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Regeneration of commercial selective catalyst reduction catalysts deactivated by Pb and other inorganic elements

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ABSTRACT

The regeneration of commercial SCR (Selective Catalyst Reduction) catalysts deactivated by Pb and other elements was studied. The deactivated catalyst samples were prepared by chemical impregnation with mixed solution containing K_2SO_4 , Na_2SO_4 , $CaSO_4$, $Pb(NO_3)_2$ and $NH_4H_2PO_4$. A novel method combining Ethylenediaminetetraacetic acid disodium salt (EDTA-2Na) and H_2SO_4 solution (viz. catalysts treated by dilute EDTA-2Na and H_2SO_4 solution in sequence) was used to recover the activity of deactivated samples, and the effect was compared with single H_2SO_4 , oxalic acid, acetic acid, EDTA or HNO_3 solutions. The surface structure, acidity and reducibility of samples were characterized by N_2 adsorption-desorption, inductively coupled plasma optical emission spectrometer (ICP-OES), scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray fluorescence (XRF), H_2 -temperature programmed section (H_2 -TPR), NH_3 -temperature programmed desorption (NH_3 -TPD) and in situ DRIFTS. Impurities caused a decrease of specific surface area and surface reducibility, as well as Brønsted acid sites, and therefore led to severe deactivation of the SCR catalyst. The use of an acid solution alone possibly eliminated the impurities on the deactivated catalyst to some extent, and also increased the specific surface area and Brønsted acid sites and promoted the surface reducibility, thus recovered the activity partially. The combination of EDTA-2Na and H_2SO_4 could remove most of the impurities and improve the activity significantly. The removal of Pb should be an important factor for regeneration. Due to a high removal rate for Pb and other impurities, the combination of EDTA-2Na and H_2SO_4 solutions provided the best efficiency.

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Introduction

Catalysts are the key to the selective catalytic reduction of Selective catalytic reduction of NH_3 (NH_3 -SCR) method, which is commonly used in coal-fired power plants for abating

nitrogen oxides (NO_x) in flue gas (Cheng et al., 2014). V_2O_5 - WO_3/TiO_2 is the main commercial catalyst used in NH_3 -SCR systems due to its high catalytic activity, high thermal stability and resistance to SO_2 (Forzatti, 2001). However, owing to the toxicity of V_2O_5 (Larsson et al., 2013), landfilling

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of spent SCR catalysts will not only waste metal resources but also pose potentially huge threats to the environment and human beings.

Due to the strict emission standards for NO_x, hundreds of coal-fired power plants have had to introduce de-NO_x technology since 2012 in China. By 2014, all coal-fired power plants in China with a capacity of about 660 GW had installed de-NO_x processes to reduce NO_x emission. Among these, the NH₃-SCR process is dominant, and the total volume of catalysts in use was about 528,000 m³. It can be predicted that other industries (i.e. waste incinerators, cement kilns, steel industries) will also use NH₃-SCR technology in the future. Many impurities in flue gas can cause the deactivation of SCR catalysts, for example, alkali metals and alkaline earth metals (Kröcher and Elsener, 2008; Kamata et al., 1999; Chen et al., 2011), heavy metals (Kröcher and Elsener, 2008; Khodayari and Odenbrand, 1998), P (Castellino et al., 2008, 2009) and S (Crocker et al., 2004; Yu et al., 2016). Generally, an SCR catalyst has a lifetime around 2–7 years, depending upon its application and placement in power plants (Argyle and Bartholomew, 2015). Huge amounts of spent SCR catalysts will thus be produced, and their treatment will be a serious problem in the near future.

The regeneration of used catalysts will be a preferable option because it could prolong the lifetime of catalysts and thus save metal resources. Regeneration of three-way automobile catalysts (TWCs) and other catalysts has drawn much attention in recent years. (López et al., 2011; Christou et al., 2006, 2007; Subramanian et al., 2011; Christou and Efstathiou, 2013). However, research on regeneration of SCR catalysts has been limited. In our recent studies, we found that a combined method (*viz.* catalysts treated by dilute NaOH and HNO₃ solutions in sequence) was effective in regeneration of a deactivated SCR catalyst used in a coal-fired power plant (Yu et al., 2016). In addition, dilute H₂SO₄ solution was an effective method for regenerating SCR catalysts deactivated by alkali metals, and dilute H₂O₂ solution seemed to be effective in regeneration of catalysts poisoned by As (Shang et al., 2012; Peng et al., 2015; Li et al., 2015; Gao et al., 2014). Municipal waste incinerators have been used in many countries to get rid of waste. Unlike the flue gas from coal fired power plants, Pb is a typical element in the flue gas from municipal waste incinerators and could lead to the deactivation of SCR catalysts (Khodayari and Odenbrand, 1998; Jiang et al., 2014, 2015). However, research on regeneration of SCR catalysts deactivated by Pb has been rare. Thus, there is still a need to explore new methods for regeneration of SCR catalysts.

