

Regeneration Study on Active Components Supplement of Waste V_2O_5 - WO_3 / TiO_2 SCR Catalyst

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ABSTRACT: The waste Selective Catalytic Reduction (SCR) catalysts were regenerated by active components supplement on the basis of alkali/acid washing treatment. Through orthogonal design, the regenerated SCR catalyst restored the denitration activity of 98.36% at optimal regeneration parameters of 6% WO_3 loaded after 1.2% V_2O_5 loaded and then calcined at 500 °C. The catalysts were characterized by XRD and H_2 -TPR techniques. The XRD patterns and the FT-IR spectrogram showed that the supplemented V_2O_5 and WO_3 were dispersed uniformly in an amorphous state on the surface of TiO_2 support which remained as the anatase phase. The H_2 -TPR characterization reported that V_2O_5 significantly affected the low-temperature activity while WO_3 mainly affected the high-temperature activity, the loading sequence of V_2O_5 before WO_3 not only enhanced the interaction between V_2O_5 and TiO_2 but also facilitated the enrichment of WO_3 on TiO_2 surface.

KEYWORDS: SCR catalyst; Deactivation; Regeneration; The orthogonal design.

INTRODUCTION

Selective Catalytic Reduction (SCR) catalyst was commonly used for flue gas denitration to control NO_x emission in thermal power plants, in which anatase TiO_2 was generally chosen as support to provide large specific surface area for dispersion, 1%~5% V_2O_5 as the main active component to form active sites for reaction, and 5%~10% WO_3 or MoO_3 as promoter component to improve the denitration activity by resisting high temperature and SO_2 poisoning [1]. Soot particles from coal combustion entered the denitration system along with flue gas, abraded the SCR catalyst, deposited on the surface, blocked the channel damaged the active site, hindered reactants adsorption, and even formed adhesive $(NH_4)HSO_4$ by the reaction of SO_2 with NH_3 reductant to aggravate the deactivation of SCR catalyst during about 3 years of De- NO_x operation [2,3]. Regeneration was considered

as the effective treatment method, which includes water washing, acid washing [4,5], alkaline washing [6-7], and impregnation of active components solution [8-11]. Yu *et al.* [6] reported that the dilute NaOH solution could effectively remove sulfate on the surface of the deactivated catalyst, and its specific surface area and pore volume of catalyst become larger using NaOH solution to wash the deactivated SCR denitration catalyst. Cao *et al.* reported the SCR catalyst washed with water or nitric acid. And it was shown that nitric washing could remove most of the ammonium salts deposited on the surface of the waste catalyst and produce crystalline WO_3 , which could effectively inhibit the agglomeration of vanadium species in the process of impregnation [4], however, it was also found that the presence of V and W elements can be detected in the cleaning solution after acid and alkali cleaning

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and regeneration, indicating the loss of active components in this process [6]. In addition, pickling and alkaline washing will reduce the mechanical strength of SCR denitration catalyst to a certain extent [12,13]. A single way of regeneration couldn't effectively restore the activity of the waste SCR catalyst, because of the complex actual operation process and multiple factors to the deactivation of SCR catalysts. Although aqueous ammonia and nitric acid washing were employed to remove alkaline impurities of K_2O , CaO , MgO , and acid impurities of Cl^- , P_2O_5 , SO_3 in our previous work, the denitration activity of SCR catalyst couldn't be effectively recovered by washing regeneration alone, attributed to that V_2O_5 and WO_3 were also leached out by aqueous ammonia and nitric acid leading to the loss of active components and a decrease in denitration activity accordingly [14]. Therefore, it is necessary to investigate the influence of different parameters of active component supplements on the denitration activity of waste SCR catalysts based on the optimal alkali/acid washing regeneration conditions.

EXPERIMENTAL SECTION

Catalyst regeneration

V_2O_5 and WO_3 active components of the waste SCR catalyst were supplemented under optimal alkali/acid washing regeneration conditions with NH_4VO_3 and $5(NH_4)_2O \cdot 12WO_3$ as precursors by equal volume impregnation method [3]. The influence of each factor the denitration activity of regenerated SCR catalysts was investigated by 4 factors and 3 levels of orthogonal design by taking the supplementary loading amount of V_2O_5 and WO_3 , loading sequence, and calcination temperature as factors shown in Table 1.

