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TPR-STUDY OF SUBSTITUTION EFFECTS ON REDUCIBILITY AND OXIDATIVE NON-STOICHIOMETRY OF $La_{0.8}A'_{0.2}MnO_{3+\delta}$ PEROVSKITES

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Abstract

$La_{0.8}A'_{0.2}MnO_{3+\delta}$ (A'=Sr, Ba, K, Cs) perovskites were studied by temperature-programmed reduction. The amount of non-stoichiometric oxygen was found to decrease from δ=0.16 for $LaMnO_{3+\delta}$ to δ=0.07 (Sr-), 0.06 (Ba-), 0.07 (K-) and 0.03 (Cs-) substituted manganites. The reducibility at low and mean-temperatures (t<500°C) increased in the sequence La<(La, Sr)≈(La, Ba)<(La, Cs)<(La, K).

Keywords: catalyst, lanthanum manganite, non-stoichiometry, perovskite, TPR

Introduction

A-site substituted lanthanum manganites are known as catalysts for the oxidation of carbon monoxide [1–3], methane [4], ethene [2], propane [5], NO–H_2 reaction [6], etc. In most cases, an enhancement of the catalytic activity as compared to the non-substituted $LaMnO_{3+\delta}$ has been found for Pb, Sr, Ca, and K substituted oxides.

According to Voorhoeve [7], catalysis by perovskites can proceed via a suprafacial or an intrafacial mechanism. For suprafacial reactions (as CO-oxidation), both $t_{2g}^3e_g^0$ (Mn^{4+}) and $t_{2g}^3e_g^1$ (Mn^{3+}) configurations are required within the framework of lanthanum manganite to achieve the highest activity [7]. The ratio between them can be controlled by the appropriate substitution of the A-site cation (La^{3+}) with lower valence ions. For intrafacial reactions (as NO reduction) the amount of reducible lattice oxygen, which is controlled by the bonding energy of oxygen, can be changed by substitution of La^{3+} cations with metals of different basicity, as alkaline and alkaline-earth metals, or by changing the Mn^{4+}/Mn^{3+} ratio.

In this paper, alkaline (K, Cs) and alkaline-earth (Sr, Ba) substituted lanthanum manganites $La_{0.8}A'_{0.2}MnO_{3+\delta}$ are characterized by temperature-programmed reduction with respect to the oxygen non-stoichiometry δ, the $Mn^{4+}/(Mn^{4+}+Mn^{3})$ ratio and the amount of reducible oxygen at low and mean temperatures (t<500°C). The results are

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

Oxide	H_2-consumption expressed as O-removed						Total	O-removed	$\frac{Mn^{4+}}{Mn^{4+}+Mn^{3+}}$	δ
	Peak 1		Peak 2		Peak 3		O-removed	below 500°C		
	T_{R1}/°C	atgr/ molgr	T_{R2}/°C	atgr/ molgr	T_{R3}/°C	atgr/ molgr	atgr/ molgr	atgr/ molgr	%	
$LaMnO_{3+\delta}$	361	0.185	460	0.070	790	0.405	0.66	0.255	32	0.16
$La_{0.8}Sr_{0.2}MnO_{3+\delta}$	334	0.184	440	0.115	790	0.375	0.67	0.300	34	0.07
$La_{0.8}Ba_{0.2}MnO_{3+\delta}$	361	0.200	440	0.090	790–850	0.370	0.66	0.290	32	0.06
$La_{0.8}K_{0.2}MnO_{3+\delta}$	264	0.090	419	0.360	748	0.420	0.87	0.450	54	0.07
$La_{0.8}Cs_{0.2}MnO_{3+\delta}$	298	0.080	361	0.270	790	0.480	0.83	0.350	46	0.03

compared with the features of non-substituted $LaMnO_{3+\delta}$ and the simple oxides La_2O_3, Mn_2O_3 and MnO_2.

Experimental

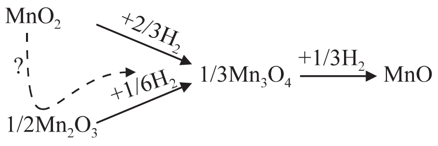
The perovskites were prepared by using metal nitrates as precursors. $Mn(NO_3)_2 \cdot 4H_2O$ (Fluka), $La(NO_3)_3 \cdot 6H_2O$ (Fluka), KNO_3 (Merck), $CsNO_3$ (Fluka), $Sr(NO_3)_2$ (Fluka), $Ba(NO_3)_2$ (Fluka), after the method given in [8]. Calculated amounts of dried nitrates were dissolved in distilled 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. La_2O_3 (Aldrich), MnO_2 (Merck) and Mn_2O_3 (prepared by decomposition of manganese nitrate at 750°C) were taken for comparison.

