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Synthetic studies of $ABB'O_3$ (A = La, Pr, Nd; B = Fe, Mn; B′ = Pd, Pt) perovskites

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Abstract

Perovskites $LaB_{1-x}B'_xO_3$, $PrB_{1-x}B'_xO_3$ and $NdB_{1-x}B'_xO_3$, where B is Fe or Mn and B′ is Pd or Pt, were synthesized by sol–gel method. Structures were characterized by powder XRD and surface areas, oxygen desorption and reduction properties were determined. The surface areas of prepared perovskites were between 10 and 29 $m^2\,g^{-1}$. The oxygen desorption and reduction studies showed behavior of the perovskites to be similar for different combinations of the A and B cations. The structures of the perovskites were characterized again after desorption (O_2-TPD) and reduction (H_2-TPR) analyses and after a heat treatment test. The XRD diffraction patterns showed that cubic structures of the perovskites were stable at elevated temperatures and under applied atmospheres.

Keywords: Perovskite; Noble metal; XRD

1. Introduction

Perovskite-type oxides have interesting magnetic, electrical, optical and catalytic properties [1]. Recent studies have focused on the catalytic properties as it has been found that perovskites may work as catalyst for exhaust gas cleaning. The structural formula of perovskite-type oxides is ABO_3 and the ideal crystal structure is cubic. In the perovskite structure, A is a larger cation than B. The A-site elements are usually rare earth or earth metals and the B-site elements transition metals of first row in the periodic table. The catalytic activity of perovskite in oxidation conditions is mainly determined by the B-site transition metals [2,3].

Perovskites can be synthesized, for example, by alkoxide [4,5], molten salt [6–8], sol–gel [9–13] or thermal decomposition [14] methods. In sol–gel method reactants are dissolved in suitable solvent, which is usually water. An intermediate product is precipitated with citric [9,11–13] or malic acid [11–13,15,16]. The solvent is evaporated and formed sol–gel is dried and calcinated after complexation.

It is possible to synthesize perovskites where both the A- and B-sites are occupied by two or more metals ($A_{1-x}A'_x$-$B_{1-y}B'_yO_3$). Small amounts of noble metal substituted at the B-site have been reported to increase the activity and selectivity of perovskites in exhaust cleaning processes [1,2,17,18]. Tanaka et al. [2,4,5] have studied the use of $LaFe_{0.95}Pd_{0.05}O_3$ and $LaFe_{0.57}Co_{0.38}Pd_{0.05}O_3$ as the catalyst for automotive applications. The B-site metal in perovskites have been proposed to migrate between the bulk structure and the surface. Palladium is in metallic state under oxidizing atmosphere and dispersed on the surface under reducing conditions. Small palladium particles on the surface of the perovskite return to solid solution after reoxidation [2,4].

The structures of perovskites are determined by powder X-ray diffraction (XRD) [10,19,20]. The purity and homogeneity of synthesized perovskites have been verified from

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the diffraction pattern. The surface areas of the synthesized perovskites can be determined by Brunauer–Emmet–Teller (BET) method [18], where the measurement is based on nitrogen adsorption. The reactivity of perovskite toward various atmospheres as a function of elevated temperatures can be studied by temperature programmed desorption (TPD), temperature programmed oxidation (TPO) and temperature programmed reduction (TPR) analysis [21]. In addition, energy dispersive X-ray (EDX) microanalysis [19] and thermogravimetric method (TG) [22], and X-ray photoelectron spectroscopy (XPS) [2] are useful techniques for exploring the perovskite catalysts.

Our aim in this study was to synthesize and characterize new $AB_{1-x}B'_xO_3$ (A = La, Pr, Nd; B = Fe, Mn; B′ = Pd, Pt) perovskite oxides and compare different synthetic techniques based on sol–gel methods. The characterizations were carried out by XRD, BET, atomic adsorption spectrometry (AAS), TPO and TPR. The TPO and TPR analyses were used to determine the temperature range of the reactivity of the synthesized perovskites and to assess the effect of different metal combinations on the reactivity.

