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The Poisoning of V$_2$O$_5$-WO$_3$/TiO$_2$ and V$_2$O$_5$-Ce(SO$_4$)$_2$/TiO$_2$ SCR Catalysts by KCl and The Partial Regeneration by SO$_2$

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Abstract: Poisoning effects by alkali metal chlorides is one of the major reasons for the deactivation of SCR catalyst in biomass-fired plants. In this study, the influence of KCl on two vanadium-based catalysts with different promoters, V$_2$O$_5$-WO$_3$/TiO$_2$ and V$_2$O$_5$-Ce(SO$_4$)$_2$/TiO$_2$, was investigated. The catalytic activity of the fresh V$_2$O$_5$-WO$_3$/TiO$_2$ was higher than that of V$_2$O$_5$-Ce(SO$_4$)$_2$/TiO$_2$ at low temperatures. V$_2$O$_5$-Ce(SO$_4$)$_2$/TiO$_2$ performed better than V$_2$O$_5$-WO$_3$/TiO$_2$ when KCl was deposited on the catalyst surface. Both poisoned catalysts were efficiently regenerated by SO$_2$ treatment. The characterization results show that the reducibility and acidity of the catalysts were weakened by KCl deposition but regenerated by SO$_2$.

Keywords: alkali-poisoning; KCl; NH$_3$-SCR; SO$_2$ regeneration

1. Introduction

NO$_x$ from exhaust emissions is an important precursor of pollution sources such as smog and acid rain, causing severe damages to the natural environment. Selective catalytic reduction (SCR), with high efficiency of NO$_x$ removal, is a wide-spread technology for reducing the emissions of NO$_x$ from the flue gas of power plants and the exhaust gas of vehicles [1–4]. NO$_x$ is reduced into harmless N$_2$ by NH$_3$ over catalysts, following Reactions (1)–(3) with different NO/NO$_2$ ratios [3,5–7]:

Standard-SCR:

$$4\text{NO} + 4\text{NH}_3 + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \quad (1)$$

Fast-SCR:

$$\text{NO} + \text{NO}_2 + 2\text{NH}_3 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O} \quad (2)$$

NO$_2$-SCR:

$$6\text{NO}_2 + 8\text{NH}_3 \rightarrow 7\text{N}_2 + 12\text{H}_2\text{O} \quad (3)$$

Biomass has been used as a renewable fuel due to its environmentally-friendly features. However, the deactivation of the SCR catalyst used in the biomass-fired/cofired boilers is faster than that of coal-fired boilers [8]. The major difference between biomass and fossil fuels is the amount of
alkali earth metals contained: it is higher in biofuels than in fossil fuels. Meanwhile, alkali earth metals are always contained in the flue gas and result in the deactivation of SCR [9].

The effect of alkali earth metals on catalysts, especially the commercial VWTi catalysts, has been investigated by many researchers. The activity of SCR catalysts gradually decreases as a result of the alkali accumulation on the catalyst [10]. The acidity of V₂O₅-WO₃/TiO₂ is affected by alkali earth metals owing to the reduction in the concentration of V=O Brønsted acid sites and the reducibility of active V^5+ sites, which play a crucial role for the SCR reaction [11–13]. The effect of alkali metals on vanadium active sites has also been confirmed by DFT calculations [11]. V₂O₅-WO₃/TiO₂ is deactivated more severely by K than Ca and Mg due to the greater decrease in the amount and stability of Brønsted acid sites [14]. The deactivation degree of V₂O₅-WO₃/TiO₂ caused by different forms of calcium follows the order: CaCO₃ > CaO > CaSO₄. SO₄²⁻ can partly mitigate the CaO deactivation effect on acid sites [15]. A general method to enhance the alkali-resistance is to deposit promoters on the catalyst surface, which can increase the number of surface acid sites and strengthen their stability, thus improving the alkali metal resistance of commercial SCR catalysts [16]. Cerium, one of the promoters, is proved to enhance V₂O₅/TiO₂ NOx conversion [17].

