Selective catalytic reduction of NO_x with NH_3 over Mo-based catalysts

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Abstract: A series of MoO_3-doped MnZr and CeZr mixed oxides catalysts were investigated for the selective catalytic reduction of NO_x by NH_3(NH_3-SCR). It was found that the added MoO_3 significantly enhanced the activity of MnZr and CeZr catalysts for NH_3-SCR of NO_x in a wide temperature range. The optimum Mo loading is different for the different support. The highly dispersed MoO_3 not only resulted in more Lewis acid and Brønsted acid sites formed on the catalyst surface, but also increased the redox property of the catalyst, all of which account for the enhanced SCR activity.

Keywords: NO_x, NH_3-SCR, MoO_3.

1. Introduction

Nitrogen oxides (NO_x) emitted from mobile and stationary source are the major air pollutants, as they cause a variety of environmentally harmful effects such as photochemical smog, acid rain and ozone depletion [1]. Selective catalytic reduction of NO_x by NH_3 (NH_3-SCR) is regarded to be the most effective method for the removal of NO_x, and V_2O_5/TiO_2-based catalyst is widely used for this process [2]. However, the toxicity of vanadium and the narrow temperature window (300-400℃) has restrained the practical application of V-based catalyst [3]. Thus, great efforts have been made to develop novel NH_3-SCR catalyst for the control of NO_x.

MoO_3 has been employed to increase the activity of V-based catalyst [4, 5]. Our previous studies also revealed that the addition of MoO_3 showed a noticeable promoting effect on the activity of Ce/TiO_2 for the NH_3-SCR [6]. The present work attempts to improve the activity of MnZr and CeZr by adding MoO_3 to develop novel non-vanadium NH_3-SCR catalysts. It was found that the addition of MoO_3 showed a noticeable promoting effect on the activity of MnZr and CeZr for the NH_3-SCR of NO_x. On the basis of the characterization results, the cause of the promoting effect of MoO_3 has been elucidated.

2. Experimental

MnZr and CeZr mixed oxides were prepared by the hydrothermal method. $Zr(NO_3)_4·5H_2O$ and $Mn(NO_3)_2$(or $Ce(NO_3)_3$) solution were dissolved in deionized water and stirred at room temperature. Then ammonia solution was added slowly to the above solution under stirring until pH is 10. The obtained suspension was transferred to a Teflon-sealed autoclave and aged at 120 ℃ for 4 h. Subsequently the precipitate was filtered and washed with deionized water. The resulting powder was dried at 120℃ for 12 h and then calcined in air at 500 ℃ for 4 h. MO_3-doped MnZr and CeZr catalysts were prepared by impregnating MnZr(or CeZr) with ammonium molybdate ($(NH_4)_6Mo_7O_{24}·4H_2O$) and oxalic acid ($H_2C_2O_4·2H_2O$) solution, then dried at 120℃ for 12h, and calcined at 500 ℃ for 4 h in air. Hereinafter these catalysts are designated by xMoMnZr(or xMoCeZr), where x is the loading of MoO_3.

The catalysts were characterized by XRD, XPS, H_2-TPR and the reaction mechanism was studied by in-situ DRIFTS.

3. Results and discussion

The NH_3-SCR activities of MnZr and xMoMnZr catalysts with different MoO_3 loading as a function of temperature were illustrated in Figure 1(a). It can be seen that the activity temperature window of MnZr catalyst is narrow. The introduction of MoO_3 leads to wider activity temperature window. As the loading of MoO_3 increased to 15%, over 90% of NO_x conversion was achieved in a wide temperature window (250-400 ℃). As shown in Figure 1(b), Compared with MoO_3 and CeZr, MoCeZr catalyst exhibited much higher activity. These results indicate that the co-existence of MoO_3 and MnZr(or CeZr) is important for the promotion of SCR activity.

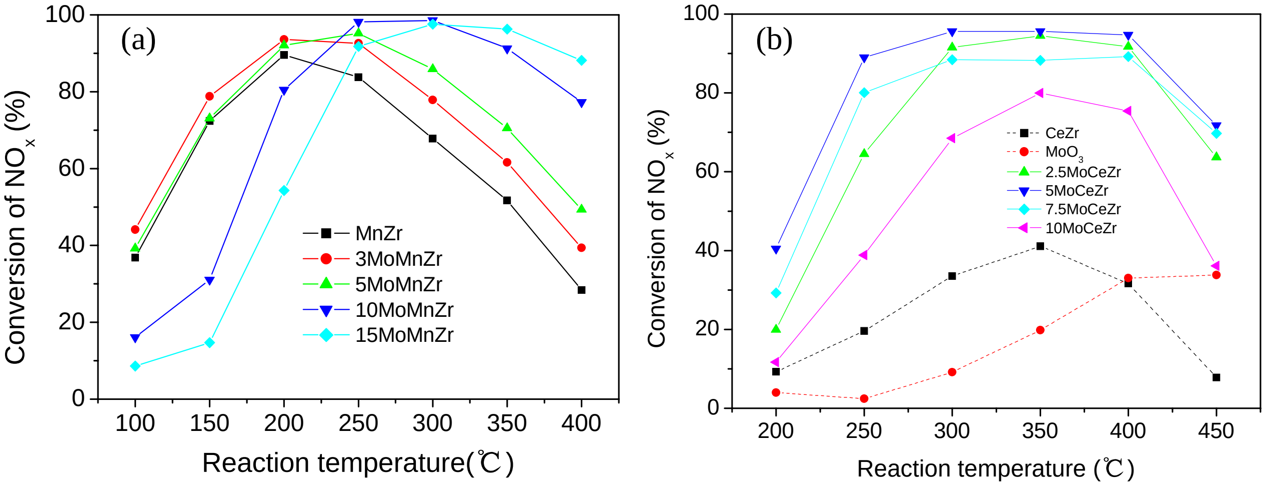

Figure 1. NH_3-SCR activities of MoMnZr(a) and MoCeZr(b) catalysts for the selective catalytic reduction of NO_x with NH_3 in the presence of oxygen. Reaction conditions: $[NO]=[NH_3]=$ 500 ppm, $[O_2]=$ 5%.

From XRD patterns, it was found that over both MoMnZr and MoCeZr catalysts MoO_3 is highly dispersed on the support. In-situ DRIFTS and H_2-TPR showed that the introduction of MoO_3 not only resulted in more Lewis acid and Brønsted acid sites formed on the catalyst surface, but also increased the redox property of the catalyst. As a result, the NH_3-SCR of NO_x was promoted.

4. Conclusions

Novel MoMnZr and MoCeZr catalysts for the selective catalytic reduction of NO_x have been developed. The co-presence of MoO_3 and MnZr(or CeZr) contributes to improving the NH_3-SCR activity. Moreover, both catalysts displayed relatively high tolerance to H_2O and SO_2. The synergetic effect between Mo and MnZr(or CeZr) contributes to the adsorption and activation of NH_3, thus leading to high catalytic activity for the NH_3-SCR of NO_x.

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