CuK_α-X-ray analysis has been performed on a HZ G4 diffractometer for all samples. Temperature-programmed reduction experiments have been carried out by using a flow device equipped with a TC-detector. The gas flow (30 ml min^{-1} NTP with 10% H_2 in N_2) passed over about 50 mg sample in a quartz reactor, then through a cold trap prior to the detector. The temperature was raised at a linear rate of 10° min^{-1} from 20 up 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 in a nitrogen flow. The hydrogen consumption was calculated from the peak area and expressed as 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 atgr O/molgr CuO was found.

Results and discussion

The XRD-diagrams show that upon substitution of 20% of the La^{3+} ions with Sr^{2+}, Ba^{2+}, K^+ or Cs^+, the samples retain the perovskite structure without extra lines.

The TPR profiles of the simple oxides are shown in Fig. 1. La_2O_3 (curve 1a) is practically unreducible at temperatures below 950°C. The manganese oxides (curves 1b and 1c) display a two-stage reduction pattern, according to the mechanism proposed by Kapteijn *et al.* [9]:



The relative hydrogen consumption of the two peaks of 2:1 for MnO_2 and 1:2 for Mn_2O_3 supports this assignment. The reduction temperatures of Mn^{4+} (331–351°C) are lower than that of Mn^{3+} (443–526°C).

The reduction profiles of the perovskites are presented in Fig. 2, and the corresponding amounts of oxygen removed in different reduction stages are given in Table 1.

$LaMnO_{3+\delta}$

The total amount of removed oxygen of 0.66 atgr/molgr and the shape of the TPR-profile points out at a two-stage reduction process described by Eq. (2):

$$La^{3+}Mn^{4+}_{2\delta}Mn^{3+}_{1-2\delta}O_{3+\delta} \rightarrow La^{3+}Mn^{3+}O_3 \rightarrow La^{3+}Mn^{2+}O_{2.5}(\equiv 0.5La_2O_3+MnO) \quad (2)$$

The oxygen excess can be calculated as $3+\delta-2.5=0.66$ that is $\delta=0.16$, which corresponds to the formula $LaMnO_{3.16}$ and a ratio $Mn^{4+}/(Mn^{4+}+Mn^{3+})$ of $2\delta=0.32$ (32%).

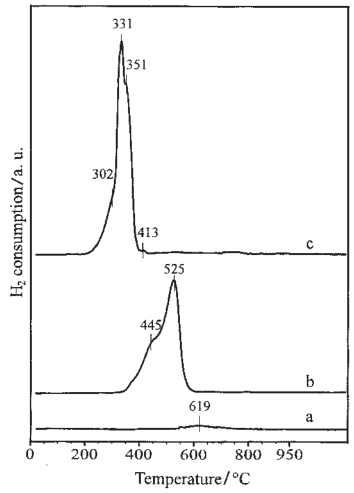


Fig. 1 TPR profiles of the oxide samples: a – La_2O_3; b – Mn_2O_3 and c – MnO_2

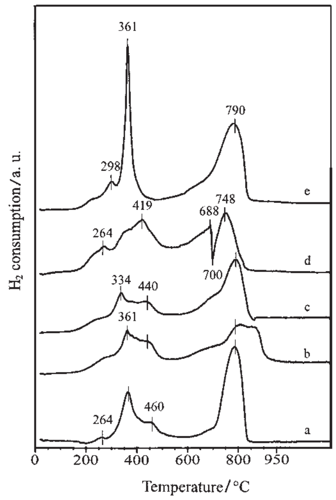


Fig. 2 TPR profiles of oxide catalysts with perovskite structure: a – $LaMnO_3$; b – $La_{0.8}Ba_{0.2}MnO_3$; c – $La_{0.8}Sr_{0.2}MnO_3$; d – $La_{0.8}K_{0.2}MnO_3$ and e – $La_{0.8}Cs_{0.2}MnO_3$

The hydrogen consumption in the first reduction stage indicates however that about 1/5 of the Mn^{3+} ions are also reduced to Mn^{2+} at mean temperatures. There are two possible reasons for this: either the surface Mn^{3+} ions, though inserted in the more stable perovskite structure, retain their reduction capability as in Mn_2O_3, or during the transition from the oxygen-rich rhombohedral phase to the nearly stoichiometric orthorhombic $LaMnO_3$ in the reducing atmosphere, a part of the lattice oxygen is released leading to a defective $LaMnO_{3-\delta}$ stable phase. Such oxides having a regular arrangement of anionic vacancies are mentioned in [10]. The final reduction of Mn^{3+} begins at about 600°C, the asymmetric shape of the reduction curve indicating a process controlled by nucleation [11].

