



Short communication

Property influence and poisoning mechanism of HgCl₂ on V₂O₅-WO₃/TiO₂ SCR-DeNO_x catalysts



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ABSTRACT

In this paper, HgCl₂ was loaded by impregnation method to study its property influence and poisoning mechanism on V₂O₅-WO₃/TiO₂ SCR-DeNO_x catalyst. For HgCl₂-containing catalysts, deactivation was observed in simulated gas stream, and its catalytic activity declined with the increase of HgCl₂ loadings. Brønsted acid sites (V—OH) and V=O bond were affected evidently by HgCl₂, new NH₃ adsorption site Cl—V—O—H was generated after HgCl₂ addition. Interactions between HgCl₂ and V₂O₅ resulted in the loss of SCR active sites, and —HgCl existed as the stable form on the bridge site. Finally, the probable schematic diagram of HgCl₂ poisoning mechanism was also proposed.

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1. Introduction

Nitrogen oxide (NO_x) emission from coal-fired power plants will cause a serious threat to the environment since it can form acid rain, photochemical smog and ozone depletion. Recent years, considerable researches were carried out and techniques on eliminating nitrogen oxide pollutions were developed. Among various NO_x control techniques, the selective catalytic reduction (SCR) of NO_x with NH₃ has been proved to be one of the most effective technology for abating NO_x emission [1,2]. Besides, investigations exhibited that SCR De-NO_x process showed evident effects on the speciation of mercury in coal combustion flue gas, which is advantageous to mercury capture [3]. V₂O₅-WO₃/TiO₂ catalysts, containing of vanadium as the active phase, tungsten as the promoter, and titanium dioxide as the supporter, are generally used in SCR process [4,5].

Mercury is one of the most toxic trace elements due to its extreme volatility, persistence and neurological health impacts [6]. Statistics showed that over 60% of mercury emission comes from coal combustion. [7]. At high temperatures, almost entire mercury will be transformed into the elemental form (Hg^{el}). When the flue gas cooling down, gaseous Hg^{el} would be converted to oxidized mercury species (Hg^{ox}) and particulate-bound mercury (Hg_p) via a series of complex reactions. Different forms of mercury and other combustion products would partly interact with the catalysts as they flowing through the

SCR system, which will result in catalytic activity decline. Then, the initial and reacted products releasing from the SCR system could be removed by subsequent equipment, such as electrostatic precipitators (ESP), fabric filter (FF), and wet flue gas desulfurization (WFGD) [8–11].

In the coal combustion flue gas, HCl is the most important species that effect Hg^{el} oxidation [12]. Several mechanisms have been proposed for catalytic mercury oxidation over SCR catalyst [13–15]. Emo et al. [16] and He et al. [15] have reported that the adsorbed Hg^{el} will react with the reactive chlorine generating from adsorbed HCl on the SCR catalysts. Sandra et al. [14] studied the adsorption and oxidation of mercury in tail-end SCR-DeNO_x plants in bench-scale investigation. The results showed that Hg^{el} was oxidized to HgCl₂ by catalyst in the presence of HCl, and HgCl₂ could be appreciably accumulated on the De-NO_x catalysts. However, these studies mainly focused on the mechanism of Hg^{el} oxidation and adsorption. The effect of HgCl₂ accumulated on V₂O₅-WO₃/TiO₂ catalyst has been ignored and hardly ever studied hitherto.

In our previous research on the synergy effect of KCl and Hg^{el} over V₂O₅-WO₃/TiO₂ catalyst [17], the authors just proposed that the formation of HgCl₂ might have influence on the catalyst, but did not elaborate its behavior on catalyst surface. Therefore, the authors systematically investigated the effect of HgCl₂ on the selective catalytic reduction of NO with NH₃ over V₂O₅-WO₃/TiO₂ catalysts in this paper. Impregnation method was used to prepare the HgCl₂-containing catalysts. The fresh and HgCl₂-containing samples were characterized by XRD, SEM, BET, XPS, NH₃-TPD, NH₃ chemisorption, FT-IR and NO reduction measurements. The purpose of this work is to explore the substantial changes causing by HgCl₂ and reveal HgCl₂-poisoning mechanism over V₂O₅-WO₃/TiO₂ catalysts.

