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Lean NO_{XX}–SnO_2–CeO_2 catalyst at low temperatures

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ABSTRACT

Mn_x–Sn_y–Ce_{1-x-y}–$O_{2\pm\mu}$ (denoted Mn–Sn–Ce–O) catalysts prepared through co-precipitation were used for NO_X storage under lean conditions at a low temperature (100 °C). The NO_X storage capacity (NSC) of the Mn–Sn–O dramatically increased after incorporating Ce. The catalyst, which has a 4:5:1 molar ratio of Mn:Sn:Ce (denoted $Mn_{0.4}Sn_{0.5}Ce_{0.1}$), exhibited a breakthrough time of 16 min and a NSC of 565.9 μmol g^{-1} at a gas hourly space velocity (GHSV) of 48,000 mL h^{-1} g^{-1}. Combining the NO adsorption/desorption results with XPS and H_2-TPR, results revealed that the NO oxidation ability of Mn–Sn–Ce–O had improved dramatically due to the Sn–Ce interactions and the surface defect oxygen species. Furthermore, the NO-TPD, NO_2-TPD and *in situ* DRIFTS data indicated that incorporate Ce into the Mn–Sn–O induced a synergistic Sn–Ce effect during NO_X storage, thereby producing more NO_2 adsorption sites on the surface.

1. Introduction

NO_X storage and reduction (NSR) technology can remove the NO_X (NO and NO_2) from the emissions of lean-burn engines [1]. Since they store and reduce NO_X to N_2, the NSR systems can be used with engines operating alternatively under lean and rich conditions. In a traditional NSR catalyst, especially, $Pt/BaO/Al_2O_3$, Pt is vital when oxidizing NO into NO_2, and BaO provides adsorption sites during NO_X storage to form metal nitrates or nitrites on the surface [2].

Currently, traditional $Pt/BaO/Al_2O_3$ catalyst containing noble metal is of high cost for commercial applications in after treatment systems for vehicle exhaust. To solve these cost-related issues, scientists have focused on cheap transition metal oxides that show excellent NO_X storage performance. Due to their excellent ability to oxidize NO at low temperatures [3], manganese-based oxide such as MnO_2–SnO_2 [1,4] and MnO_X–ZrO_2 [5,6] were investigated; ABO_3-type perovskites, such as Ti-doped $BaFe_{1-x}Ti_xO_{3-y}$ [7] and $La_{1-x}Sr_xCoO_3$ [8] also exhibit good de-NO_X performance under lean burn conditions. Nevertheless, neither traditional $Pt/BaO/Al_2O_3$ nor transition metal oxide catalysts have satisfactory NO_X storage capacity at low temperatures (≤150 °C) due to their poor NO oxidation abilities, which is a key step during NO_X storage [9]. The process for converting NO to NO_2 is primarily limited by kinetics and mass transfer below 350 °C [10–13]. Therefore large amounts of NO_X cannot be removed efficiently at low temperatures or during the cold-start stage.

Our group [4] found that MnO_X–SnO_2 catalysts have large NO_X storage capacity at 100 °C due to the oxidizing ability of MnO_X and the strong interaction between the SnO_2 and NO. Among the various Mn_n–$Sn_{(1-n)}O_x$ catalysts (n is the molar ratio of Mn/(Mn + Sn), $n = 0, 1, 2, 3, 4, 5$), $Mn_{0.4}Sn_{0.6}$ displayed the best NO_X storage performance with a NSC of 3290 μmol g^{-1}. On the other hand, Ce-based catalysts have also been investigated due to their moderate basicity [14,15] and oxygen storage capacity between Ce^{3+} and Ce^{4+} [16,17]. Previous studies indicated that MnO_X–CeO_2 prepared through co-precipitation method could provide numerous NO_X adsorption sites on the MnO_X–CeO_2 surface during NO adsorption [18], and on MnO_X–CeO_2 system Ce provided active adsorption sites on the surface [19]. Therefore, incorporating Ce into MnO_X–SnO_2 to enhance

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the NO_X storage ability is highly expected. We attempted to incorporate Ce into binary $Mn_{0.4}Sn_{0.6}$ metal oxides to enhance its de-NO_X ability at low temperatures.