The process of waste SCR catalyst regeneration was as follows taking V loaded before W for example, the loaded sequences of W loaded before V, V, and W meantime was similar. The designed NH_4VO_3 was weighed and dissolved in oxalic acid solution completely until appearing light blue, the regenerated SCR catalysts under optimal alkali/acid washing conditions were impregnated in the above solution for 30 min with ultrasonic treatment and then stood at room temperature for 5 h, dried at $110\text{ }^\circ\text{C}$ for 10 h, calcined at designed temperature for 3 h to obtain the V_2O_5 supplemented samples. The designed $5(NH_4)_2O \cdot 12WO_3$ was weighed and dissolved in oxalic acid solution completely, the V_2O_5 supplemented samples

were impregnated in the above solution for 30 min with ultrasonic treatment, and then stood at room temperature for 5 h, dried at $110\text{ }^\circ\text{C}$ for 10 h, calcined at the designed temperature for 3 h to obtain the V_2O_5 and WO_3 supplemented samples, and then ground and sieved to 40 ~ 60 mesh for reserved.

Characterization

The crystal structure of regenerated SCR catalysts was measured by X-ray diffraction (XRD, Riga Ku/Mini Flex 600, Japan). The bonding of functional groups on the catalyst's surface was tested by FT-IR (Nicolet IS50, America). H_2 -TPR test was carried out on a chemisorption instrument (Chemisorb 2720, America), 10% H_2/Ar mixture gas has introduced to the system at 30 mL/min rate after being purged by Ar at $300\text{ }^\circ\text{C}$ for 2 h and cooled to room temperature, the temperature was programmed to $1050\text{ }^\circ\text{C}$ at $10^\circ\text{C}/\text{min}$ rate.

Evaluation of Denitration Activity

The denitration performance of regenerated SCR catalysts was evaluated in a fixed-bed reactor. The simulated gas of 600 ppm NO, 600 ppm NH_3 , 5 vol.% O_2 , and N_2 (as the balance gas) was accurately controlled by mass flow meters and imported into the reactor with a loaded 0.3 g catalyst. The concentration of NO in the inlet and outlet gas was measured by a flue gas analyzer (KM9106, Kane) between 240 and $390\text{ }^\circ\text{C}$ in intervals of $30\text{ }^\circ\text{C}$ for maintained 30 min, and the denitration activity was calculated by NO conversion of the percentage of the difference between the inlet and the outlet NO concentration divided by the inlet NO concentration.

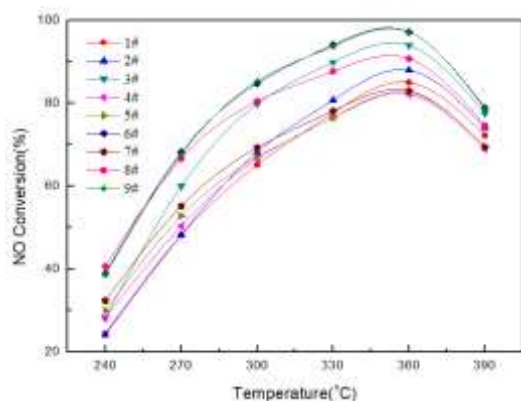
RESULTS AND DISCUSSION

Denitration activity and orthogonal analysis

The active components reduced by V_2O_5 reacted with acid and alkali and WO_3 dissolved in alkali when acidic and alkaline impurities were removed in the alkali/acid washing treatment. Therefore, the active components of V_2O_5 and WO_3 should be supplied in order to effectively recover the activity of waste SCR catalysts. Based on the optimal conditions of 0.05mol/L aqueous ammonia and then $0.15\text{mol}\cdot\text{L}^{-1}$ nitric acid for each washing 10 min, orthogonal active components supplement regeneration was designed as shown in Table 1 to investigate the influence of different parameters. The denitration activity

Table 1: Orthogonal design for active components supplement regeneration.