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2. Experimental

2.1. Catalyst preparation

The fresh V_2O_5 - WO_3 / TiO_2 catalyst with V_2O_5 (1.0 wt.%) and WO_3 (5.0 wt.%) loadings was prepared by impregnation method referring to our previous paper [17].

The $HgCl_2$ -containing catalysts were prepared by impregnation with different concentrations of $HgCl_2$ aqueous solution on the fresh V_2O_5 - WO_3 / TiO_2 catalysts. The samples were impregnated in ultrasonic vibration instrument at 60 °C for 2 h, dried at 110 °C for 12 h and then calcined at 250 °C for 5 h. The $HgCl_2$ -containing catalysts were denoted as xHg -VWTi, where x is the theoretical mass percentage of $HgCl_2$. The actual Hg content (wt.%) in the obtained $HgCl_2$ -containing catalysts was also detected by Inductively Coupled Plasma (ICP) and listed in Table 1.

In the XRD patterns (not showed), only anatase TiO_2 was detected, and no peaks related to V_2O_5 , WO_3 and Hg-species were detected. Besides, agglomeration phenomenon was observed in $HgCl_2$ -containing catalysts in the morphology test.

2.2. Catalytic performance test

Catalytic measurements were carried out referring to our previous research [17]. According to the research [14,15], HCl appreciably limits $HgCl_2$ adsorption on the catalyst surface and performs severe influence on catalyst nature. Therefore, no HCl was feed and the influent gas mixture consisted of 500 ppmv NO, 500 ppmv NH_3 , 4.4 vol.% O_2 , 5 vol.% H_2O and N_2 as the balance.

2.3. Characterization of catalysts

The powder X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) surface areas, Scanning Electron Micrograph (SEM), Fourier Transform Infrared spectra (FT-IR), Temperature-programmed Desorption of NH_3 (NH_3 -TPD) and NH_3 -chemisorption characterization referred to our previous paper [17]. X-ray photoelectron spectra (XPS) measurements were examined using Thermo Scientific ESCALAB 250 with Al $K\alpha$ X-ray (1486.6 eV, 150 W). The observed spectra were corrected with the C1s binding energy (284.6 eV).

3. Results and discussion

3.1. SCR activity performance

The NO removal efficiency of V_2O_5 - WO_3 / TiO_2 catalysts with different $HgCl_2$ loading amount at different temperatures was illustrated in Fig. 1. The fresh catalyst performed the greatest SCR activity and went better with the increase of temperature. However, the NO conversion decreased with the increase of $HgCl_2$ loadings at testing temperatures. The catalytic activities reduced by approximate 50% at 200 °C and 25% at 250 °C respectively after loading 0.5 wt.% $HgCl_2$. Notably, the disparity of $deNO_x$ activities was narrowed with the growth of temperature from 300 to 450 °C. Parts of the reason may be that $HgCl_2$ has a boiling point

Table 1

$HgCl_2$ contents and BET surface areas of all catalysts.

Samples	$HgCl_2$ content (wt.%)			S_a (m^2/g)	V_p (cm^3/g)	D_p (nm)
	Theoretical	Actual	After reaction			
VWTi	–	–	–	82.9	0.32	15.43
xHg -VWTi	0.01	–	–	79.6	0.31	15.38
	0.1	0.037	–	78.0	0.30	15.02
	0.5	0.216	0.104	77.0	0.31	15.85

S_a , surface areas; V_p , pore volume; D_p , pore diameter; x , theoretical $HgCl_2$ content (0.01, 0.1, 0.5).