In this article, the regeneration of commercial SCR catalysts treated by mixed solutions containing K₂SO₄, Na₂SO₄, CaSO₄, Pb(NO₃)₂ and NH₄H₂PO₄ was investigated. H₂SO₄, oxalic acid, HNO₃, acetic acid and Ethylenediaminetetraacetic acid (EDTA) solutions were used to regenerate the deactivated samples. A novel method combining Ethylenediaminetetraacetic acid disodium salt (EDTA-2Na) and H₂SO₄ solutions was also used for regeneration of deactivated samples. The activities of samples regenerated by different methods were compared and the fresh, deactivated and regenerated samples were characterized by N₂ adsorption-desorption, X-ray diffraction (XRD), X-ray fluorescence (XRF), H₂-temperature programmed reduction (H₂-TPR), scanning electron microscopy

(SEM), NH₃-temperature programmed desorption (NH₃-TPD), *in situ* diffuse reflectance infrared Fourier transform spectroscopy (*in situ* DRIFTS) and an inductively coupled plasma optical emission spectrometer (ICP-OES).

1. Experimental

1.1. Catalyst samples

The catalyst used in the experiment was a honeycomb commercial SCR catalyst with wall thickness of 0.90 mm and pitch of 7.70 mm. For sample preparation, fresh catalyst (Fresh) samples cut into pieces with 16 channels (about 3.2 × 3.2 × 5.0 cm) were impregnated with a 500 mL aqueous mixed solution containing K₂SO₄ (2 wt.%), Na₂SO₄ (2 wt.%), Pb(NO₃)₂ (2 wt.%), NH₄H₂PO₄ (2 wt.%) and CaSO₄ (saturated). The wet samples (De) were then dried in air at 120°C for 2 hr. followed by calcination at 600°C in air for 5 hr. The deactivated samples were first impregnated with 1 L regeneration solution for 5 min under ultrasound and then washed (continuous air stirring, 100 mL/min, 0.05 MPa) at 25°C for a certain time. Afterward, the samples were dried at 120°C for 2 hr. The detailed methods are shown in Table 1.

1.2. Activity measurements

The catalytic activity tests for SCR of nitric oxide (NO) by NH₃ were evaluated in a fixed-bed quartz reactor (Φ10 mm × 600 mm). The catalyst sample (20–40 mesh, 1.2 mL) was placed in the middle of the reactor. The total gas flow rate was 1250 mL/min (STP) and consisted of NO (700 ppm), NH₃ (700 ppm) and O₂ (4%) in N₂. A flue gas analyzer (T-350, Testo Company, Germany) was used to measure the concentrations of O₂ and NO. N₂O at the outlet of the reactor was detected by gas chromatography (7890A, Agilent Technologies, USA). The conversion of NO was obtained by the following equation:

$$x = \frac{C_{\text{NO,in}} - C_{\text{NO,out}}}{C_{\text{NO,in}}} \times 100\% \quad (1)$$

where $C_{\text{NO,in}}$ and $C_{\text{NO,out}}$ are the NO concentrations of the simulated gas stream at the inlet and outlet of the reactor, respectively.

Table 1 – Methods for regeneration of deactivated samples.

Sample	Method
Re-1	0.01 mol/L H ₂ SO ₄ , 30 min
Re-2	0.01 mol/L oxalic acid, 30 min
Re-3	0.01 mol/L acetic acid, 30 min
Re-4	Saturated Ethylenediaminetetraacetic acid (EDTA), 30 min
Re-5	0.01 mol/L HNO ₃ , 30 min
Re-6	0.01 mol/L Ethylenediaminetetraacetic acid disodium salt (EDTA-2Na), 15 min + 0.01 mol/L H ₂ SO ₄ , 15 min
Re-7	0.02 mol/L Ethylenediaminetetraacetic acid disodium salt (EDTA-2Na), 15 min + 0.02 mol/L H ₂ SO ₄ , 15 min
Re-8	0.04 mol/L Ethylenediaminetetraacetic acid disodium salt (EDTA-2Na), 15 min + 0.04 mol/L H ₂ SO ₄ , 15 min

1.3. Catalyst characterization

Nitrogen adsorption–desorption: catalyst surface area and pore size were characterized by a NOVA 2000e surface area and pore size analyzer (Quantachrome, USA) using nitrogen adsorption at liquid nitrogen temperature (-196°C). Prior to the analysis, samples were degassed at 300°C under vacuum for 3 hr.

