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# Dynamic structural changes of perovskite-supported metal catalysts during cyclic redox treatments and effect on catalytic CO oxidation

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## ABSTRACT

CaTiO<sub>3</sub>- and BaTiO<sub>3</sub>-supported Ag and Pt catalysts were subjected to cyclic oxidation and reduction treatments and their surface structures were investigated using X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The CO oxidation reactions over the Ag and Pt catalysts showed that the oxidized Ag/oxide catalysts performed better in CO oxidation than the reduced ones did, whereas the reduced Pt/oxide catalysts had higher CO oxidation activity than that after oxidation treatment. The XRD and XPS measurements revealed that the oxidation treatment helped to improve the dispersion of Ag nanoparticles, but their metallic state was retained, which enhanced CO oxidation. In contrast, the surfaces of the Pt nanoparticles were dominated by PtO<sub>2</sub> after the oxidation treatment, which lowered the CO oxidation activity compared with that of the reduced Pt catalyst.

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## 1. Introduction

Perovskite oxides (ABO<sub>3</sub>) have important applications in heterogeneous catalysis because of their unique crystal structures and chemical properties. Perovskite oxides can be directly used to catalyze many reactions, e.g., BaMO<sub>3</sub> (M = Pb, Bi, Sn) for catalytic combustion of methane [1], LaMO<sub>3</sub> (M = Cr, Mn, Fe, Co, Ni) for oxidation of propylene [2], and LaCoO<sub>3</sub> for CO oxidation [3]. The A and B sites in the ABO<sub>3</sub> structure can both be partially substituted by other cations to form A<sub>1-x</sub>A'<sub>x</sub>B<sub>1-y</sub>B'<sub>y</sub>O<sub>3-δ</sub> (A' = noble metal, B' = transition metal) composite oxides, which show excellent performances in many catalytic reactions. For instance, LaFe<sub>0.57</sub>Co<sub>0.38</sub>Pd<sub>0.05</sub>O<sub>3</sub> [4] and LaFe<sub>0.95</sub>Pd<sub>0.05</sub>O<sub>3</sub> [5] catalysts are used in automotive emissions

control, and LaMO<sub>3</sub> (M = Mn, Fe, Co, and Ni) [6] and La<sub>0.6</sub>Sr<sub>0.4</sub>CoO<sub>3-δ</sub> [7] catalysts give high performances in solid-oxide fuel-cells. Making use of their high chemical and thermal stabilities, these oxides can be used as supports for high-temperature catalytic reactions, e.g., Pt/La<sub>0.7</sub>Sr<sub>0.2</sub>Ce<sub>0.1</sub>FeO<sub>3</sub> [8] and Pt/La<sub>0.5</sub>Ce<sub>0.5</sub>MnO<sub>3</sub> [9] catalysts in lean-deNO<sub>x</sub> reaction, and Ag/LaMnO<sub>3</sub> [10] and Pd/LaMnO<sub>3</sub> [11,12] catalysts in the total oxidation of methane.

In perovskite-based catalysts, the surface structure of the catalyst depends sensitively on the pretreatment conditions. The chemical composition, atomic structure, and chemical state of the catalyst surface often exhibit dynamic changes in various gaseous environments. Among many pretreatment conditions, reduction and oxidation are the most frequently used processes

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es. The redox pretreatments affect the surface structure and, thus, the activity of the catalyst. Changes in the catalyst structure in response to various redox pretreatments may help in understanding the mechanisms of catalyst activation and deactivation [13,14]. For example, Nishihata et al. [4,5] have proposed “intelligent” catalysts, in which perovskite  $\text{LaFe}_{0.57}\text{Co}_{0.38}\text{Pd}_{0.05}\text{O}_3$  and  $\text{LaFe}_{0.95}\text{Pd}_{0.05}\text{O}_3$  catalysts were successfully used in automotive emissions control. When the catalysts were subjected to oxidizing conditions, noble metal atoms were incorporated into the perovskite lattice, and the activity decreased significantly. In contrast, the noble metal ions segregated on the oxide surfaces to form metal nanoparticles under reducing conditions, accompanied by an increase in the activity. During the reaction, the catalysts were subjected to alternating oxidation and reduction conditions, and the noble metal underwent reversible structural changes between metal cations in the oxide lattice and metal nanoparticles on the oxide surface, which prevented the sintering of metal particles and achieved self-regeneration of the catalysts. Scott group studied the treatment-structure-reactivity relationships of  $\text{BaCe}_{0.95}\text{Pd}_{0.05}\text{O}_3$  catalysts [15,16]. They found that Pd atoms were doped in  $\text{BaCeO}_3$  lattice after oxidation treatments, which produced a large number of oxygen vacancies in the oxide and enhanced CO oxidation activity. Under reducing conditions, Pd segregated on the surface to form nanoparticles, which caused a decrease in the CO oxidation activity. The Nishihata’s group and Susannah’s group have demonstrated opposite dependences of reactivity on redox treatments in perovskite-based catalysts, and the difference has not been explained very well. Here, we studied the structure and CO oxidation activity of Pt and Ag catalysts supported on perovskite oxides. Opposite dependences of the catalytic performance on the redox treatment was observed for the perovskite-supported Pt and Ag catalysts. Based on structural investigations, the different structural changes in the supported Pt and Ag catalysts in response to the redox treatments were used to explain their different catalytic behaviors.

