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Structural transformations in cubic structure of Mn/Co perovskites in reducing and oxidizing atmospheres

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Abstract

ABO_3 ($A = \mathrm{La, Pr}$; $B = \mathrm{Mn, Co}$), $AB_{1-x}B'_xO_3$ ($A = \mathrm{La, Pr}$; $B = \mathrm{Mn, Co}$; $B' = \mathrm{Co, Pd}$), and $AB_{1-x-y}Co_yPd_xO_3$ ($A = \mathrm{La, Pr}$; $B = \mathrm{Fe, Mn}$) ($x = 0.05, 0.37$; $y = 0.38$) perovskites were synthesized via malic acid complexation. O_2-TPD, O_2-TPO, and H_2-TPR treatments were carried out to study the oxidation and reduction behavior of the synthesized perovskites. $LaCo_{0.95}Pd_{0.05}O_3$, $PrCo_{0.95}Pd_{0.05}O_3$, and $PrCoO_3$ perovskites had the highest desorption, oxidation, and reduction activity within the studied perovskite series. Powder XRD studies revealed structural transformation of the cubic structure of all synthesized perovskites except $LaFe_{0.57}Co_{0.38}Pd_{0.05}O_3$ in H_2/Ar atmosphere when the temperature was over 400 °C. The decomposed structure reverted to the original perovskite structure under oxidizing atmosphere. This reversion was accompanied by increased oxygen desorption activity. It was noticed that the Co and Mn combinations in the B-site of the perovskites structure decreased the thermal stability of the synthesized perovskites.

Keywords: Perovskite; Structural transformation; Decomposition; TPR; TPD; TPO

1. Introduction

Today perovskites are under wide interest because of their magnetic [1–3], electrical [1,3], optical [3], and catalytic [4–6] properties. One use of perovskite-type oxides is as catalyst in exhaust gas cleaning process [4–8] and methane combustion [9, 10]. Recent studies of perovskite as catalyst have focused on the exhaust gas cleaning processes. These studies have suggested that with the perovskite based catalysts reasonable exhaust gas cleaning activity can be achieved with low noble metal loading. The structure formula of perovskites is ABO_3, where the A-site metals are usually rare earth metal or earth metal and the B-site elements are first row transition metals. The thermal stability of the perovskite is determined by both the A-site and B-site cations. The activity in oxidation and reduction reactions is mainly determined by the transition metals in the B-site. The thermal stability and activity of perovskite improves when the B cation is partially substituted by noble metal [3,5,11,12].

The thermal stabilities and reduction-oxidation activities of perovskite have been reported in the literature [3,11,13–15]. Studies of $LnCoO_3$ (Ln = lanthanide) perovskite have shown that the hydrogen reduction of cobalt increases from La to Eu with decreasing ionic radius of the lanthanide [3,16]. The stability of the perovskite structure increases with the size of the lanthanide ion. Partial replacement of La by a lower oxidation state ion such as Sr ($La_{1-x}Sr_xCoO_3$) changes the stability of the perovskite. It is possible to increase the concentration of Co^{4+} and the oxygen vacancies by increasing the amount of strontium. Because Co^{4+} is unstable, this change favours the diffusion of lattice oxygen from the bulk structure to the surface of the perovskite as charge compensator.

The effect of the B-site cation on the thermal stability of perovskite oxide has been studied with a series of $LaBO_3$ ($B = \mathrm{V}$, Mn, Fe, Co, Ni) perovskites in reducing atmosphere [17]. Secondary products, La_2BO_4 ($B = \mathrm{V}$, Fe, Co, Ni) and $La_2Co_2O_5$,

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were formed during heat treatment. Although the secondary products were formed in reducing atmosphere, it was suggested that a perovskite catalyst where lanthanum is the A-site metal and cobalt is in the B-site has improved catalytic activity. Activity of the perovskite is improved by partially replacement of the A-site metal (La) with ions of different valency such as Sr or Ce [18]. However as also noted above, the substitution may decrease the stability of the perovskite.