Great efforts have been focused on the regeneration of poisoned catalysts and many methods were proposed [18,19], such as water-washing and SO₂-treatment. SO₂ usually appears in the flue gas and leads to SCR catalysts deactivation. NH₄HSO₄ is deposited on the surface through the reaction among SO₂, H₂O, and NH₃, plugging the catalyst pores at low temperatures [20–22]. Ce-based oxide catalytic activity can be significantly enhanced through SO₂-treatment, and the surface acidity of catalyst is strengthened through impregnation with H₂SO₄ solution [22,23]. It is of great interest to study the regeneration of alkali metals-poisoned catalysts through SO₂ treatment.

The impact of KCl on the V₂O₅-WO₃/TiO₂ and V₂O₅-Ce(SO₄)₂/TiO₂ catalysts (denoted as VWTi and VCeTi, respectively) was studied. The catalyst poisoning in stationary NOx sources applications (biomass fired/cofired boilers) was simulated. Experiments were conducted to investigate the regeneration of the poisoned catalysts through SO₂ treatment. The fresh, poisoned, and regenerated catalyst samples were characterized by H₂-TPR and NH₃-TPD experiments. The catalytic activity of the fresh VWTi was higher than that of VCeTi at low temperature, while VCeTi performed better than VWTi when KCl was deposited on the catalyst. SO₂-treatment could efficiently regenerate the poisoned catalysts, especially the VCeTi catalyst.

2. Results and Discussion

2.1. Poisoning Effect of KCl on VWTi Catalyst

Figure 1 illustrates the performance of the VWTi catalyst with different KCl deposition contents under different calcination temperatures. The catalytic activity of VWTi catalysts decreased with increasing of the molar ratio of n(K)/n(V) (i.e., the molar ratio of KCl and V₂O₅), although the calcination temperature (T_{calc}) was different (T_{calc} = 320 and 370 °C; T_{calc} = 20 °C higher than the highest test temperature). Obviously, the catalytic activity decreased significantly owing to the KCl deposition. It indicates that VWTi is susceptible to the alkali species as KCl; especially when the molar ratio of n(K)/n(V) is 1.5, the NO conversion decreased by more than 50%. The results are consistent with the poisoning phenomenon that occur during the operation of a biomass power plant: the catalytic activity decreases due to the deposition and accumulation of KCl. The alkali metal ions (K⁺) evaporated from the fuel will absorb on the catalysts surface and form solid KCl particles on the catalyst surface [9]. Moreover, a parallel tendency of the VWTi catalysts calcinated at 345, 395, and 420 °C was obtained and N₂-selectivity (>95%) of VWTi catalysts was barely affected by KCl. Figure 2 depicts the NO conversion of poisoned VWTi with different T_{calc}. Fluctuations were clearly observed with different T_{calc}, while all the VWTi catalysts activities dropped due to KCl deposition. The highest point of NO conversion can be explained by the fact that NO conversion of fresh VWTi peaked at 370 °C. The reason for the decrease of NO conversion at 345 °C is that diffusion of small KCl clusters on the catalyst surface led to increasing interface per unit mass of KCl, which is equivalent to the covering of likely active catalytic sites [24–26]. The decreased degree of NO conversion at 345 °C was
weakened obviously at elevated n(K)/n(V). Therefore, the two effects, of alkali metal and the NO conversion fluctuations of fresh catalysts, together led to the results demonstrated in Figure 2.

Figure 1. Effects of three n(K)/n(V) ratios on activity of V_2O_5-WO_3/TiO_2 catalyst calcinated at: (a) 320 °C; and (b) 370 °C.

Figure 2. NO conversion of three n(K)/n(V) of KCl poisoned V_2O_5-WO_3/TiO_2 catalysts at different T_{calc}. The test temperature was 300 °C.

