Catalysis Communications 40 (2013) 47–50

Contents lists available at SciVerse ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

A Ce–Sn–O_x catalyst for the selective catalytic reduction of NO_x with NH_3

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ARTICLE INFO

Article history:
Received 7 March 2013
Received in revised form 20 May 2013
Accepted 22 May 2013
Available online 31 May 2013

Keywords:
Ce–Sn–O_x catalyst
NH_3-SCR
Anti-poisoning
Synergistic effect

ABSTRACT

A series of Ce–Sn–O_x catalysts prepared by the facile coprecipitation method exhibited good catalytic activity in a broad temperature range from 100 °C to 400 °C for the selective catalytic reduction of NO_x with NH_3 at the space velocity of 20,000 h^{-1}. The $Ce_4Sn_4O_x$ catalyst calcined at 400 °C showed high resistance to H_2O, SO_2, K_2O and PbO under our test conditions. The better catalytic performance was associated with the synergistic effect between CeO_2 and SnO_2, which strengthened the NH_3 and NO_x adsorption capacity on the surface of the catalyst.

1. Introduction

Nitrogen oxides are widely thought to be a major source of air pollution, because they can contribute to acid rain, photochemical smog, ozone depletion and endangering human health [1]. Selective catalytic reduction of NO_x with NH_3 (NH_3-SCR) is an effective and economical method to reduce NO_x emissions. Nowadays the most widely used catalyst is V_2O_5–WO_3/TiO_2 or V_2O_5–MoO_3/TiO_2 for NO_x control. However, there are some inevitable problems that remain in this catalyst, such as the toxicity of vanadium species, a relatively narrow temperature window (300–400 °C) and the weak ability to resist metal oxides (e.g., K_2O and PbO) poisoning in the practical application [2–5].

Cerium-based oxides catalysts with the superiority of unique oxygen storage capacity and excellent redox properties have received much attention for their use in NH_3-SCR reaction. In recent years, a series of Ce-based catalysts have been reported such as MnO_x–CeO_2 [6], ceria modified MnO_x/TiO_2 [7], WO_3/CeO_2–ZrO_2 [8], CeO_2/TiO_2 [9–11], CeO_2/Al_2O_3 [12], Ce–P–O [13], Ce–W mixed oxides et al. [14], all of these catalysts have exhibited a variety of catalytic activity under different conditions.

Alternatively, SnO_2 has been widely used as an oxidation catalyst as it can reversibly undergo between Sn^{4+} and Sn^{2+}. Thus it can improve the redox efficiency and enhance the oxygen storage capacity of CeO_2 by substituting part of Ce^{4+} with Sn^{4+}. Sasikala et al. synthesized the Ce–Sn mixed oxides that showed better activity for CO oxidation reaction [15]. Chang et al. found that SnO_2-modified MnO_x–CeO_2 catalyst can improve the SCR performance and enhance the resistance to SO_2 [16]. In this study, the Ce–Sn–O_x catalysts were prepared by the coprecipient method. Brunauer–Emmett–Teller (BET), X-ray diffraction (XRD), NH_3-temperature-programmed desorption (NH_3-TPD) and the *in situ* diffuse reflectance infrared Fourier transform spectroscopy (*in situ* DRIFTS) were performed for the catalysts. The influences of H_2O, SO_2, K_2O and PbO were also investigated respectively.

2. Experimental

2.1. Catalyst preparation

The Ce–Sn–O_x catalyst was synthesized by the co-precipitation method using $(NH_4)_2Ce(NO_3)_6$ and $SnCl_4 \cdot 5H_2O$ as precursors and 25 wt% $NH_3 \cdot H_2O$ as precipitator. The catalysts were signed as $Ce_aSn_bO_x$-M, where the a/b represented the Ce/Sn molar ratio and M denoted the calcination temperature (°C). Pure CeO_2 and SnO_2 were also prepared using the same method for parallel experiment purpose.

2.2. Characterization of catalysts

The BET results were measured by N_2 adsorption at 77 K using a Micromeritics Tristar-3000 system. XRD patterns were recorded on a Rigaku D/max 2500 with Cu Kα radiation. NH_3-TPD was utilized to study the catalyst acidity on a Micromeritics Auto Chem II 2920 instrument. The *in situ* DRIFTS experiments were performed on a Fourier transform infrared spectrometer (Nicolet Nexus 670) equipped with an *in situ* diffuse reflection chamber and high sensitivity mercury–cadmium–telluride detector.

