Short Communication

Selective catalytic reduction of NOx by NH3 over MoO3-promoted CeO2/TiO2 catalyst

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ABSTRACT

The addition of MoO3 enhanced the activity of CeO2/TiO2 catalyst for the selective reduction of NOx with NH3. The MoO3-promoted CeO2/TiO2 exhibited higher activity than CeO2/TiO2 even in the co-presence of H2O and SO2. This is because the introduction of Mo to the Ce10Ti catalyst can inhibit the adsorption of H2O and SO2 as well as the formation of sulfate species on the catalyst surface, thus alleviating the poisoning effect of H2O and SO2.

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1. Introduction

Nitrogen oxides (NOx) are serious pollutants that cause not only the formation of acid rain but also photochemical smog. Selective catalytic reduction of NOx with NH3 (NH3-SCR), using V2O5–WO3(MoO3)/TiO2 as catalyst, has attracted much attention as a practical method to remove NOx emitted from stationary sources [1]. However, the toxicity of vanadium and the narrow temperature window (300–400 °C) has restrained the practical application of V-based catalyst [2]. For the above reasons, it is desirable for developing novel NH3-SCR catalyst with no vanadium but high deNOx performance.

Recently, Ce-based catalyst seems to be promising for the NH3-SCR of NOx [3–5]. Ce/TiO2 catalyst prepared by impregnation method was reported to be active for the NH3-SCR of NOx [6]. Gao et al. [7] also found that Ce/TiO2 is active for this reaction. However, the presence of SO2 leads to a noticeable decrease of the deNOx activity [7,8]. From a practical point of view, the ability of resistance against H2O and SO2 is important for any catalyst with potential deNOx application. Chen et al. [9] found that the addition of W results in the enhancement of the activity of Ce/TiO2 catalyst. Moreover, its resistance against H2O and SO2 was also improved due to the existence of W. Recently we found that the addition of MoO3 can improve the activity of Ce/TiO2 catalyst in the absence of H2O and SO2 [10]. However, the effects of the H2O and SO2 as well as the impregnation preparation procedure on the catalytic performance of MoO3-promoted Ce/TiO2 catalyst remain unclear.

In this study, it was found that CeO2–MoO3/TiO2 is more active than CeO2/TiO2 even in the co-presence of H2O and SO2. The impregnation preparation procedure also influences the catalytic performance. On the basis of the characterization results, the cause of the promoting effect of MoO3 has been proposed.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by the impregnation method, and Degussa AEROSIL TiO2 P25 was used as support. 10 wt.% CeO2/TiO2 (Ce10Ti) catalyst was prepared by impregnating TiO2 with a proper amount of cerium nitrate (Ce(NO3)3·6H2O) solution, then stirred for 4 h, followed by drying at 120 °C and calcinations at 500 °C for 4 h in the air. 5 wt.% MoO3/TiO2 (Mo5Ti) catalyst was prepared by the same method as described above using ammonium molybdate ((NH4)6Mo7O24·4H2O) and oxalic acid (H2C2O4·2H2O) solution instead. Ce10Mo5Ti catalyst was prepared by impregnating Mo5Ti powder with an aqueous solution of cerium nitrate, stirred for 4 h, then dried at 120 °C and calcined at 500 °C for 4 h in air. Mo5Ce10Ti catalyst was prepared according to the opposite procedure, where Ce10Ti powder was impregnated with ammonium molybdate and oxalic acid solution.

2.2. Catalytic activity measurement

The activity measurements were carried out in a fixed-bed quartz reactor using a 0.12 g catalyst of 40–60 meshes. The feed gas mixture...
contained 500 ppm NO, 500 ppm NH3, 5% O2 and helium as the balance gas. The total flow rate of the feed gas was 300 cm3·min−1, corresponding to a GHSV of 128,000 h−1. In order to investigate the effects of H2O and SO2 on the activity of the catalyst, 5% H2O and/or 50 ppm SO2 was introduced into the reaction gas mixture. The reaction temperature was increased from 200 to 400 °C. The composition of the product gas which was produced by the reaction of NH3 with nitrate at high temperatures [3]. Consequently, the addition of MoO3 showed a promoting effect on the activity and the change in impregnation preparation procedure affected the catalytic performance of MoO3-promoted Ce10Ti catalyst.