2.2. Comparison of Alkali Resistance of VCeTi and VWTi Catalysts

Figure 3 shows the influence of different T_{calc} and molar ratios of n(K)/n(V) on the V_2O_5-Ce(SO_4)_2/TiO_2. As illustrated in these figures, the fresh V_2O_5-WO_3/TiO_2 performed better than the fresh V_2O_5-Ce(SO_4)_2/TiO_2 at low temperature in terms of activity, whereas their activities were approximately equal at high temperature. Moreover, the NO conversion of all catalysts decreased due to KCl loading. Higher alkali loading imposed a stronger poisoning influence on both VWTi and VCeTi catalysts. One exception is that the VCeTi catalyst was slightly more strongly deactivated when the deposition ratio was 1.0, rather than 1.5, at the calcination temperature of 320 °C. VWTi was sensitive to alkali metal such as potassium, as discussed in Section 2.1, while VCeTi possessed a better alkali resistance than VWTi. It in demonstrated in Figure 3 that the VCeTi catalyst exhibited a superior NO conversion than VWTi after poisoning at the test temperature; the explanation for this might be the superior oxidation properties of Ce^{4+} and acidity of SO_4^{2-} [23]. The same experiments were also conducted on poisoned VWTi and VCeTi calcinated at 345, 395 and 420 °C, respectively, and the results are consistent with those discussed above. Figure 4 demonstrates a comparison of poisoned VCeTi calcinated at different temperatures. It can be noticed that the poisoned VCeTi catalytic activity decreased slightly with T_{calc} changing. What is more interesting is that activities of VCeTi catalysts barely changed at n(K)/n(V) = 1.0, 1.5. Based on the experimental results, it can be concluded that VCeTi catalysts possess superior alkaline resistance in a wide calcination temperature window.
Figure 3. Comparison of activities between $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ and $\text{V}_2\text{O}_5\text{-Ce(SO}_4\text{)}_2/\text{TiO}_2$ catalyst samples with KCl deposition at different $T_{\text{calc}}$: (a)320 °C; and (b)370 °C.

Figure 4. NO conversion of three n(K)/n(V) of KCl poisoned $\text{V}_2\text{O}_5\text{-Ce(SO}_4\text{)}_2/\text{TiO}_2$ catalyst at different $T_{\text{calc}}$. The test temperature was 300 °C.

2.3. The Regeneration of the Poisoned Catalysts

The regeneration of poisoned catalysts has been investigated by many researchers, and many effective methods have been proposed [27–30]. SO$_2$ is always contained in the flue gas [27,28]. Consequently, experiments were conducted to explore the regeneration of poisoned catalysts by SO$_2$ treatment. Figure 5a indicates that the catalytic activity of poisoned VWTi catalysts was dramatically enhanced after SO$_2$ treatment, even though the activity was still slightly lower than the fresh catalyst. The catalytic activity of regenerated catalysts peaked at $T_{\text{calc}} = 370$ °C, and then decreased at elevated temperature. The regeneration of poisoned VWTi catalysts with 0.5 and 1.0 n(K)/n(V) molar ratios was also investigated. The catalysts with the low molar ratio of n(K)/n(V) possessed a higher NO conversion than the catalysts with the high molar ratio of n(K)/n(V) after regeneration. This observation validates that the deactivation arose from KCl and can be regenerated to some extent.

The SO$_2$ treatment on poisoned VCeTi catalysts was also employed, and experimental results are plotted in Figure 5b. The activity of poisoned VCeTi was promoted after SO$_2$ treatment, and barely fluctuated after $T_{\text{calc}} = 320$ °C. It is more interesting that the activity of the regenerated catalyst was even better than that of the fresh catalyst. The reasons for this are more Brønsted acid sites were formed from potassium sulfate and active sites emerged due to surface sulfation by SO$_2$ [29]. As reported, the number of Bronsted acid sites increased because the surface sulfates on TiO$_2$ were converted to bidentate surface species (acidic S−OH groups) [30–33], and the reaction rate increased as a result of more Bronsted acid sites [34].
Figure 4+32 nhanced (integral m for poisoned 2, w, w, ed positions Ce of fresh VCeTi catalyst with the activity results. Peak which temperatures shifted As shown in therefore, the regeneration of poisoned VCe exhibited a superior surface acidity through regeneration [39,40]. The g acid, and the increased Brønsted acid sites strengthen sites slightly, whereas the peak position results of VCeTi catalysts. As for the poisoned VCeTi catalyst, the intensity of the TPD peak area (from 1020 to 245 to 4547 for VWTi, while from 21,862 to 13,912 for VCeTi). Therefore, the regeneration of poisoned VCeTi catalysts by SO2-treatment is not obvious.