V ₂ O ₅ load amount / %	WO ₃ load amount / %	Load Sequence	Calcined temperature / °C
0.4	2	W after V	400
0.8	4	V after W	500
1.2	6	V, W Meantime	600

**Fig. 1 Denitration activity of active components supplement regenerated catalysts.**

curves of active components supplement regeneration catalysts illustrated in Fig. 1. It could be found that NO conversion increased rapidly before 360 °C and then decreased slightly with a temperature rising from 240 °C to 390 °C. It might be due to NH₃ oxidized by incomplete combustion oxygen in the flue gas to form NO, NO₂, and N₂O at a higher temperature, these side reactions result in the concentration alternated between NH₃ and NO, thus more NO was detected in outlet gas and denitration activity decreased accordingly. It also could be found that the active components V₂O₅ and WO₃ were supplemented successively, and the denitration activity of the regenerated SCR catalysts had significantly recovered and reached the maximum of 97.28%. Compared with other catalysts, 6#, 9#, and 3# showed better denitration activity at high temperatures, whose supplementary loading of WO₃ was the same as 6%, indicating WO₃ supplement was very important for the denitration activity recovery of waste SCR catalyst, which might provide additional active sites for SCR reaction [15].

Considering all the regenerated catalysts reached the maximum NO conversion at 360 °C, based on which orthogonal analyzed according to Integral Balance Method and shown in Table 2, in which *R*, *K_i*, and *k_i* referred to the extremum difference of each factor, the sum of

all factors, and the average value of each factor at the same level. The factor sequence according to *R* affected the denitration activity was: WO₃ loaded amount, loading sequence, V₂O₅ loaded amount, and calcination temperature. The optimal conditions according to *K* and *k* values for the active components supplement regeneration was as 1.2% V₂O₅ loaded before 6% WO₃ loaded and then calcined at 500 °C.

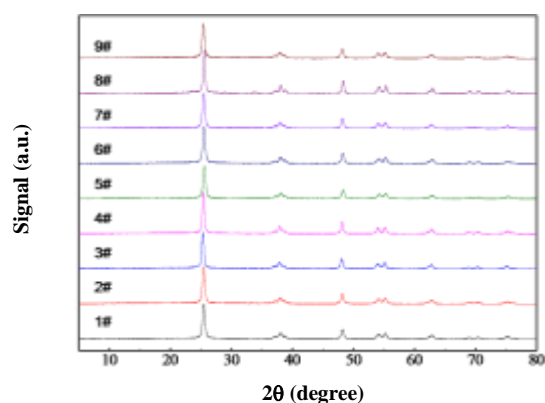
Crystal structure, functional groups, and active sites

Fig. 2 shows the XRD patterns of regenerated catalysts, it could be found that: the characteristic diffraction peaks of all the regenerated catalysts were similar only with some differences in the sharpness, which indicated that the crystal phase of TiO₂ support was not transformed and maintained still anatase phase after active components supplement regeneration, and the active components of V₂O₅ and WO₃ were also well dispersed on the surface of TiO₂ support in the amorphous state [16].

H₂-TPR curves of regenerated SCR catalysts were shown in Fig. 3. Two reduction peaks appeared in all catalysts: peaks within 400 °C and 600 °C attributed to the reduction of V⁵⁺ → V³⁺, [17-19] and peak within 750 °C and 900 °C attributed to the reduction of tungsten oxide. It could be found that: the peak position (indicated reduction difficulty) of V₂O₅ and WO₃ moved to high temperature and the peak area (indicated reduction amount, i.e. hydrogen consumption) increased gradually with the increase of the loading amount of active components, the temperature migration and hydrogen consumption of WO₃ active component were more obvious than V₂O₅, due to V₂O₅ was only about 2% while WO₃ about 10% in the total catalyst. Taking 1#, 2# and 3# catalysts with the same 1.2% V₂O₅ loaded as an example, the reduction amount of 3# with 6% WO₃ loaded was the largest, 2# with 4% loaded was the second, and 1# with 2% loaded was the smallest. Obviously, the larger the loaded amount of active components, the larger the metal oxide particles formed on the surface of the catalyst, which require a higher temperature

Table 2: Orthogonal analysis of active components supplement regenerated catalysts.