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http://dx.doi.org/10.1016/j.catcom.2013.05.024

2.3. Activity test

The SCR activity measurements were carried out in a fixed bed quartz reactor (inner diameter 10 mm), which contained 0.45 mL catalyst under atmospheric conditions. A K-type thermocouple (o.d.1 mm) was directly immersed into the catalyst bed from the bottom of the reactor and connected to a programmable temperature controller to monitor the reaction temperature. The composition of the model flue gas was: 500 ppm NO, 500 ppm NH_3, 5 vol% O_2, 5 vol% H_2O (when used), 100 ppm SO_2 (when used), banlance N_2, and 150 mL min^{-1} total flow rate, yielding a GHSV of 20,000 h^{-1}. The water vapor was introduced by an injection pump (LSP01-1A, LongerPump Inc) and an evaporator. The concentrations of NO and NO_2 in the inlet and outlet gas were measured by an online chemiluminescent NO/NO_x analyzer (Model 42i-HL, Thermo Inc). The datum was collected after 1 h when the SCR reaction had reached a steady state. NO_x conversion was calculated by using: NO_x conversion $= (1-[NO_x]_{out}/[NO_x]_{in}) \times 100\%$; with $[NO_x] = [NO] + [NO_2]$.

3. Results and discussion

3.1. NH_3-SCR activity test

Fig. 1A presented the influences of calcination temperature on NO conversions over $Ce_4Sn_4O_x$ catalysts. It can be seen that the $Ce_4Sn_4O_x$-400 showed the best activity in the whole temperature range. The $Ce_4Sn_4O_x$-300 exhibited lower conversion from 100 °C to 400 °C, which might be associated with some tin ions being incorporated into the ceria lattice. Whereas with the calcination temperature increased the decline of low-temperature activity was possibly related to the sintering effect. Based on the results above, the optimal calcination temperature was chosen at 400 °C, the effects of the Ce/Sn molar ratio on the activity of $Ce_aSn_bO_x$-400 catalysts were shown in Fig. 1B. Clearly, both pure SnO_2 and pure CeO_2 exhibited limited SCR activity in the entire temperature scope. With the Ce/Sn molar ratio being 1:4, the reaction temperature window was greatly broadened with more than 96% NO conversion being achieved from 250 °C to 400 °C. As the Ce/Sn molar ratio increased to 4:4, the low-temperature (<250 °C) catalytic activity was improved significantly. However, further increase of the Ce/Sn ratio to 4:1 resulted in a decrease of NO_x conversion in the tested temperature range. This may be connected with the decrease of active sites on the surface of catalyst [14].

3.2. The effects of impurities on NH_3-SCR activity

The flue gases often contain a certain concentration of SO_2, water vapor, K_2O and PbO, which can decrease the catalytic activity and the operational life of the catalysts, hence it is essential to evaluate the resistance to the deactivation caused by these compounds.

The influences of 100 ppm SO_2 and 5 vol% H_2O on the performance of the $Ce_4Sn_4O_x$-400 were investigated at 300 °C and the results were illustrated in Fig. 2A. Before adding SO_2 or/and H_2O the reaction was stabilized for 3 h, after stopping them the reaction continues to be recorded for 4 h. It could be seen that a slight NO conversion decline occurred during 100 ppm SO_2 was added 1–6 h and then became stable, after removing SO_2 the conversion recovered to 97.5%. When 5 vol% water vapor was introduced into the stream, the NO conversion kept at about 97% during the tested period, after stopping the water vapor the conversion restored to 99%. When the 100 ppm SO_2 and 5 vol% H_2O were injected into the feed gases at the same time, NO conversion decreased a little more, but the NO conversion still maintained at about 92%. The above results suggested that the catalyst had certain SO_2/H_2O durability.

In order to evaluate the impacts of PbO and K_2O on the performance of Ce–Sn–O_x catalyst, here we prepared V_2O_5–WO_3/TiO_2 catalyst and supported 2.5 wt% PbO or 3.0 wt% K_2O to carry out the parallel test. As shown in the Fig. 2B, the $Ce_4Sn_4O_x$-400 catalyst performed much higher resistance to the PbO or K_2O than V_2O_5–WO_3/TiO_2 in the whole temperature range. Gao et al. and Khodayari et al. proved that doping K_2O or PbO could reduce the surface acidity separately [4,5]. The good tolerance to the K_2O or PbO poisoning of the $Ce_4Sn_4O_x$-400 catalyst can probably be associated with the acidity that was enhanced by the introduction of SnO_2.