In our previous study [12] the lanthanum and the praseodymium perovskites, where the B-site metal combination was $Mn_{1-x}Pd_x$, showed promising desorption and reduction properties. The aims of this study were to synthesize La/Pr perovskites with different combinations of B-site metals (Co, Fe, Mn, Pd) and to observe the effect of combinations of metals at the B-site on the thermal stabilities and reactivity of ABO_3 ($A = La, Pr$; $B = Mn, Co$), $AB_{1-x}B'_xO_3$ ($A = La, Pr$; $B = Mn, Co$; $B' = Co, Pd$), and $AB_{1-x-y}Co_yPd_xO_3$ ($A = La, Pr$; $B = Fe, Mn$) ($x = 0.05, 0.37$; $y = 0.38$) perovskites in different atmospheres. Since the temperatures and existing atmospheres in various exhaust cleaning processes fluctuate it is important to understand how different kinds of perovskites behave under these reaction conditions and what would be the most effective metal combination for the certain catalytic process. The thermal stabilities of Mn/Co perovskites and effect of Co to the oxidation and reduction behavior were studied by temperature programmed desorption (TPD), oxidation (TPO), and reduction (TPR).

2. Experimental

2.1. Preparation of perovskites

The manganese and cobalt perovskites were synthesized by malic acid complexation [12,19]. The reactants for the A- (La, Pr) and B-site (Mn, Co, Pd) metals were commercially available nitrates. The stoichiometric amounts of reactants were dissolved in water. After all solids were dissolved the malic acid was added in solution, and the pH was adjusted to 3 with NH_3. The water was evaporated in a rotavapor at 70 °C. The formed viscous intermediate products were dried in a sandbath at 150 °C for 4 h. The intermediate product was calcinated in air at 750 °C for 5 h.

2.2. Characterization

A Bruker-AXD D8 Advance X-ray powder diffractometer (CuK_α) was used to determine the structures and the crystallite size of the perovskites. The scanning rate was $0.6° min^{-1}$. The amount of palladium was determined by atomic adsorption spectrometry (AAS, Varian SpectrAA-220). Brunauer–Emmet–Teller (BET) surface areas were measured with a Micromeritics ASAP 2010 device. The perovskite samples were evacuated at 350 °C overnight and the BET measurements were carried out with nitrogen adsorption.

Oxygen temperature programmed desorption (O_2-TPD) and hydrogen temperature programmed reduction (H_2-TPR) measurements were carried out on a Micromeritics AutoChem 2910 device. The perovskite samples were pretreated in a purified oxygen stream at 500 °C for 30 min. The samples were cooled down to 40 °C and the stream was changed to purified helium. The samples were flushed for 3 h in helium stream before the O_2-TPD test was performed. Temperature was increased at $10 °C min^{-1}$. After the O_2-TPD measurement, the perovskite samples were cooled down to 40 °C in helium stream, and the H_2-TPR test was carried out. The reducing gas was 10% H_2/Ar mixture and the rate of temperature increase was $10 °C min^{-1}$ in the test. After the H_2-TPR test the structure of the reduced perovskite was determined by powder XRD and the samples were re-oxidized (950 °C, $\Delta T = 10 °C min^{-1}$) after structure analyse.

Oxygen temperature programmed oxidation (O_2-TPO) and hydrogen temperature programmed reduction (H_2-TPR) measurements were carried out as well. The perovskite samples were pretreated in a purified helium stream at 500 °C for 30 min and cooled to 40 °C. The stream was then changed to 9% O_2/He mixture gas and the O_2-TPO test was performed. The rate of temperature increase was $10 °C min^{-1}$. After O_2-TPO measurement, the samples were cooled down to 40 °C in helium stream and the H_2-TPR test was carried out as described above.

3. Results

Study of the structures of the synthesized perovskites by powder XRD showed that the cubic structure of perovskite was formed in all cases. Properties of the synthesized perovskites are summarized in Table 1. The BET surface areas were be-

Table 1
Data obtained from the synthesized perovskites

Perovskite	Calcination temperature (°C)	Surface area ($m^2 g^{-1}$)	Amount of noble metal (%)	a (Å)	Crystallite size (nm)
$LaMnO_3$	750	19.76	–	3.84	26.2
$LaCo_{0.95}Pd_{0.05}O_3$	750	11.45	2.1	3.81	18.4
$LaMn_{0.57}Co_{0.38}Pd_{0.05}O_3$	750	10.14	2.2	3.85	29.3
$LaFe_{0.57}Co_{0.38}Pd_{0.05}O_3$	750	15.52	2.1	3.88	13.2
$PrMnO_3$	750	17.84	–	3.86	25.5
$PrCoO_3$	750	5.97	–	3.75	50.7
$PrMn_{0.63}Co_{0.37}O_3$	750	18.30	–	3.83	26.1
$PrCo_{0.95}Pd_{0.05}O_3$	750	5.97	2.0	3.88	50.6
$PrMn_{0.57}Co_{0.38}Pd_{0.05}O_3$	750	10.37	1.4	3.82	31.6

a—length of the edge of the lattice cell.