## 2. Experimental

### 2.1. Catalyst preparation

$\text{BaTiO}_3$  (BTO)-supported Pt and Ag catalysts were prepared using a sol–gel method [17]. Typically, 2.0 g of  $\text{BaCO}_3$  were dissolved in glacial acetic acid in a molar ratio of 1:10. In parallel, appropriate amounts of titanium(IV) butoxide, acetylacetone, and butanol in molar ratios of 1:2:5 were mixed to form a uniform solution. The  $\text{BaCO}_3$  solution was added dropwise to this solution, and the mixture was stirred vigorously for 1 h. Then, 1 ml of 0.5 mol/L  $\text{AgNO}_3$  or 1 ml of 0.5 mol/L  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  solution was added to the obtained solution and stirred at 50 °C. The resulting gel was dried at 100 °C for 10 h in an oven, and then calcined in air at 800 °C for 2 h. The obtained samples were designated as oxidized samples (M/BTO-Oxidized). The reduced samples (denoted by M/BTO-Reduced) were obtained by heating the oxidized samples in  $\text{H}_2$  at 800 °C for 2 h. The reduced samples were calcined in air at 800 °C for 2 h, produc-

ing the reoxidized samples (M/BTO-Reoxidized).

$\text{CaTiO}_3$  (CTO)-supported metal catalysts were prepared using a similar sol–gel method [18]. Tetrabutyl titanate,  $\text{Ca}(\text{NO}_3)_2$ , and citric acid were dissolved in anhydrous ethanol and dispersed ultrasonically. Then 1 ml of  $\text{AgNO}_3$  solution (0.5 mol/L) or  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  solution (0.5 mol/L) was added to the mixture. Using the same drying and calcining processes, the oxidized samples were obtained (M/CTO-Oxidized). Reduced (M/CTO-Reduced) and reoxidized samples (M/CTO-Reoxidized) were obtained using the same processes as for the M/BTO samples. In all the catalysts, the molar ratio of Ag or Pt to the oxide support was set at 0.05.

### 2.2. Catalyst characterization

X-ray diffraction (XRD) measurements were performed using a Rigaku D/MAX-RB X-ray diffractometer with  $\text{Cu } K\alpha$  radiation ( $\lambda = 0.15418$  nm), operated at 40 kV and 200 mA at room temperature, with a scanning rate of 5°/min. X-ray photoelectron spectroscopy (XPS) studies were carried out using a VG ESCALAB MK2 instrument with an Al  $K\alpha$  excitation source ( $h\nu = 1486.6$  eV). The analyzer mode was set at a constant pass energy of 20 eV.

### 2.3. Catalyst activity

CO oxidation was carried out in a laboratory-built four-channel microreactor, in which four samples can be evaluated in parallel. The products were analyzed using an online six-channel mass spectrometer (Omnistar GSD 301 O2&GSS 300). The reaction gas consisted of 1% CO, 20%  $\text{O}_2$ , and 79% He. The gas hourly space velocity was calculated to be 12000 ml/(g·h). The catalytic performance was evaluated using a temperature-programmed reaction process, with the reaction temperature ramped from room temperature to 300 °C at a ramping rate of 1 °C/min. For quantitative analysis of the CO conversion, one of the four channels was kept empty to have reference signals from the input reactants [19]. The bed temperature when the CO conversion reached 90% is denoted by  $T_{90}$ .

## 3. Results and discussion

### 3.1. Structural change of Ag/ $\text{ABO}_3$ catalysts with redox treatments

The structural changes in the BTO- and CTO-supported Ag catalysts with cyclic oxidation and reduction treatments were investigated using XRD (Fig. 1). The XRD patterns for the BTO and Ag/BTO samples are shown in Figure 1A. Diffraction peaks from the cubic BTO structure are clearly visible in each pattern (JCPDS 86-1570), suggesting that a well-crystallized perovskite structure was obtained using the sol-gel method. After the oxidation and reduction treatments, the patterns of all Ag/BTO samples show obvious peaks of metallic Ag ( $2\theta = 38.2^\circ, 44.5^\circ, 64.5^\circ$ ; JCPDS 01-1167), and no diffraction peaks from  $\text{Ag}_2\text{O}$  are observed. In addition, the main BTO peaks have not shifted in

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