This work aimed to investigate the NO_X storage properties of a novel Mn–Sn–Ce–O ternary metal oxide catalyst with different metal ratios and to explore the mechanism for NO_X storage. XRD, BET, XPS, NO and NO_2 adsorption/desorption experiments, as well as *in situ* DRIFTS measurements were used to characterize the structure, redox properties and storage capacities of the catalysts.

2. Experimental methods

2.1. Catalyst preparation

Mn–Sn–Ce–O catalysts with various Sn/(Mn + Sn + Ce) ratios were synthesized using a redox co-precipitation method. During preparation, the catalyst precursors ($MnSO_4·H_2O$, $(NH_4)_2S_2O_8$, $SnCl_4·5H_2O$ and $Ce(NO_3)_3·6H_2O$) were mixed with 150 mL deionized water in a beaker. Subsequently, 25% ammonia was dropwise added into the solution as a precipitator. Afterwards, the mixture was stirred at 50 °C for 1 h. After filtration, the precipitate was washed 3 times with deionized water, dried at 110 °C overnight, and calcined at 500 °C for 4 h in air. Finally, the samples were crushed and sieved to 40–60 meshes for the NO_X adsorption experiments. The catalysts were denoted $Mn_xSn_yCe_z$, where x, y, z present the molar ratios of Mn/(Mn + Sn + Ce), Sn/(Mn + Sn + Ce) and Ce/(Mn + Sn + Ce).

$$S_2O_8{}^{2-} + Mn^{2+} + 4NH_3·H_2O \rightarrow 2SO_4{}^{2-} + MnO_2 + 2H_2O + NH_4{}^{+} \quad (1)$$

$$S_2O_8{}^{2-} + 2e^{-} = 2SO_4{}^{2-} \quad E^{\theta} = 2.01\,V \quad (2)$$

$$Mn^{2+} + 2H_2O = MnO_2 + 4H^{+} + 2e^{-} \quad E^{\theta} = 1.23\,V \quad (3)$$

Above equations show the chemical reactions during sample preparation. Eq. (1) shows that the molar ratio of $MnSO_4·4H_2O$ and $(NH_4)_2S_2O_8$ was kept at 1:1. Eqs. (2) and (3) indicate the redox reactions during preparation.

2.2. Characterizations

The X-ray diffraction (XRD) patterns of the catalysts were obtained with a Bruker D8 Advance X-ray diffractometer (Rigaku, D/max-2200, Japan) using Cu Kα (k = 1.5418 Å) radiation and operated at 40 kV and 40 mA. The scanning range was 10–90° with a step size of 8° min^{-1}.

The BET surface areas and average particle sizes were measured by N_2 adsorption/desorption experiments at 77.3 K while using a Micromeritics ASAP2020. Before the analysis, samples were degassed at 300 °C for 4 h. The specific surface area was determined from the linear portion of the Brunauer–Emmett–Teller (BET) equation at P/P_0 in the range of 0.05–0.35, and average particle sizes was determined by the Barrett–Joyner–Halenda (BJH) method using the desorption branches in 0.35–0.95 partial pressure range.

The X-ray photoelectron spectroscopy (XPS) data were obtained with a VG Scientific ESCALab 220i-XL electron spectrometer using 300 W Mg Kα radiation. The base pressure was 3×10^{-9} mbar, and the C 1s (284.8 eV) line was used as the binding energies reference. The Mn 2p, Sn 3d, Ce 3d and O 1s spectra were measured for the Mn–Sn–Ce–O oxides.

