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Short communication

Porous bimetallic $Mn_2Co_1O_x$ catalysts prepared by a one-step combustion method for the low temperature selective catalytic reduction of NO_x with NH_3

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ABSTRACT

The porous $Mn_2Co_1O_x$ catalysts are prepared by a one-step combustion (CB) method for low temperature deNO$_x$ process. This catalyst displays an excellent NH_3-SCR activity, achieving 100% NO_x conversion at 150–300 °C. In addition, the catalyst shows high N_2 selectivity, wide operating temperature window, high stability, and high H_2O and SO_2 resistance. The crystalline phase of $CoMn_2O_4$, porous structure and large specific surface areaare beneficial for the deNO$_x$ activity. The catalyst exists abundant Mn^{4+}, Co^{3+} and surface adsorbed oxygen species, which improve the catalyst's redox ability. Plenty of acid sites from the strong interaction of manganese and cobalt oxide enhance the catalyst performance.

1. Introduction

Nitrogen oxides emitted from thermal power plants are currently considered as the main sources of a series of environmental issues [1, 2]. Selective catalytic reduction (SCR) with NH_3 is a well-proven technique to reduce NO_x emissions [3]. Nowadays the most widely used catalyst is V_2O_5–WO_3(MoO_3)/TiO_2 for NO_x control. However, there are some inevitable problems for this catalyst, such as the toxicity of VO_x, a relatively narrow temperature window (300–400 °C) and the deactivation caused by dust and SO_2 [4]. Therefore, it is vital for us to develop the low-temperature SCR catalysts which can be located the downstream of the desulfurizer and the electrostatic precipitator [5,6].

Transition metal (Fe, Cr, Ce, and Mn) oxide catalysts have been explored intensively in the low-temperature SCR reaction [7,8]. Mn-based oxide catalysts with the superiority of unique activities at low temperature and excellent redox properties have received much attention [9–11]. But due to the high sulfur sensitivity of the Mn-based catalysts, which can induce a severe deactivation, researchers have studied modified Mn-based catalysts by doping the other transition metal oxides [7,12]. Chen et al. showed that Mn–Cr mixed oxide catalysts yielded 98.5% NO_x conversion and high SO_2 tolerance at 120 °C because of the formation of $CrMn_{1.5}O_4$ phase [7]. Lian et al. indicated that $Mn_2Nb_1O_x$(500) could obtain 94% NO_x conversion and 96% N_2 selectivity at 125 °C [12]. Wan et al. found that the Ni(0.4)–MnO_x catalyst showed 85% of NO conversion at 95 °C and 100% from 120 to 240 °C [13]. Although the research obtained some achievements, it is still important to discover new Mn-based catalysts, which have superior catalytic activity, high SO_2 tolerance and stability.

Cobalt oxides have long been studied widely in the field of catalysts, due to the terrific redox properties and morphology characteristics [14–16]. Previous researches have already noted that the coupling of Mn and Co oxides has improved the catalytic activity for the oxidation of n-hexane [17–18]. But there have been few reports on Mn–Co mixed oxides for SCR of NO_x with NH_3. In this study, a series of Mn–Co oxide catalysts, prepared by the one-step combustion method, were examined for the deNO$_x$ performance and they were the potential catalysts for the low temperature deNO$_x$ process with high resistance to SO_2 poisoning.

2. Experiments

2.1. Catalyst preparation

The $Mn_2Co_1O_x$ catalyst powders were synthesized using a one-step combustion (CB) method [19]. Stoichiometric amounts of $Mn(NO_3)_2 \cdot 4H_2O$ (A) and $Co(NO_3)_2 \cdot 6H_2O$ (B) (the mole ratio of A and B was 2:1) were used as the metal precursors. Glycine and citric acid were used to assist combustion so that the catalysts can get the porous structure. The detailed process could be found in the Supplementary Data. The obtained oxides were denoted $Mn_2Co_1O_x$ (CB). Pure MnO_x and CoO_x were also prepared using the same procedure.

