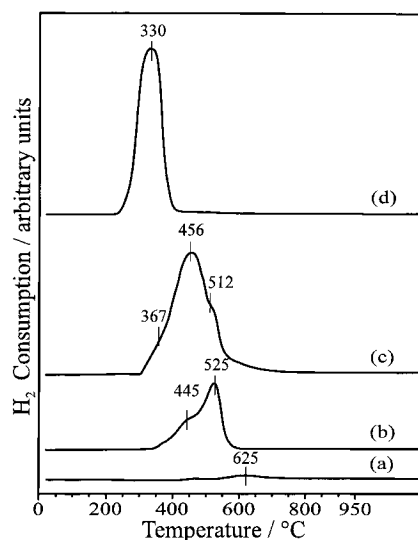


Fig. 1. TPR profiles of the catalyst samples: (a) ZnO; (b) Mn_2O_3 ; (c) NiO and (d) CuO.

nese oxides displayed a two-stage reduction pattern according to the mechanism proposed by Kapteijn et al. [10]. The first reduction temperature of Mn^{4+} in MnO_2 was $302\text{--}331^\circ\text{C}$ [9] while for Mn^{3+} in Mn_2O_3 it was 445°C (Fig. 1). The reduction of nickel oxide occurs approximately in the same temperature range as that of the trivalent manganese oxide, i.e. at higher temperatures than the tetravalent manganese. The shoulder at 367°C arises from the reduction of Ni^{3+} , which is always present in NiO samples, calcined in air at 600°C [8]. Zinc oxide is essentially not reduced in the temperature range of $20\text{--}950^\circ\text{C}$ under the conditions of our TPR runs. Copper oxide is reduced in a single step at 330°C to metallic copper, in the same temperature range as Mn^{4+} .

The reduction profiles of the perovskites are displayed in Fig. 2 and the amounts of lattice oxygen removed corresponding to the reduction peaks are given in Table 1.

3.1. $\text{LaMnO}_{3+\delta}$

The discussion of the TPR spectra, leading to the formula $\text{LaMnO}_{3.16}$ and the ratio $\text{Mn}^{4+}/(\text{Mn}^{4+}+\text{Mn}^{3+})$ of 0.32 (32%), is given in a previous paper [9]. The main reduction stages are Mn^{4+} to Mn^{3+} (361°C) and Mn^{3+} to Mn^{2+} (790°C).

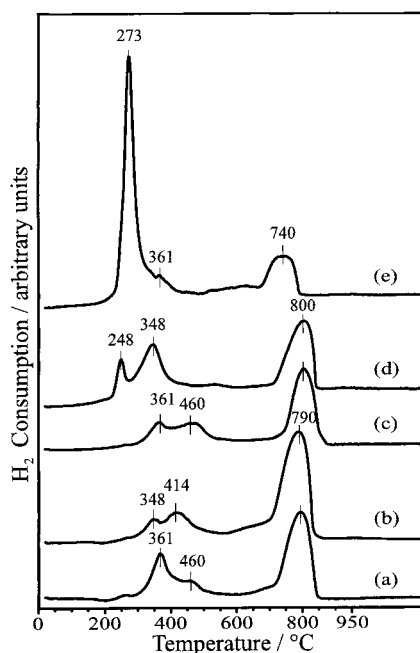
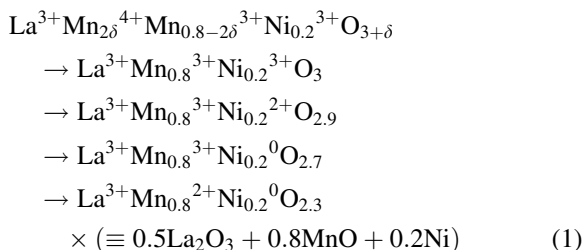


Fig. 2. TPR profiles of oxide catalysts with perovskite structure: (a) LaMnO_3 ; (b) $\text{LaMn}_{0.8}\text{Ni}_{0.2}\text{O}_{3+\delta}$; (c) $\text{LaMn}_{0.8}\text{Zn}_{0.2}\text{O}_3$; (d) $\text{LaMn}_{0.8}\text{Cu}_{0.2}\text{O}_3$ and (e) $\text{LaMn}_{0.5}\text{Cu}_{0.5}\text{O}_3$.