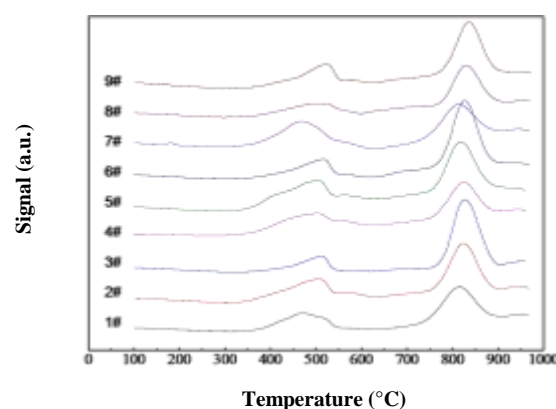
Sample No.	V ₂ O ₅ / %	WO ₃ / %	Loading sequence	Calcined temp. / °C	NO conversion / %
1#	0.4	2	W after V	400	85.08
2#	0.4	4	V after W	500	88.06
3#	0.4	6	V, W Meantime	600	94.02
4#	0.8	2	V after W	600	82.22
5#	0.8	4	V, W Meantime	400	82.70
6#	0.8	6	W after V	500	97.28
7#	1.2	2	V, W Meantime	500	83.08
8#	1.2	4	W after V	600	90.83
9#	1.2	6	V after W	400	97.23
K ₁	267.16	250.38	273.19	265.01	
K ₂	262.21	261.59	267.51	268.42	
K ₃	271.14	288.53	259.80	267.07	
k ₁	89.05	83.46	91.06	88.34	
k ₂	87.40	87.20	89.17	89.47	
k ₃	90.38	96.18	86.60	89.02	
R	2.98	12.71	4.46	1.14	

**Fig. 2: XRD patterns of active components supplement regenerated catalysts.**

to reduce, the more complex active species that existed on the catalyst, the more H₂ was consumed in the reduction process, and then the larger reduction peak area appeared.

Effect of regeneration parameters on denitration activity

Fig. 4a showed the histogram of denitration activity of regenerated SCR catalysts with different WO₃ loaded. It could be found that denitration activity was continuously

**Fig. 3: H₂-TPR curves of active components supplement regenerated catalysts.**

improved with the increase of WO₃ loaded. WO₃ was considered an active promoter in SCR catalysts to increase the brønsted acid sites on the surface of the catalysts and improve the thermal stability of the support TiO₂ to inhibit its sintering or crystal phase transformation. *Aleman et al.* found that the specific surface area of SCR catalysts increased with WO₃ loading increased when V₂O₅ loading was fixed, which meant more reactants could be adsorbed [20].