3.2. Effect of H2O and SO2

The effect of H2O and SO2 on the activities of Ce10Ti, Ce10Mo5Ti and Mo5Ce10Ti catalysts was investigated and the results are shown in Fig. 2A. Compared with Fig. 1, it can be seen that the activity of Ce10Ti catalyst was seriously suppressed by the presence of H2O and SO2. Only about 50% NOx conversion was obtained in the presence of H2O (or H2O and SO2) at 300 °C. Although the presence of H2O and SO2 also leads to the decrease of the NOx conversion over Ce10Mo5Ti catalyst, the conversion is much higher than that obtained over Ce10Ti catalyst. At 300 °C, 84% and 75% NOx conversions were obtained in the presence of H2O and co-presence of H2O and SO2, respectively.

![Fig. 2. (A) Effect of H2O and SO2 on the NOx conversion over Ce10Ti, Ce10Mo5Ti and Mo5Ce10Ti catalysts. (B) The response of the NOx conversion over Ce10Mo5Ti catalyst at 300 °C to the intermittent feed of H2O and SO2. Reaction conditions: [NO] = [NH3] = 500 ppm, [O2] = 5%, [H2O] = 5%, [SO2] = 50 ppm, GHSV = 128,000 h−1.](image-url)
Ce10Mo5Ti exhibited noticeably higher activity than Mo5Ce10Ti catalyst in the presence of H2O. And below 300 °C the NOx conversion over Ce10Mo5Ti in the presence of H2O is even higher than that of Ce10Ti catalyst in the absence of H2O. In the co-presence of H2O and SO2 100% N2 selectivity can be obtained over these catalysts (see Fig. S1).

Fig. 2B illustrated the response of the NOx conversion over Ce10Mo5Ti catalyst at 300 °C to the intermittent feed of H2O and SO2. The coexistence of H2O and SO2 induced a gradually decrease of NOx conversion and the conversion was decreased to 71% from 93% in 10 h. After stopping H2O and SO2, the NOx conversion was increased to 87%. The loss of SCR activity could be ascribed to the deposit of sulfate on the catalyst surface [11].

3.3. Effect of O2

It is well recognized that oxygen plays an important role in the NH3-SCR of NOx [12]. The effect of oxygen on catalytic activity was studied in this work. As shown in Fig. S2, the NOx conversion is only 34% over Ce10Mo5Ti catalyst at 300 °C in the absence of oxygen. However, the conversion was increased significantly when 1% oxygen was introduced into the reactants. With the oxygen concentration further increasing, the NOx conversion was seldom changed. This indicates that oxygen plays a significant promoting role in the SCR reaction. Similar promoting effect was also observed over MnOx–CeO2 catalyst by Qi and Yang [12].

The presence of oxygen can be adsorbed and activated on the surface of Ce10Mo5Ti catalyst thus forming the surface chemisorbed oxygen species, which was reported to be highly active for the NH3-SCR of NOx [13].

3.4. Catalyst characterization

Fig. 3 showed the XRD patterns of Ce10Ti, Ce10Mo5Ti and Mo5Ce10Ti catalysts. For all the catalysts, the anatase phase was the main phase [2], and only a little rutile phase appeared [14]. The peak ascribed to crystalline MoO3 was not observed for Ce10Mo5Ti and Mo5Ce10Ti catalysts, indicating that the molybdenum oxide was highly dispersed on the surface of TiO2. A weak peak of cubic CeO2 crystallites was observed over Ce10Ti catalyst [15]. This peak becomes a little bit higher over Mo5Ce10Ti catalyst, and the most noticeable peak ascribed to CeO2 appeared over Ce10Mo5Ti catalyst, indicating that the introduction of Mo could induce the crystallite of CeO2 and over Ce10Mo5Ti catalyst the crystallization is more apparent. The cubic CeO2 can contribute to the activation of NH3 [16], thereby enhancing the SCR activity. On the other hand, it could be more susceptible to H2O and SO2 than the highly dispersed CeO2. Therefore, Ce10Mo5Ti is more sensitive to the presence of H2O and SO2 than Ce10Ti at 200 °C (see Figs. 1 and 2A).