3.2. $\text{LaMn}_{0.8}\text{Ni}_{0.2}\text{O}_{3+\delta}$

The total amount of removed oxygen points to a reduction process that brings nickel to the metallic state. LaNiO_3 is also known to be reduced to La_2O_3 and Ni, in two stages, the first one between 150 and 400°C ($\text{Ni}^{3+} \rightarrow \text{Ni}^{2+}$), and the second one between 400 and 560°C ($\text{Ni}^{2+} \rightarrow \text{Ni}^0$) [5]. The reduction of the substituted perovskite can be thus written as

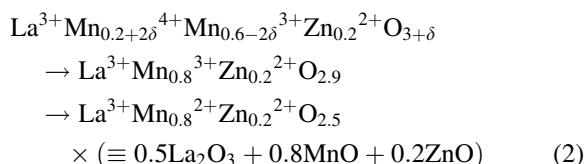


The amount of removed oxygen of $0.7+\delta=0.78$ leads to the formula $\text{LaMn}_{0.8}\text{Ni}_{0.2}\text{O}_{3.08}$ and the corresponding $\text{Mn}^{4+}/(\text{Mn}^{4+}+\text{Mn}^{3+})$ ratio of $2\delta/0.8=0.2$ (20%). By introducing nickel, a cation of the same valence as manganese, in the perovskite lattice the

oxygen non-stoichiometry, and consequently the amount of tetravalent manganese, are diminished. A possible explanation of this phenomenon is the absence of the Jahn–Teller distortion of the Ni^{3+} ions, which renders unnecessary the transformation of a part of the distorted Mn^{3+} cations into undistorted Mn^{4+} in order to achieve an energetically more stable configuration. The appearance of the TPR-profile suggests that only about a half of the Ni^{2+} cations are reduced below 560°C, as in LaNiO_3 , while the rest undergo reduction at higher temperatures (>600°C) together with Mn^{3+} cations.

3.3. $\text{LaMn}_{0.8}\text{Zn}_{0.2}\text{O}_{3+\delta}$

The TPR profile of this perovskite is identical to that of $\text{LaMnO}_{3+\delta}$, the only difference being the relative amount of hydrogen consumption corresponding to the peak at 361°C (reduction of Mn^{4+}). This points out to the same reduction sequence as in $\text{LaMnO}_{3.16}$



The value of oxygen non-stoichiometry is thus $0.5+\delta=0.53$, leading to the formula $\text{LaMn}_{0.8}\text{Zn}_{0.2}\text{O}_{3.03}$ and the corresponding $\text{Mn}^{4+}/(\text{Mn}^{4+}+\text{Mn}^{3+})$ ratio of $(0.2+2\delta)/0.8=0.325$ (32.5%). Substitution of manganese for zinc reduces the oxidative non-stoichiometry while keeping the Mn^{4+} content constant. This finding is similar to the effect of lanthanum substitution for divalent alkaline-earth cations [9]. The presence of Zn^{2+} ions also causes an increased reduction of Mn^{3+} at mean temperatures (the peak at 460°C), which indicates an increased anionic mobility. A possible explanation for this peculiarity could be the strong distortion around the Zn^{2+} cations (usually in the tetrahedral co-ordination) situated in the octahedral sites of the perovskite lattice.

3.4. $\text{LaMn}_{0.8}\text{Cu}_{0.2}\text{O}_{3+\delta}$ and $\text{LaMn}_{0.5}\text{Cu}_{0.5}\text{O}_{3+\delta}$

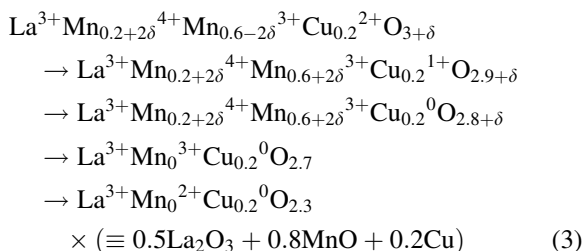
The TPR spectra and the corresponding H_2 -consumption indicate a complete reduction of the copper ions to the metallic state. Hence the reduction process for the 20% substituted perovskite can

Table 1
TPR results and characterisation of Mn-substituted perovskite oxides regarding their reducibility and oxygen non-stoichiometry

Oxide	H ₂ -consumption expressed as O-removed per mole oxide						Total O-removed (mol/mol)	O-removed below 500°C (mol/mol)	(Mn ⁴⁺)/ (Mn ⁴⁺ + Mn ³⁺) (%)	δ
	Peak 1		Peak 2		Peak 3					
	T_{R1} (°C)	mol/mol	T_{R2} (°C)	mol/mol	T_{R3} (°C)	mol/mol				
LaMnO _{3+δ}	361	0.185	460	0.07	790	0.405	0.66	0.255	32	0.16
LaMn _{0.8} Ni _{0.2} O _{3+δ}	348	0.07	414	0.16	790	0.55	0.78	0.23	20	0.08
LaMn _{0.8} Zn _{0.2} O _{3+δ}	361	0.09	460	0.14	790	0.30	0.53	0.23	32.5	0.03
LaMn _{0.8} Cu _{0.2} O _{3+δ}	248	0.07	348	0.28	790	0.39	0.74	0.35	35	0.04
LaMn _{0.5} Cu _{0.5} O _{3+δ} ^a	273	0.52	361	0.08	740	0.24	0.84	0.60	36	-0.16

