Selective catalytic reduction of NOx with NH3 over Mo-based catalysts

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Abstract: A series of MoO3-doped MnZr and CeZr mixed oxides catalysts were investigated for the selective catalytic reduction of NOx by NH3(NH3-SCR). It was found that the added MoO3 significantly enhanced the activity of MnZr and CeZr catalysts for NH3-SCR of NOx in a wide temperature range. The optimum Mo loading is different for the different support. The highly dispersed MoO3 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: NOx, NH3-SCR, MoO3.

1. Introduction

Nitrogen oxides (NOx) 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 NOx by NH3 (NH3-SCR) is regarded to be the most effective method for the removal of NOx, and V2O5/TiO2-based catalyst is widely used for this process [2]. However, the toxicity of vanadium and the narrow temperature window (300-400°C) has restrained the practical application of V-based catalyst [3]. Thus, great efforts have been made to develop novel NH3-SCR catalyst for the control of NOx.

MoO3 has been employed to increase the activity of V-based catalyst [4, 5]. Our previous studies also revealed that the addition of MoO3 showed a noticeable promoting effect on the activity of Ce/TiO2 for the NH3-SCR [6]. The present work attempts to improve the activity of MnZr and CeZr by adding MoO3 to develop novel non-vanadium NH3-SCR catalysts. It was found that the addition of MoO3 showed a noticeable promoting effect on the activity of MnZr and CeZr for the NH3-SCR of NOx. On the basis of the characterization results, the cause of the promoting effect of MoO3 has been elucidated.

2. Experimental

MnZr and CeZr mixed oxides were prepared by the hydrothermal method. Zr(NO3)4·5H2O and Mn(NO3)2(or Ce(NO3)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 °C for 4 h. Subsequently the precipitate was filtered and washed with deionized water. The resulting powder was dried at 120°C for 12 h and then calcined in air at 500 °C for 4 h. MoO3-doped MnZr and CeZr catalysts were prepared by impregnating MnZr(or CeZr) with ammonium molybdate ((NH4)6Mo7O24·4H2O) and oxalic acid (H2C2O4·2H2O) solution, then dried at 120°C for 12h, and calcined at 500 °C for 4 h in air. Hereinafter these catalysts are designated by xMoMnZr(or xMoCeZr), where x is the loading of MoO3.

The catalysts were characterized by XRD, XPS, H2-TPR and the reaction mechanism was studied by in-situ DRIFTS.

3. Results and discussion

The NH3-SCR activities of MnZr and xMoMnZr catalysts with different MoO3 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 °C). 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$_2$O 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$_x$.

References