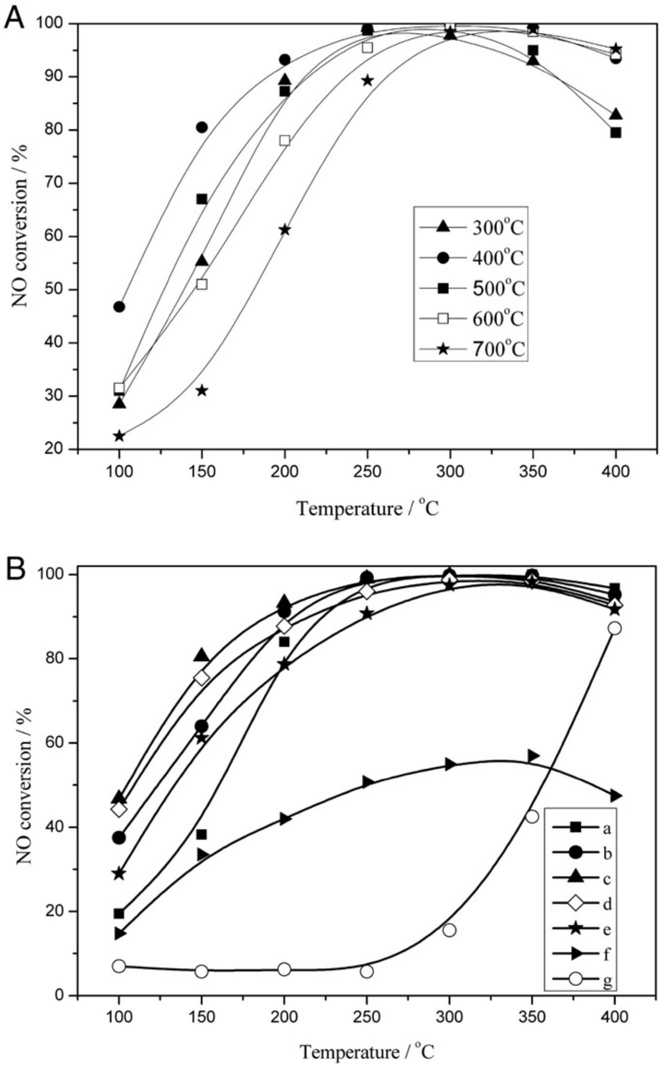

Fig. 1. (**A**) The influences of calcination temperature on the NH_3-SCR activity over $Ce_4Sn_4O_x$ catalysts under GHSV of 20,000 h^{-1}. (**B**) The effects of Ce/Sn molar ratios on the NH_3-SCR activity over Ce–Sn–Ox catalysts under GHSV of 20,000 h^{-1}. (a) Ce_4SnO_x – 400, (b) $Ce_4Sn_2O_x$-400, (c) $Ce_4Sn_4O_x$-400, (d) $Ce_2Sn_4O_x$-400, (e) $CeSn_4O_x$-400, (f) CeO_2-400, (g) SnO_2-400.

3.3. XRD patterns

The XRD was carried out to investigate the $Ce_4Sn_4O_x$ catalysts and the patterns were displayed in Fig. 3. As for the $Ce_4Sn_4O_x$ catalyst calcined at 300 °C, the diffraction peaks attributed to SnO_2 were not shown and only broad peaks due to CeO_2 were observed. It might suggest that some SnO_2 were wrapped in the CeO_2 or the SnO_2 were mainly existing in the amorphous. The typical diffraction peaks that belonged to cassiterite SnO_2 at 2θ values of 26.66, 33.97, 51.84° were found when the calcined temperature reached 400 °C. When the calcination temperature was further increased from 500 °C to 700 °C, the diffraction peaks attributed to CeO_2 and SnO_2 became much narrower and sharper. The average crystallite sizes of CeO_2 and SnO_2 were also calculated by Scherrer equation, the CeO_2 average crystallite sizes of