^a All quantities are referred to the formula LaMn_{0.5}Cu_{0.5}O_{3+ δ} though the real oxide contains some La₂CuO₄ and CuO.

be written as



The oxygen excess is $\delta=0.04$, that means $\text{LaMn}_{0.8}\text{Cu}_{0.2}\text{O}_{3.04}$ and the ratio $\text{Mn}^{4+}/(\text{Mn}^{4+}+\text{Mn}^{3+})$ of 0.35 (35%). From this point of view, copper substitution produces almost the same effect as zinc substitution.

Unlike copper oxide, where Cu^{2+} is reduced to Cu^0 in a single step, in the 20%-substituted lanthanum manganite the copper cations appear to follow a two-step reduction with Cu^{1+} as intermediate, as indicated by the size of the first reduction peak. The second step occurs at the same time with Mn^{4+} reduction to Mn^{3+} . The reduction of Mn^{3+} seems to take place entirely at high temperatures. The relative good stability of copper in the perovskite lattice against low temperature (<300°C) reduction to metallic copper can be regarded as a convenient feature of the low substituted manganites, by avoiding sintering of copper during oscillations of working environment.

The accurate interpretation of the TPR curve of $\text{LaMn}_{0.5}\text{Cu}_{0.5}\text{O}_{3+\delta}$ is rendered difficult by the presence of La_2CuO_4 and CuO . If the final reduction point is considered $0.5\text{La}_2\text{O}_3+0.5\text{MnO}+0.5\text{Cu}$ ($\equiv\text{LaMn}_{0.5}\text{Cu}_{0.5}\text{O}_2$), the total amount of removed oxygen is $1+\delta=0.84$, that is $\delta=-0.16$, which leads to the stoichiometry $\text{LaMn}_{0.5}\text{Cu}_{0.5}\text{O}_{2.84}$. The real value of δ should be lower in absolute value, since the La:O ratio in La_2CuO_4 is 1:2 whereas in LaMnO_3 it is 1:3, which means that a part of this apparent oxygen deficiency is due to the presence of La_2CuO_4 . In fact, the stoichiometry found by Gallagher et al. [1] for the pure perovskite phase was $\text{LaMn}_{0.5}\text{Cu}_{0.5}\text{O}_{2.93}$, while Rojas et al. [11] have prepared $\text{LaMn}_{0.5}\text{Cu}_{0.5}\text{O}_{3.00}$. By examining the TPR curve it appears that copper cations in high-substituted manganites are reduced to metal in a single step similar to copper oxide but at lower temperatures. Another striking feature is the lowering of the reduction temperature of Mn^{3+} , which can be caused by the high permeability of the lattice arising from the removal of a great

amount of oxygen during copper reduction. Generally speaking, the stability of this perovskite against reductive environment seems to be poor, though its ability to release a great part of the lattice oxygen could make it very suitable for intrafacial catalysis.

4. Conclusions

In conclusion, the following remarks regarding the features of B-site substituted manganites in relation to their potential use as oxidation catalysts may be stated on the basis of TPR studies.

1. Manganese substitution for divalent (Zn^{2+} , Cu^{2+}) cations in lanthanum manganite leads to the lowering of oxidative non-stoichiometry by keeping the $\text{Mn}^{4+}/(\text{Mn}^{4+}+\text{Mn}^{3+})$ ratio constant, while trivalent cation (Ni^{3+}) substitution produces the diminution of both oxidative non-stoichiometry and Mn^{4+} content. Therefore the latter, containing a higher amount of Mn^{3+} sites is likely to adsorb gas-phase oxygen to a higher extent.
2. The Ni^{3+} and Zn^{2+} substituted manganites display a poorer reducibility at low and mean temperatures (<500°C) as compared to non-substituted lanthanum manganite, while Cu^{2+} substituted perovskites release at relatively low ($\cong 250$ –270°C) temperature an important amount of lattice oxygen, which increases with the ratio Cu/Mn. The ease of reduction, which is desirable from the point of view of intrafacial catalytic reactions, represents at the same time a disadvantage for the stability of the catalyst in reducing atmospheres, especially for the higher substituted perovskites.

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