Inhibition Effects of Pb on Selective Catalytic Reduction of NO with NH_3 over Commercial Vanadia-based Catalysts

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Abstract: The V_2O_5-WO_3/TiO_2 catalyst applied in municipal solid waste incinerators usually faces the problem of deactivation by lead produced during the combustion of municipal solid waste. Therefore, a series of Pb-poisoned V_2O_5-WO_3/TiO_2 catalysts were prepared by a wet impregnation method in this study. The physicochemical properties of catalyst were detected by NH_3-TPD and *in situ* FTIR. The results show that the reactions between Pb and Lewis acid sites and Brønsted acid sites contribute to the inhibition effects of Pb on selective catalytic reduction of NO with NH_3 over commercial V_2O_5-WO_3/TiO_2 catalyst.

Keywords: SCR, Commercial Catalyst, Deactivation, Lead.

1. Introduction

Nitrogen oxides (NO_x) emitted from automobiles, coal-fired power plant and municipal solid waste(MSW) incinerators can cause a variety of environmentally harmful effects such as acid rain, photochemical smog and ozone depletion. The number of MSW incinerators for generating electricity power has increased in recent years. V_2O_5-WO_3/TiO_2, as the main catalyst used for the selective catalytic reduction of NH_3 (NH_3-SCR), is commonly applied in MSW incinerators for abating nitrogen oxides (NO_x) in flue gas to meet the strict discharge standards. However, there are large amounts of lead produced during the combustion of MSW and deposit on the catalyst with ash which could bring about deactivation of V_2O_5-WO_3/TiO_2 catalyst. Therefore, it is important to study the deactivation of V_2O_5-WO_3/TiO_2 by lead.

2. Experimental

The commercial catalyst used in the study with vanadium pentoxide loading of 2.45% and tungsten trioxide loading of 3.18% was ground and sieved to 60–80 mesh. The samples poisoned by lead oxide were prepared by impregnating the commercial catalyst particles into $Pb(NO_3)_2$ aqueous solutions of different concentrations. The Pb poisoned catalysts were denoted as D-Pb-x, where x represented the molar ratio of Pb to vanadium pentoxide. The catalytic activities of fresh and D-Pb-x samples were evaluated by the fixed bed reactor in the laboratory. The temperature-programmed desorption of ammonia (NH_3-TPD) experiments were carried out on the combination of a Quantachrome ChemBET-3000TPR-TPD chemisorption analyzer and mass spectrum (Ametek, DYCOR LC-D200, USA). The Fourier transform infrared spectroscopy (FT-IR) was characterized by Bruker Vertex 70 (Bruker, VERTEX 70, Germany).

3. Results and discussion

Figure 1 shows the SCR activity of the fresh and Pb-poisoned catalyst in the temperature range of 250-450 °C. The NO_x conversion of fresh catalyst keeps around 90% at the temperature range of 250-380°C and decreases dramatically as the temperature is higher than 400 °C. The Pb-poisoned catalyst exhibits obviously lower activity than the fresh catalyst within the whole temperature range.

It has been recognized that the surface acidities of catalysts play an important role in the SCR of NO with NH_3. It is regarded to be crucial for the SCR reaction that NH_3 is adsorbed on the catalyst surface. Hence, NH_3-TPD experiments were performed to investigate the effect of Pb on the surface acidities of V_2O_5/TiO_2 catalysts, as shown in Figure 2. All curves were fitted into three peaks, the lower one ranging from 180 to 250 °C is attributed to NH_3 desorption from weak acid sites; the second peak at 250–300 °C is ascribed to medium acid sites; and the higher temperature peak at 300 °C is related to NH_3 desorption of strong acid sites. In the figure 2, with doping of Pb, most NH_3 adsorbed on the weak acid sites desorbed at low temperature while the peaks ascribed to medium acid sites and strong acid sites decrease remarkably which implies that the reaction between strong acid sites and Pb contributes to the deactivation effects of Pb on the catalyst to some degree.