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For comparison, the $Mn_2Co_1O_x$ particles were prepared by co-precipitation (CP) method, noted as $Mn_2Co_1O_x$ (CP), according to literature with some modification [20].

2.2. Catalyst characterization

The obtained products were characterized by X-ray diffraction (XRD, Rigaku Ultima IV, Cu Ka radiation, 40 kV, 40 mA). The morphology was characterized using a scanning electron microscope (SEM, QUANTA FEG 250). The specific surface area and pore size distribution were determined by N_2 adsorption–desorption measurements at 77 K using a Quantachrome Instrument ASIQM000-1-MP. Prior to N_2 adsorption, the samples were degassed at 300 °C for 4 h. X-ray photoelectron spectroscopy (XPS) was carried out on a PHI QUANTERA-II from Japan Ulvac-PHI INC using 25 W Al-Kα radiation. The binding energies were referenced to the C 1s line at 284.8 eV.

H_2 temperature programmed reduction (H_2-TPR) and NH_3 temperature programmed desorption (NH_3-TPD) were performed on a Quantachrome Chembet Pulsar. The H_2 consumption was quantified by a thermal conductivity detector (TCD). Prior to H_2-TPR experiment, 50 mg of catalysts was pretreated with He with a total flow rate of 30 $mL\cdot min^{-1}$ at 450 °C for 1 h, then heated in 5% H_2/Ar (30 $mL\cdot min^{-1}$) from room temperature to 800 °C with a ramping rate of 10 $°C\cdot min^{-1}$. For the NH_3-TPD experiments, the catalysts (100 mg) were pretreated at 450 °C for 1 h in flowing He, then was exposed at 80 °C to NH_3 until saturation followed by purging with He for 30 min to remove adsorbed species. Finally, the reactor temperature was raised to 800 °C at a rate of 10 $°C\cdot min^{-1}$ for NH_3 desorption.

2.3. Catalytic activity measurement

The NH_3-SCR activity tests were performed in a fixed-bed quartz reactor with an inner diameter of 8 mm under the following condition: 1000 ppm NH_3, 1000 ppm NO, 5 (vol)% O_2, 10 (vol)% H_2O (when used), 100 ppm SO_2 (when used) and balance N_2, 0.3 g catalyst (60–100 mesh), the flow rate was 500 $mL\cdot min^{-1}$, thus the GHSV of 30,000 h^{-1} was obtained. The outlet NO_x was monitored by a gas analyzer (MRU VARIO PLUS, Germany), the NH_3 and N_2O were monitored by a Benchtop Gas Analysis System (HPR-20 QIC). From the concentration of the gases at steady state, NO_x conversion was calculated according to the following equation:

$$NO_x \text{ conversion } (\%) = \frac{[NO_x]_{in} - [NO_x]_{out}}{[NO_x]_{in}} \times 100\%.$$

The N_2 selectivity in SCR reaction was calculated according to the following equation [21]:

$$S_{N_2} = \left(1 - \frac{2[N_2O]_{out}}{[NO_x]_{in} + [NH_3]_{in} - [NO_x]_{out} - [NH_3]_{out}}\right) \times 100\%$$

where $[NO_x] = [NO] + [NO_2]$.

3. Results and discussion

3.1. Low-temperature activity for NO_x conversion and N_2 selectivity of $Mn_2Co_1O_x$ (CB), $Mn_2Co_1O_x$ (CP), MnO_x (CB), CoO_x (CB)