ICP-OES: about 0.1 g of the catalyst sample was digested by a mixture of HNO_3 and HF , and then the concentrations of Na, K, Ca, P and Pb were determined by ICP-OES (Optima 7000DV, PerkinElmer, USA).

XRD: the crystalline structures of metal oxides were studied using a wide angle X'Pert Pro XRD diffractometer (PANalytical B.V., Netherlands) with $\text{CuK}\alpha$ radiation (40 kV, 40 mA) monochromatized with a graphite monochromator. The samples were scanned over the 2-theta range 10 to 80° with a step size of 0.02° .

XRF: the concentrations of Ti, V, W and S were detected by an XRF spectrometer (Axios-MAX, PANalytical B.V., Netherlands). The catalyst samples were crushed and ground to less than 200 mesh. About 3.0 g samples of the powders were pressed with boric acid, then the pellets were analyzed by an XRF spectrometer.

H_2 -TPR: the temperature programmed reduction profile of catalysts was characterized with a Quantachrome ChemBET-3000 TPR-TPD chemisorption analyzer. A 30 mg sample was preheated under a stream of helium at 500°C for 1 hr and then cooled to 200°C . The temperature was progressively increased up to 900°C at $10^{\circ}\text{C}/\text{min}$ in a stream of 5% H_2/Ar and the TCD signal was recorded.

NH_3 -TPD: NH_3 -TPD was also carried out on the Quantachrome ChemBET-3000 TPR-TPD chemisorption analyzer, and the signal of NH_3 was detected by mass spectrometry (DYCOR LC-D100, Ametek Company, USA). A 50 mg sample was preheated under a stream of helium at 500°C for 1 hr and then cooled to 50°C , then the gas flow was changed to 5% NH_3/Ar for 30 min. Then the carrier gas was switched to helium and the sample was purged at 100°C for 1 hr to remove weakly adsorbed NH_3 . The temperature then progressively increased up to 600°C at $10^{\circ}\text{C}/\text{min}$.

SEM: the morphology of catalysts was imaged using a Hitachi S-4800 scanning electronic microscope (Hitachi, Japan). Small flat pieces cut from catalyst samples were coated by sputtering with platinum for imaging.

1.4. In situ DRIFTS experiment

In situ DRIFTS of catalyst NH_3 adsorption was performed by using a Bruker Vertex 70 infrared spectrometer with an MCT detector cooled by liquid nitrogen. Prior to NH_3 adsorption, the powdered catalyst sample was preheated in the reaction cell at 500°C for 1 hr under a N_2 flow (50 mL/min), and then cooled to 50°C . Afterwards, the sample was exposed to 3000 ppm NH_3/N_2 for 15 min and then purged with N_2 for 15 min. DRIFTS spectra were collected at 50°C before and after NH_3 saturation. The spectrum was obtained by subtracting the background contribution from the collected spectrum. All the spectra were collected at a resolution of 4 cm^{-1} by accumulating 100 scans.

2. Results and discussion

2.1. Catalytic activity

The NO conversion for Fresh, De and regenerated samples is shown in Fig. 1a. Under the experimental conditions, the Fresh sample exhibited the best activity, with the maximum NO conversion rate of 94.9% (380°C). After the commercial SCR catalyst was doped with impurities, a noticeable deactivation was observed. The De sample showed poor activity with a maximum NO conversion of only 44.6% (380°C), significantly less than that of Fresh sample. The various regeneration methods increased the activity considerably, and the activity of regenerated samples could be ordered as follows: $\text{Re-3} < \text{Re-1} < \text{Re-2} < \text{Re-4} < \text{Re-5} < \text{Re-6} < \text{Re-7} < \text{Re-8}$. Though dilute H_2SO_4 solution has been thought to be an effective method for regeneration of aged SCR catalysts (Shang et al., 2012; Gao et al., 2014), in this experiment, the effect of H_2SO_4 solution was only higher than that of acetic acid solution and