The H2 consumption of fresh and poisoned catalysts was obtained through H2-TPR experiments. As shown in Figure 7a, VWTi catalyst exhibited two TPR peaks: TPR Peak (1) at low temperatures shifted towards high temperatures with the deposition of KCl, whereas TPR Peak (2) at high temperatures did not change. Peak (1) was assigned to the reduction of V5+ to V3+ and W6+ to W4+ [41], which revealed that the redox ability of V and W was decreased after deposition of KCl, consistent with the activity results. Peak (2) belongs to the reduction of W4+ to W6+ [42]. The H2 consumption peak of fresh VCeTi catalyst contained two overlapped reduction peaks, which can be assigned to V3+ and Ce4+, respectively, and a synergistic effect between Ce4+ and V5+ appeared due to the adjacent peak positions. Through the deposition of KCl, a deviation of the TPR reduction peak was observed, the
former peak being related to the reduction of V$^{5+}$ to V$^{3+}$, while the latter being assigned to the reduction of Ce$^{4+}$ to Ce$^{3+}$ [17,43,44]. It is reported that oxygen vacancies are yielded with the conversion of Ce$^{4+}$ to Ce$^{3+}$ [45]. Oxygen vacancies are beneficial to catalytic activity, thus making VCeTi catalysts perform better than VWTi.

![NH$_3$-TPD profiles of the fresh poisoned and regenerated catalysts](image)

**Figure 6.** NH$_3$-TPD profiles of the fresh poisoned and regenerated: (a) V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst; and (b) V$_2$O$_5$-Ce(SO$_4$)$_2$/TiO$_2$ catalyst.

![H$_2$-TPR profiles of catalysts at three n(K)/n(V) ratios](image)

**Figure 7.** H$_2$-TPR profiles of catalysts at three n(K)/n(V) ratios: (a) V$_2$O$_5$-WO$_3$/TiO$_2$; and (b) V$_2$O$_5$-Ce(SO$_4$)$_2$/TiO$_2$.  

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3. Materials and Methods

3.1. Catalyst Synthesis

1 wt.% V₂O₅–5 wt.% WO₃/TiO₂ and 1 wt.% V₂O₅–11.74 wt.% Ce(SO₄)₂/TiO₂ (11.74 wt.% Ce(SO₄)₂ was calculated according to 5 wt.% CeO₂) were synthesized by the impregnation method. Ammonium vanadate (NH₄VO₃, Aladdin, AP) and ammonium metatungstate ((NH₄)ₓHₓWₓO₆ₓ·xH₂O, Aladdin, AP), used as the precursors of V₂O₅ and WO₃, respectively, were dissolved in deionized water, acidified by oxalic acid, and then vigorously stirred at 60 °C for 30 min. After impregnation of V- and W-precursor on TiO₂ (Degussa, P25, Sₜₜ = 55 m²/g) in a desired proportion, the synthesized samples were dried at 120 °C for 12 h, and subsequently calcinated at 500 °C for 5 h. V₂O₅–Ce(SO₄)₂/TiO₂ was prepared by the same method. Ceric sulfate (Ce(SO₄)₂·4H₂O, Aladdin AP) was the precursor of Ce(SO₄)₂. The detailed synthesis procedure is described in our previous work [46]. The poisoned catalyst was synthesized by impregnation. Potassium chloride (KCl, AP), the alkaline reactant, was dissolved in deionized water and sufficiently stirred, and then mixed with the prepared powdery catalyst according to the molar ratios of n(K)/n(V) = 0.5, 1.0 and 1.5. The catalyst was subsequently dried and then calcinated at 320, 345, 370, 395 and 420 °C to simulate the varying poisoning situations that occur in biomass-fired plants under different operating temperatures.