X-ray photoelectron spectra (XPS) analysis was conducted to elucidate the surface nature of the active sites over the catalyst systems. As shown in Fig. 4A, the Mo 3d5/2 peak was centered at 232.7 and 232.5 eV for Mo5Ce10Ti and Ce10Mo5Ti catalysts respectively, corresponding to Mo6+ state [17]. The complex spectrum of Ce3d was decomposed into eight components with the assignment defined in Fig. 4B. The sub-bands labeled u′ and v′ represent the 3d104f1 initial electronic state corresponding to Ce3+, and those labeled u″, u‴, u‴, v″ and v‴ represent the 3d104f0 initial electronic state corresponding to Ce4+ [2]. It can be seen that the redox pair of Ce3+/Ce4+ exists in the three catalysts. For Ce10Mo5Ti catalyst, the surface concentration of Ce is 2.4%, which is higher than that of Mo5Ce10Ti (2.0%) and Ce10Ti (2.3%) catalysts. More amount of Ce exists on the surface could contribute to improving the NH3-SCR activity.

3.5. In situ DRIFTS

Previous studies have shown that the adsorption of NH3 on the catalyst surface plays an important role in the NH3-SCR process [11,12]. Therefore, the adsorption of NH3 on Ce10Ti and Ce10Mo5Ti catalysts in the co-presence of H2O and SO2 was studied by in situ DRIFTS. Fig. 5A showed the DRIFT spectra of NH3 adsorption over Ce10Ti catalyst in the co-presence of H2O and SO2 at different temperatures. Compared with the DRIFT spectra of NH3 adsorption in the absence of H2O and SO2 [10], it can be seen that two new peaks centering at 1608 and 1363 cm−1 appear, which can be assigned to the adsorption of H2O [18,19] and the deposited sulfate species [18].
Lewis acid sites, which was reactive species in the NH3-SCR process, the decrease of the NH3-SCR activity [20]. The sulfate species can also inhibit the adsorption of H2O and SO2 as shown in Fig. 2A. In addition, more noticeable adsorption band of NH3 on Brønsted acid sites (1488 cm⁻¹) [23] can be observed over Ce10Mo5Ti catalyst (see Fig. 5B). Previous research showed that Brønsted acid site is beneficial for the adsorption of NH3 and SO2, thus promoting the SCR activity [24,25]. All these are the mechanistic cause of the higher activity of Ce10Mo5Ti catalyst than Ce10Ti catalyst in the co-presence of H2O and SO2.

4. Conclusions

CeO2-MoO3/TiO2 showed higher activity than CeO2/TiO2 for the selective catalytic reduction of NOx with NH3. More importantly, the resistance against H2O and SO2 was also improved due to the addition of MoO3. It was suggested that the role of added MoO3 is to inhibit the adsorption of H2O and SO2 as well as the formation of sulfate species on the catalyst surface, thus alleviating the poisoning effect of H2O and SO2. In addition, it leads to the formation of Brønsted acid sites and the crystallization of CeO2, which contribute to the adsorption and activation of NH3, respectively, thus promoting the NH3-SCR to proceed.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2013.11.032.

References


Fig. 5. DRIFT spectra of Ce10Ti (A) and Ce10Mo5Ti (B) in the flow of 500 ppm NH3 + 5% H2O + 50 ppm SO2 at different temperatures.

respectively. The adsorbed H2O can block the active sites thus leading to the decrease of the NH3-SCR activity [20]. The sulfate species can also cover the active sites thus poisoning the deNOx catalyst [1]. In our previous report [10], the peaks (1595 and 1170 cm⁻¹) ascribed to asymmetric and symmetric bending vibrations of the coordinated NH3 linked to Lewis acid sites [21,22] were observed over Ce10Ti catalyst in the absence of H2O and SO2. It is evident that these peaks were absent in the co-presence of H2O and SO2 (see Fig. 5A). Therefore, the co-presence of H2O and SO2 inhibits the formation of coordinated NH3 on Lewis acid sites, which was reactive species in the NH3-SCR process, resulting in the decrease of the NOx conversion.

By the comparison of Fig. 5A and B, it can be seen that the intensity of the peaks ascribed to the adsorption of H2O and sulfate species over Ce10Mo5Ti catalyst were weaker than those over Ce10Ti catalyst. This fact indicates that the introduction of Mo to the Ce10Ti catalyst could inhibit the adsorption of H2O and SO2 as well as the formation of sulfate species on the catalyst surface, thus alleviating the poisoning effect of H2O and SO2 as shown in Fig. 2A.