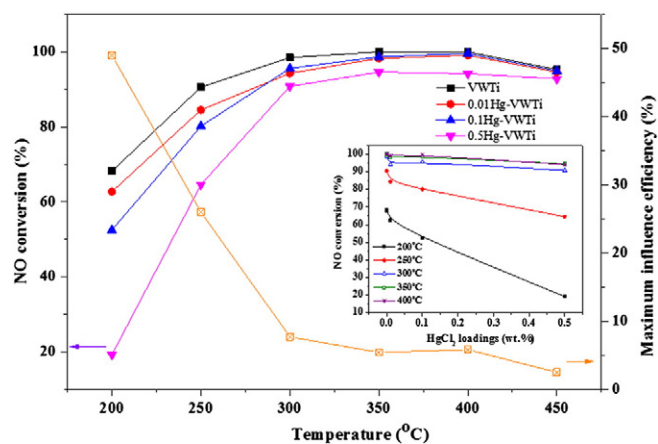


Fig. 1. NO conversion with different $HgCl_2$ loading amount at different temperatures over V_2O_5 - WO_3 / TiO_2 catalysts.

approximately at 300 °C, thus $HgCl_2$ on the catalyst surface will evaporate as the increase of reaction temperature. But in the temperature range of 300–400 °C, there is still a difference of 10% for 0.5Hg-VWTi sample, meaning a negative influence of $HgCl_2$ on catalytic activities. Yang et al. [18] found the similar tendency in the study of V_2O_5 -based catalyst properties after its mercury oxidation experiment. Besides, the catalyst activity as the function of time on stream did not change at stationary temperature for hours (not showed).

3.2. Characterization of catalysts

3.2.1. BET results

Table 1 summarized the surface areas (S_a), pore volume (V_p) and mean pore diameter (D_p) for all catalysts. The surface areas of samples decreased from 82.9 m^2/g (VWTi) to 77.0 m^2/g (0.5Hg-VWTi), and with the increase of $HgCl_2$ loading content, the BET value declined. This result expressed the same tendency with the catalytic activity. However, the pore volume presented almost the same value, while 0.5Hg-VWTi catalysts showed the biggest D_p (15.85 nm). Combining with the morphology results, this behavior can be explained as follows: the impregnation of $HgCl_2$ caused catalyst agglomeration, vanishing initial micro-pores and forming accumulated pores, which resulted in the decrease of surface areas and the increase of mean pore diameter.

3.2.2. NH_3 -TPD and NH_3 chemisorption

Surface acidity over V_2O_5 - WO_3 / TiO_2 catalysts was considered to be crucial in the selective catalytic reduction process. One of the most important steps for SCR is the adsorption of NH_3 on the catalyst surface [19–21]. The curves of NH_3 -TPD were depicted in Fig. 2 for exploring the surface acidity changes of V_2O_5 - WO_3 / TiO_2 catalysts causing by $HgCl_2$. When the temperature was below 350 °C, the evolution of ammonia occurred with two main NH_3 desorption peaks attributed to weakly adsorbed NH_3 in Brønsted acid site [22,23]. This NH_3 species could be more easily desorbed at low temperature. However, it is obviously that NH_3 desorption peaks and desorption temperature of 0.5Hg-VWTi sample is lower than that of fresh, which implies much less and easier NH_3 desorption. This phenomenon suggested that $HgCl_2$ decreased the surface acid sites of V_2O_5 - WO_3 / TiO_2 catalyst. For VWTi, another ammonia desorption peak corresponding to strongly adsorbed NH_3 in Lewis acid site exhibited at 503 °C. It is much less than weakly adsorbed NH_3 amount, meaning Brønsted acid sites played the leading role in NO reduction process. However, a new NH_3 desorption peak centered at 429 °C appeared in 0.5Hg-VWTi catalyst. This new NH_3 adsorption sites might be dominant for SCR reaction. It could be the reason of its negligible deactivation for $HgCl_2$ -containing catalyst at temperature from 300 to 450 °C, which is in good accordance with the catalyst activity variation.

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