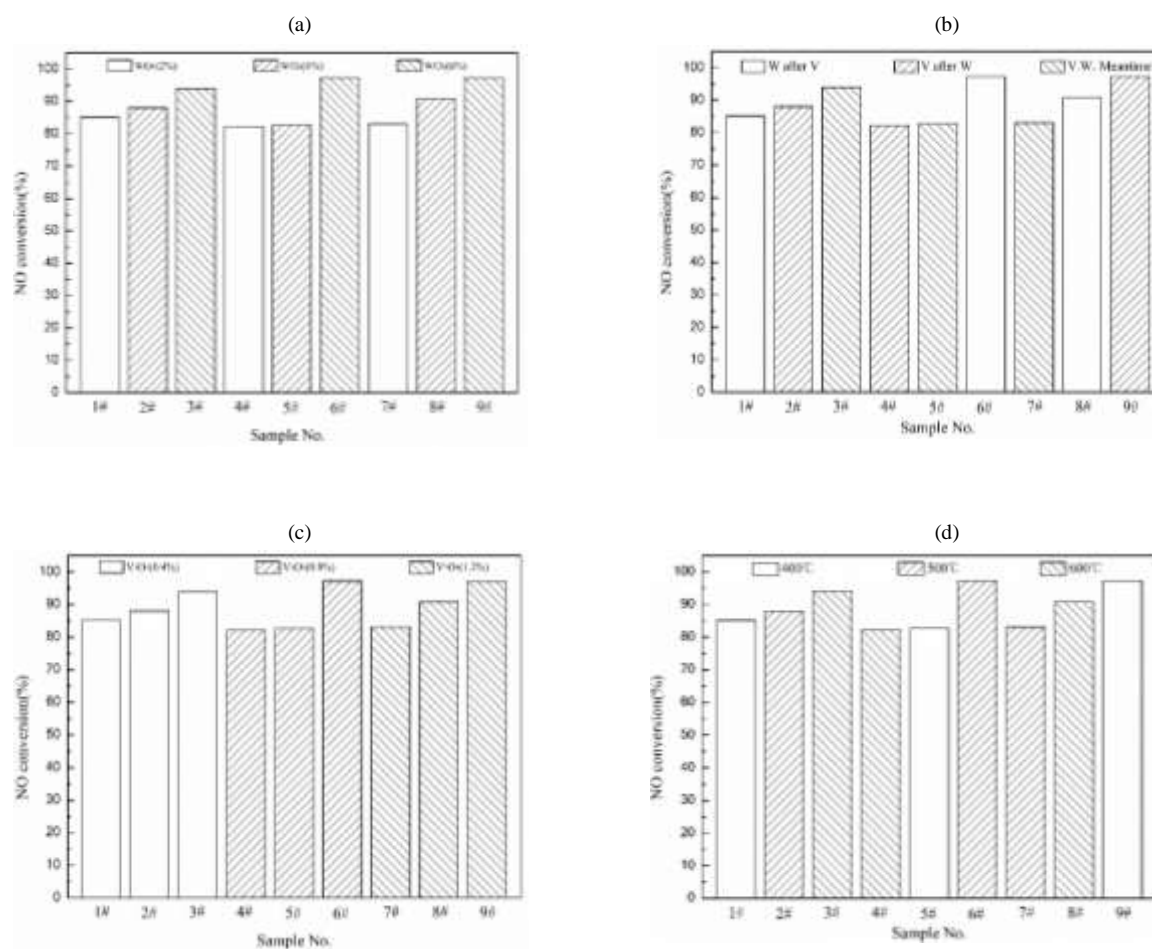


Fig. 4: Effect of different parameters on the denitration activity of regenerated SCR catalysts a: WO_3 loading, b: loading sequence, c: V_2O_5 loading, d: calcination temperature.

Furthermore, SCR catalysts loaded with WO_3 alone showed high denitration activity at high temperatures by providing another active site for SCR reaction. Although WO_3 might distribute on the catalyst surface inhomogeneity leading to agglomeration and crystallization, which would have a negative impact on denitration activity. However, 6% WO_3 loaded catalysts of 3#, 6#, and 9# were uniformly dispersed on the surface of catalysts (see XRD patterns in Fig. 2), so higher WO_3 loading was beneficial to the denitration reaction of regenerated catalysts.

Fig. 4b showed the denitration activity histogram of regenerated SCR catalysts in different loading sequences. It could be found that WO_3 loaded after V_2O_5 illustrated better denitration activity, V_2O_5 loaded after WO_3 middle, while V_2O_5 and WO_3 loaded meantime poor. The higher denitration activity of 3# might be attributed to the larger amount of WO_3 loaded.

The interaction between the first loaded component and the TiO_2 support was stronger naturally in the calcination process, conducting to improve the denitration activity. The loading amount of WO_3 is several times higher than that of V_2O_5 , so WO_3 loaded after V_2O_5 had little effect on interaction with TiO_2 support, conducting to the stronger interaction between V_2O_5 and TiO_2 support, while WO_3 loaded before V_2O_5 detriment to weaker interaction of V_2O_5 with TiO_2 .

Figure 4c showed the denitration activity histogram of regenerated SCR catalysts with different V_2O_5 loading. It could be found that the denitration activity of the catalysts with 1.2% V_2O_5 loaded was relatively better than others. Obviously, the more V_2O_5 loaded, the more Brønsted and Lewis acid sites could be provided, and then higher denitration activity obtained. The low denitration activity of 7# might be due to the lowest loading of WO_3 .

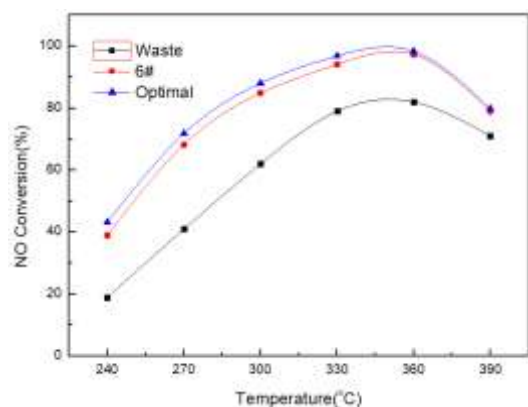


Fig. 5: Denitration activity of optimal, 6# regenerated, and waste SCR catalysts.