$La_{0.8}Sr_{0.2}MnO_{3+\delta}$ and $La_{0.8}Ba_{0.2}MnO_{3+\delta}$

By considering the total amount of removed oxygen the reduction of alkaline-earth substituted manganites is likely to follow the scheme:

$$La^{3+}_{0.8}A'^{2+}_{0.2}Mn^{4+}_{0.2+2\delta}Mn^{3+}_{0.8-2\delta}O_{3+\delta} \rightarrow La^{3+}_{0.8}A'^{3+}_{0.2}Mn^{3+}O_{2.9} \rightarrow La^{3+}_{0.8}A'^{2+}_{0.2}Mn^{2+}O_{2.4} \\ (\equiv 0.4La_2O_3+0.2A'O+MnO) \tag{3}$$

which leads to the formula $La_{0.8}Sr_{0.2}MnO_{3.07}$ and $La_{0.8}Ba_{0.2}MnO_{3.06}$ and to the corresponding values of the $Mn^{4+}/(Mn^{4+}+Mn^{3+})$ ratio of 0.34 (34%) and 0.32 (32%), respectively. The partial substitution of La for Sr or Ba is thus charge-compensated by lowering the oxidative non-stoichiometry, while keeping the content of tetravalent manganese practically unchanged. This result agrees with those of Andersen *et al.* [12] who used wet chemical methods to determine the stoichiometry of $La_{1-x}Sr_xMnO_{3+\delta}$. The onset of reduction takes place at lower temperatures (180–190°C) than with the non-substituted perovskite (~220°C) and the low-temperature shoulder at ~260°C is more pronounced. This indicates an enhanced reducibility of alkaline-earth substituted manganites which can be accounted for by the lower Mn–O bonding energy [7]. Another difference with respect to the non-substituted perovskite is the increased reduction of Mn^{3+} in the 600–700°C temperature range, which points out to a greater mobility of lattice oxygen.

$La_{0.8}K_{0.2}MnO_{3+\delta}$ and $La_{0.8}Cs_{0.2}MnO_{3+\delta}$

The extent of the H_2-consumption indicates that alkaline cations undergo reduction during TPR-runs. The process can be written as follows:

$$La^{3+}_{0.8}A'^{1+}_{0.2}Mn^{4+}_{0.4+2\delta}Mn^{3+}_{0.6-2\delta}O_{3+\delta} \rightarrow La^{3+}_{0.8}A'^{1+}_{0.2}Mn^{3+}O_{2.8} \rightarrow La^{3+}_{0.8}A'^{0}_{0.2}Mn^{3+}O_{2.7} \\ \rightarrow La^{3+}_{0.8}A'^{0}_{0.2}Mn^{2+}O_{2.2} (\equiv 0.4La_2O_3+0.2A'+MnO) \tag{4}$$

which by taking into account the H_2-consumption leads to the stoichiometry $La_{0.8}K_{0.2}MnO_{3.07}$ and $La_{0.8}Cs_{0.2}MnO_{3.03}$. The corresponding content of Mn^{4+} related to the total $(Mn^{4+}+Mn^{3+})$ amount is 0.54 (54%) and 0.46 (46%), for the K- and Cs-substituted perovskites, respectively. The charge compensation for monovalent cations is achieved both by reducing the oxidative non-stoichiometry and by increasing the

Mn^{4+} content. The reducibility of lanthanum manganite is further enhanced upon substitution with alkali metals, as the amounts of removed oxygen show (Table 1). The appearance of the reduction process at low and mean temperatures is quite different: the K-substituted perovskite releases lattice oxygen progressively over the entire range of 180–500°C, while the Cs-substituted, after a gradual reduction between 180 and 300°C displays suddenly a strong peak at 360°C which can be accounted for by the simultaneous reduction of Cs^{1+} and Mn^{4+}. The subsequent reduction of the former shows at ~700°C an 'inverse' peak. This can be accounted for by the vaporization of metallic potassium from the sample, which produces in the TC-cell a signal equivalent to an injection of hydrogen. Potassium vaporization occurred also in the gravimetric TPR-experiments of Vogel *et al.* over $La_{0.8}K_{0.2}MnO_3$ [13], and is confirmed by the fact that upon re-oxidation of the sample, the second TPR-run doesn't display such an 'inverse' peak.

As a result of TPR studies on A-site substituted lanthanum manganites, the following conclusions regarding their prospects as catalytic materials may be inferred:

1. Alkali and alkali-earth substituted lanthanum manganites show an enhanced reducibility at low and mean temperatures as compared to the non-substituted perovskite. This fact may be profitable for their use as catalysts in intrafacial reactions.

2. The charge compensation upon substitution with divalent alkaline-earth cations is achieved by reducing the oxidative non-stoichiometry, while keeping the $Mn^{4+}/(Mn^{4+}+Mn^{3+})$ ratio constant. For suprafacial reactions this allows to study the influence of the variable basicity of A' cations on the adsorption capacity of Mn-sites.

3. The substitution with monovalent alkali cations is charge-compensated both by lowering the oxygen non-stoichiometry and by increasing the $Mn^{4+}/(Mn^{4+}+Mn^{3+})$ ratio. The great capability of these perovskites to release an important amount of lattice oxygen at low and mean temperatures makes them interesting for intrafacial catalysis, though the vaporization of potassium at high temperatures rises possible difficulties regarding the practical use of this metal substitute.

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