The temperature-programmed reduction (TPR) experiments were conducted on a Micromeritics ChemiSorb 2720 using approximately 50 mg samples. After a pretreatment at 300 °C under argon for 1 h, the samples were cooled to room temperature. The reducing gas, which is a mixture of 10% H_2/Ar flowing at 40 mL min^{-1}, was used to reduce the catalysts with heating from room temperature to 1000 °C at 10 °C min^{-1}.

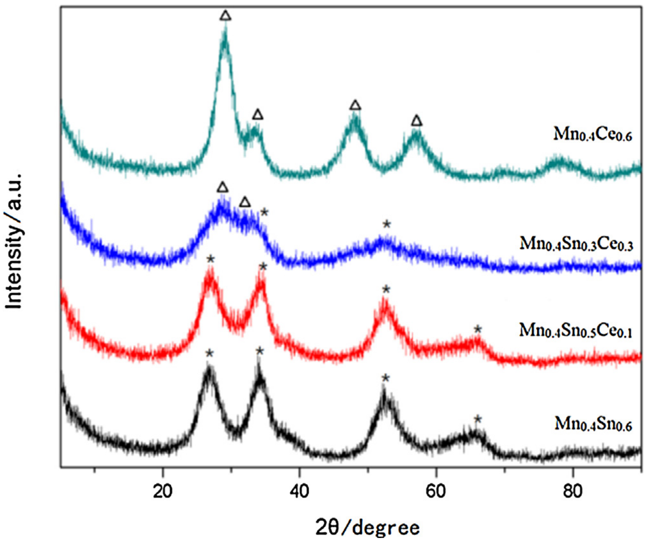

Fig. 1. XRD patterns of the Mn–Sn–Ce–O series of catalysts (Δ – CeO_2;* –SnO_2).

The *in situ* diffuse reflectance infrared Fourier transform spectra (DRIFTS) experiments from the NO adsorption and desorption were recorded on a NICOLET 6700-FTIR. The samples were finely ground and placed in the sample cell. The feed gas streamed into the cell at 100 mL min^{-1}. Before the NO adsorption, the samples were initially heated to 500 °C under N_2 and O_2 for 30 min. The background spectra were collected after holding at one desired temperature for 15 min. The spectra reported here were collected after holding for 30 min. In all cases, the IR spectra were recorded over 32 scans at a resolution of 4 cm^{-1}.

2.3. NO_X storage performance

The NO adsorption/desorption experiments were carried out in a quartz reactor under normal atmospheric pressure. The samples (0.5 g) were pretreated using 8% O_2/N_2 (400 mL min^{-1}) at 500 °C for 60 min before they were cooled to 100 °C under N_2. When the temperature stabilized at 100 °C, a mixed gas (400 mL min^{-1}) including 500 ppm NO and 8% O_2 with the balance composed of N_2, was introduced for reaction with the samples over 60 min. Afterwards, the mixed gas was replaced with pure nitrogen (400 mL min^{-1}) to remove the weakly adsorbed species on the catalyst surfaces. Next, temperature-programmed desorption (TPD) experiments were performed by increasing the temperature from room temperature to 500 °C at 10 °C min^{-1} under 400 mL min^{-1} N_2. The concentrations of NO and NO_2 in the outlet stream were recorded by an online FT-IR spectrometer (MKS, MultiGas 2030HS).

Similarly, NO_2 adsorption/desorption experiments were carried out. The NO_X storage capacity and NO_2 storage capacity, which were calculated based on the integrated areas of the NO-TPD and NO_2-TPD profile, respectively, were used to characterize the NO_X storage ability and surface NO_2 adsorption sites.

3. Results and discussion

3.1. Physical characterizations of the catalysts

The XRD patterns of the Mn–Sn–Ce–O catalysts are shown in Fig. 1. The typical peaks of rutile SnO_2 (JCPDS #1-0657) appeared in the $Mn_{0.4}Sn_{0.6}$ and $Mn_{0.4}Sn_{0.5}Ce_{0.1}$. After increasing the Ce