The NO_x conversion and N_2 selectivity of $Mn_2Co_1O_x$ (CB), $Mn_2Co_1O_x$ (CP), MnO_x (CB) and CoO_x (CB) catalysts are shown in Fig. 1. CoO_x (CB) showed negligible activity, but MnO_x exhibited a relatively higher catalytic activity of 80% NO_x conversion at 200 °C (Fig. 1A). $Mn_2Co_1O_x$ (CB) and $Mn_2Co_1O_x$ (CP) catalysts both achieve excellent deNOx efficiency, especially for $Mn_2Co_1O_x$ (CB). Meanwhile, $Mn_2Co_1O_x$ (CB) had the highest N_2 selectivity, approximately 100% N_2 selectivity at 100–250 °C, compared with $Mn_2Co_1O_x$ (CP), MnO_x (CB) and CoO_x (CB). The N_2 selectivity of $Mn_2Co_1O_x$ (CB) had a tiny decline with temperature increasing, but still remaining 90% at 350 °C; and the $Mn_2Co_1O_x$ (CB) catalyst owned the wider operation temperature window compared with $Mn_2Co_1O_x$ (CP), which implies the better catalytic activity for $Mn_2Co_1O_x$ (CB) than that of $Mn_2Co_1O_x$ (CP). Compared with MnO_x and CoO_x catalysts, the outstanding activity for the $Mn_2Co_1O_x$ catalysts can be due to some synergistic effect between Mn and Co species. Compared with $Mn_2Co_1O_x$ (CP) catalysts, the high catalytic activity of the $Mn_2Co_1O_x$ catalysts can be owed to the abundant Brønsted and Lewis acid sites, which will be investigated further in the subsequent experiment.

3.2. Analysis of XRD, SEM and BET

The XRD patterns of Mn–Co oxide catalysts are depicted in Fig. S1 of the

Supplementary Information (SI). MnO_x (CB) and CoO_x (CB) samples represent Mn_3O_4 and Co_3O_4, and $Mn_2Co_1O_x$ (CB) and $Mn_2Co_1O_x$ (CP) catalysts belong to the spinel structure $CoMn_2O_4$. The $Mn_2Co_1O_x$ (CB) catalysts have the higher crystallinity, which may be a reason of the better NO conversion of the $Mn_2Co_1O_x$ (CB) catalysts.

The SEM images of the $Mn_2Co_1O_x$ (CB) and $Mn_2Co_1O_x$ (CP) catalysts are shown in Fig. 2. The $Mn_2Co_1O_x$ (CB) catalysts present polyporous

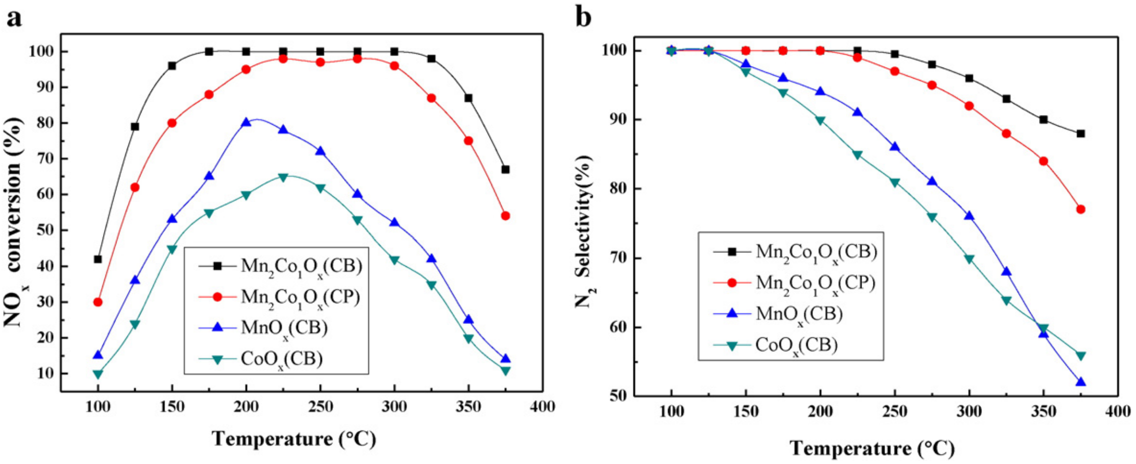

Fig. 1. (A) SCR activity and (B) N_2 selectivity of $Mn_2Co_1O_x$ (CB), $Mn_2Co_1O_x$ (CB), MnO_x (CB) and CoO_x (CB), calcined at 450 °C. Reaction conditions: [NO] = [NH_3] = 1000 ppm, [O_2] = 5(vol)%, N_2 balance, and GHSV = 30,000 h^{-1}.