The types of acid sites are also important to NH_3-SCR reaction besides the concentration of surface acid sites. In order to distinguish the difference of acid sites on the catalyst, the fresh, D-Pb-0.4 and D-Pb-0.4-S were detected by *In-situ* FTIR with NH_3 in N_2 balance for a range of time. The *In-situ* FTIR spectra are shown in the figure 3. In the figure 3a, the spectra of fresh catalyst, three bands from 3000 to 3400 cm^{-1}, bands located from 1150 to 1300 cm^{-1} and the band at 1602 cm^{-1} are ascribed to NH_3 adsorbed on the Lewis acid sites[1,2]. The band at 1656 cm^{-1} is assigned to NH_3 adsorbed on the Brønsted acid sites[3]. However, the *In-situ* FTIR spectra of D-Pb-0.4 shows that the bands at 1606 cm^{-1}, 1150-1300 cm^{-1} and 1682 cm^{-1} decrease obviously. It implies that the doped Pb affects the Lewis acid sites and Brønsted acid sites.

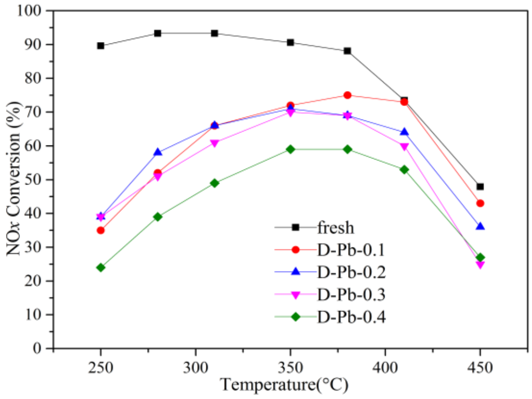

Figure 1. NO conversion of the fresh and poisoned catalysts

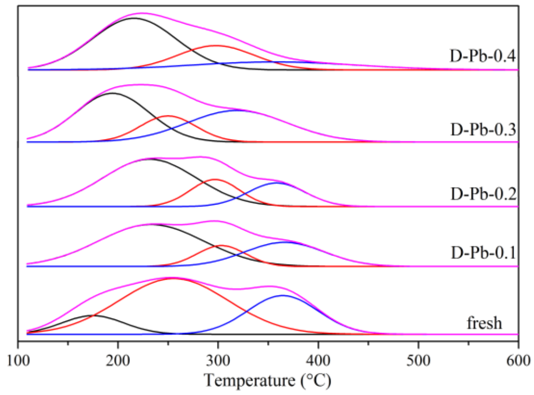

Figure 2. NH_3-TPD profiles of fresh catalyst and D-Pb-x

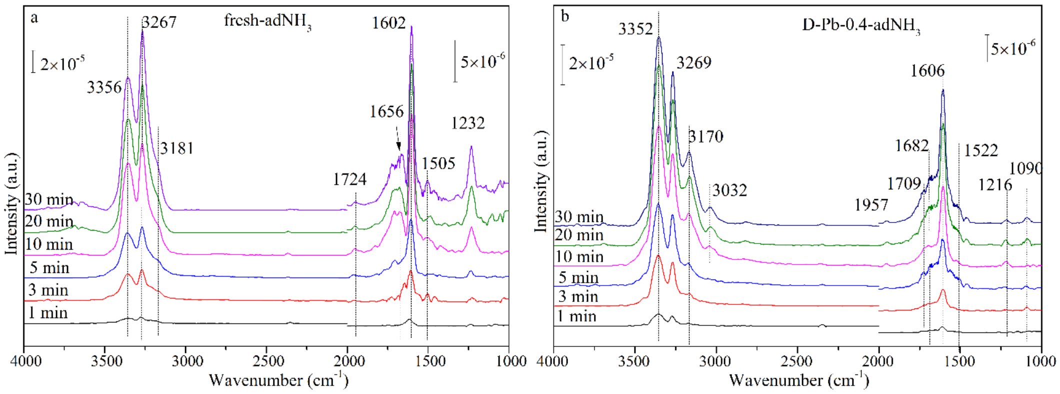

Figure 3. *In situ* FTIR spectra of fresh catalyst and D-Pb-0.4

4. Conclusions

The study is focused on the inhibition effects of Pb on the commercial catalyst. Results show that the activity of V_2O_5-WO_3/TiO_2 catalyst is decreased by Pb evidently. Pb could react with surface Lewis acid sites and Brønsted acid sites of commercial SCR catalysts, which may be the main reason for the deactivation of SCR catalysts.

References

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