Since the histogram in Fig. 5 was drawn based on the data of 360 °C, at which all the regenerated SCR catalysts displayed the highest denitration activity, thus it reflected the denitration activity of catalysts at high temperatures after 300 °C. However, it could be found that the catalysts with 1.2% V_2O_5 loaded showed significantly high denitration activity than others at low temperatures through analysis of NO conversion before 300 °C in Fig. 1. Considering the above discussion of the effect of WO_3 loading amount on denitration activity, the conclusion could be found that: V_2O_5 loading amount contributed to denitration activity at low temperature (corresponding to the reduction peak of V_2O_5 at low temperature in Fig. 3) and WO_3 loading amount to denitration activity at high temperature (corresponding to the reduction peak of WO_3 at low temperature in Fig. 3).

Fig. 4d showed the denitration activity histogram of regenerated SCR catalysts with different calcination temperatures. It could be found that: calcination temperature had no significant effect on denitration activity, because all the supplementary active components of V_2O_5 and WO_3 stably dispersed on TiO_2 support and keeping the chemical valence of V and W (see XRD patterns in Figure 2) with in the investigated calcination temperature range of 400 °C to 600 °C.

The denitration activity of the regenerated SCR catalysts calcined at 400 °C was lower than 500 °C and 600 °C, the reason 500 °C was selected as the optimal calcination temperature was that: lower temperature implied less energy consumption in terms of regeneration cost, the specific surface area and acid activity number would inevitably be decreased and then denitration activity

also decreased with the increase of calcination temperature on the other hand. Higher denitration activity of 9# calcined at 400 °C was obviously related to a large number of active components loaded (see Table 3).

Validation of denitration activity of SCR regenerated catalyst under optimal conditions

The optimal conditions for the active components supplement regeneration were obtained as 1.2% V_2O_5 loaded before 6% WO_3 loaded and then calcined at 500 °C through orthogonal analysis in 3.1 section, which was different from the nine catalysts investigated in the experiment and most similar to 6# only V_2O_5 loaded amount of 0.8% replaced by 1.2%. Therefore, the optimal regenerated SCR catalyst was prepared and activity evaluated, whose denitration activity was compared with that of 6# and waste SCR catalyst shown in Fig. 4.

It could be found that: with the increase of V_2O_5 loaded from 0.8% to 1.2%, the denitration activity of the optimal regenerated catalyst was reached up to 42.57% by increasing about 4% at 240 °C and up to 98.36% by increasing more than 1% at 360 °C compared with that of 6#, and improved significantly by increasing about 15% at 240 °C and more than 13% at 360 °C with that of waste SCR catalyst, proving the active components supplement regeneration process could effectively restore the denitration activity and achieve the reuse purpose of the waste SCR catalyst.

CONCLUSIONS

The optimal active components supplement regeneration parameters was obtained through orthogonal design as 1.2% V_2O_5 loaded before 6% WO_3 loaded and then calcined at 500 °C, at which the denitration activity of the regenerated SCR catalyst was significantly improved and reached up to 98.36% by increasing more than 13% at 360 °C compared with the waste SCR catalyst.

The characterization indicated that: TiO_2 support of all regenerated SCR catalysts remained anatase crystal phase, and the active components supplemented could be well dispersed on the surface of TiO_2 support in an amorphous state. The denitration activity of the regenerated SCR catalysts increased with the increase of V_2O_5 and WO_3 loaded. V_2O_5 significantly affected the low-temperature activity while WO_3 mainly affected the high-temperature activity, the synergy between them realized the denitration

the activity of regenerated SCR catalysts. The loading sequence of V_2O_5 before WO_3 not only enhanced the interaction between V_2O_5 and TiO_2 but also facilitated the enrichment of WO_3 on TiO_2 surface, and calcined at $500\text{ }^\circ\text{C}$ could remain the anatase crystal phase of TiO_2 support, both of them were advantaged to denitration activity of regenerated SCR catalysts.

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