2. Experimental

2.1. Preparation of perovskites

The $AB_{1-x}B'_xO_3$ ($x = 0.020$–0.047) perovskites were prepared by malic acid complexation [11–13]. The reactants for the A-site metals (La, Pr, Nd) and B-site metals (Fe, Mn) were nitrates. $PdCl_2$, $Pd(NO_3)_3$ and $PtCl_2$ were used as precursors for the B′-site. Commercially available reagents were used. Stoichiometric amounts of the nitrates and the noble metal were dissolved in water. The malic acid was added in solution after all solids were dissolved and the pH was adjusted to 3 with NH_3. The water was evaporated in a rotavapor at 70 °C or in a vacuum line until the viscous intermediate product was obtained. After drying 4 h in a sandbath at 150 °C or in vacuum line at 85 °C, the malic acid intermediate products were calcinated in air. The calcination temperatures were 550 and 750 °C. The calcination time was 5 h.

2.2. Characterization

The structure of the prepared perovskite was determined by an X-ray powder diffractometer (Bruker-AXD D8 Advance) using Cu-K_α radiation. Scanning rate was $0.6° \min^{-1}$. The amounts of palladium and platinum were determined by AAS (Varian SpectrAA-400 and 220) using an air–acetylene flame.

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. About 70 mg of perovskite sample was used for each test. In the O_2-TPD test the catalyst sample was pretreated in a purified oxygen stream at 500 °C for 30 min, followed by cooling to 40 °C. The sample was then flushed with a stream of purified helium for 3 h. The rate of temperature increase during the measurement was $10\,°C\,\min^{-1}$. After the O_2-TPD test the sample was cooled down to room temperature (RT) in helium stream and then the H_2-TPR test was carried out. In the H_2-TPR test the reducing gas was 10% H_2/Ar mixture. The rate of the temperature increase was $10\,°C\,\min^{-1}$.

Brunauer–Emmet–Teller (BET) surface areas were determined with a Micromeritics ASAP 2010 device. The perovskite samples (~ 150 mg) were evacuated at 350 °C overnight and the BET measurements were carried out by nitrogen adsorption.

3. Results and discussion

3.1. Synthesis of perovskites

Stoichiometric amounts of reactants were dissolved in water followed by addition of malic acid and subsequent adjustment of pH with NH_3. Different methods were used to remove the excess of solvent and dry the intermediate. When a vacuum line was used in evaporating and/or drying, the process was slow because the volatile solvent caused the cold trap to freeze. Use of a rotavapor to remove excess of solvent followed by drying treatment in a sandbath was the most effective method to prepare the intermediate.

Properties of the prepared perovskites are summarized in Table 1. Comparison of $LaFe_{1-x}Pd_xO_3$ perovskites prepared by different methods showed surface areas to be $\sim 20\%$ larger when the rotavapor and sandbath method was used (method 2). Although the amount of palladium was smaller, this method of synthesis was preferred in subsequent work because large surface area was more important factor than large amount of palladium.

Teraoka et al. [11–13] reported the use of chlorides as metal precursors for the B′-site. In view of the solubility of noble metal reactants and the negative effect of chloride in the exhaust catalyst, we tested palladium nitrate in addition to chlorides as the palladium source. No change of the cubic structure was seen in diffraction pattern and the perovskite surface areas were slightly increased (Table 1). On the basis of these results, palladium nitrate was chosen as the reactant for the B′-site for the perovskites containing palladium.

BET surface areas of synthesized perovskites ranged between 10 and 29 $m^2\,g^{-1}$ depending on the calcination temperature. Table 1 shows that the surface area decreased by about 10 $m^2\,g^{-1}$ when the calcination temperature was increased from 550 to 750 °C. The decrease at higher temperature is in good agreement with studies of Teraoka et al. [11–13] who found BET surface areas to decrease when the calcination temperature was increased. The impurity peaks