3.2. Catalytic Performance

The NH₃-SCR reactivity tests were completed on a quartz tube where the catalyst was placed in, and the feed gas of selected composition went through the tube. Meanwhile, the tube was heated by electric furnace. A thermocouple was injected to the bed of the catalyst to monitor the temperature, which was recorded and used in this paper. The feed gas contained 500 ppm NH₃, 500 ppm NO, and 5 vol% O₂ with N₂ as the balance gas. A catalyst sample of 0.5 g with the particle size of 40–60 mesh was used, and the gas hourly space velocity (GHSV) for all experiments was 150,000 mL·g⁻¹·h⁻¹. The gas compositions were measured by Protea ProtIR 204M online flue gas analyzer. The value of NO conversion was calculated as follows:

\[
\text{NO conversion} \% = \left(1 - \frac{[\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}}\right) \times 100
\]

3.3. Regeneration Methods

The poisoned catalysts were treated in a quartz tube with a stream of 1000 mL/min mixed gas contained 500 ppm SO₂, 5 vol% O₂ and N₂ as the carrier, under different temperatures (320, 345, 370, 395 and 420 °C, according to the Tₜₜ), for 1 h.

3.4. Catalyst Characterization

A PX200A equipment was employed for NH₃ temperature-programmed desorption of ammonia (NH₃-TPD). Powder catalyst (0.2 g) was purged in an atmosphere of 50 mL/min He while the temperature was heated up to 400 °C at 10 °C/min. The purging time was 10 min; then, the sample was cooled gradually down to 100 °C and saturated with 50 mL/min NH₃ and 50 mL/min He for 30 min. After saturation, the sample was purged with pure He at 50 mL/min until the thermal conductivity detector (TCD) signal was stabilized. The signal was collected while the temperature was raised to 500 °C (slope of 10 °C/min).

H₂-temperature programmed reduction (H₂-TPR) was conducted using the PX200A instrument. The catalyst (0.2 g) was purged with pure He at 200 °C for 30 min, and then H₂/Ar mixture gas (10 vol% H₂) was pumped into the reactor with a rate of 50 mL/min. Thirty minutes later, the sample was cooled to ambient temperature in pure He and subsequently heated to 800 °C at a rate of 10 °C/min under 10 vol% H₂/Ar. The values of H₂ consumption were obtained through TCD.
4. Conclusions

This systematic experimental investigation focused on the effects of KCl and SO$_2$ on V$_2$O$_5$-WO$_3$/TiO$_2$ and V$_2$O$_5$-Ce(SO$_4$)$_2$/TiO$_2$. V$_2$O$_5$-WO$_3$/TiO$_2$ and V$_2$O$_5$-Ce(SO$_4$)$_2$/TiO$_2$ were calcinated at different temperatures. Their catalytic activities were inhibited by KCl loading with different molar ratios. The characterization afterwards showed that the reducibility and acidity of V$_2$O$_5$-WO$_3$/TiO$_2$ and V$_2$O$_5$-Ce(SO$_4$)$_2$/TiO$_2$ were remarkably decreased by KCl. V$_2$O$_5$-Ce(SO$_4$)$_2$/TiO$_2$ exhibited a superior alkali metal resistance to V$_2$O$_5$-WO$_3$/TiO$_2$; the poisoned catalytic activity can be efficiently regenerated through SO$_2$ treatment. V$_2$O$_5$-Ce(SO$_4$)$_2$/TiO$_2$ even possessed a better activity than the fresh catalyst.

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