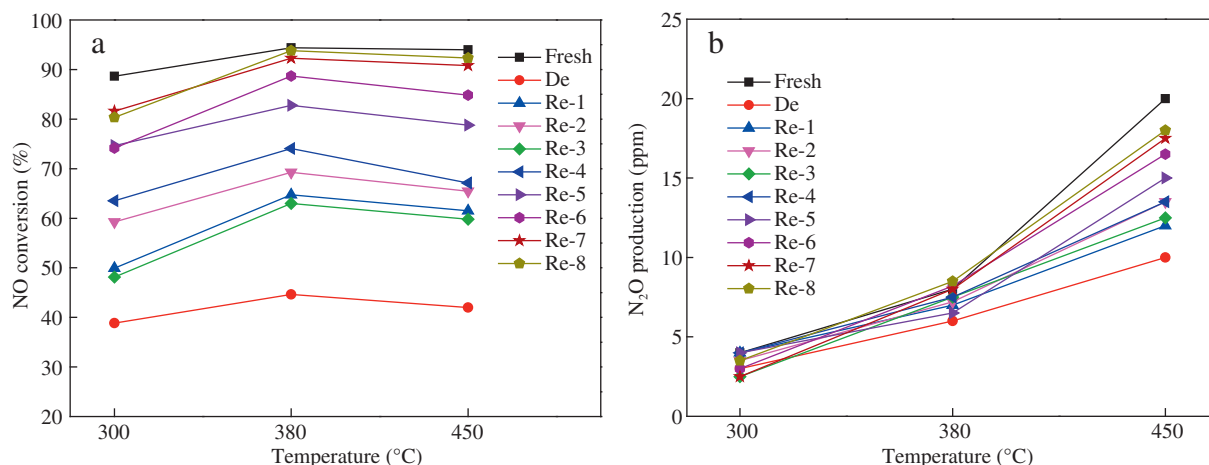


Fig. 1 – nitric oxide (NO) conversion and N_2O production of samples. (a) nitric oxide (NO) conversion; (b): N_2O production. Re-1-Re-8 refer to Table 1.

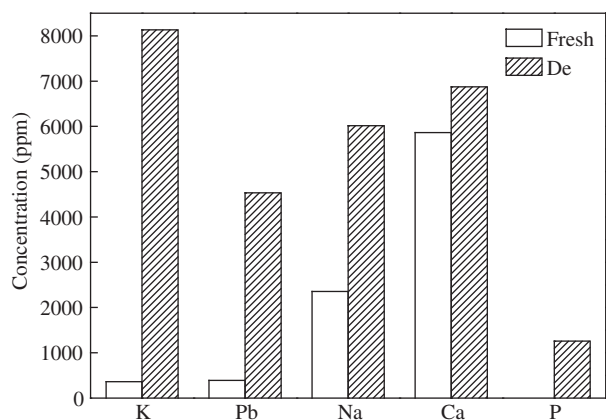


Fig. 2 – ICP results of fresh and deactivated catalysts (De). ICP: inductively coupled plasma.

markedly lower than those of other methods. Dilute HNO_3 solution showed a better regeneration effect among the acid solutions and the maximum NO conversion could reach 82.7% (380°C), which was about 87% of that of the Fresh sample. The samples regenerated by combining EDTA-2Na and H_2SO_4 solutions showed a higher activity, and the regeneration effect increased with the solution concentration. A maximum NO conversion of 93.7% (380°C, Re-8) could be obtained, similar to that of the Fresh sample. The NO conversion of the Re-8 sample at 300°C was about 80.3%, lower than that of the fresh catalyst (88.6%), but still distinctly higher than that of the deactivated sample (38.8%). It could be concluded that the combination of EDTA-2Na and H_2SO_4 solutions was an effective method for regeneration of SCR catalysts.

N_2O is the main byproduct of NH_3 -SCR, and it contributes to global warming and the depletion of stratospheric ozone (Xu et al., 2015). The production of N_2O for each sample was measured and the results are shown in Fig. 1b. The production of N_2O increased with temperature and the production of N_2O for the Fresh sample increased from 2.6 ppm to 21.5 ppm as the temperature increased from 300 to 450°C. When the samples were doped with impurities, the production of N_2O decreased greatly. The production of N_2O increased after the sample was regenerated by the washing solutions. It seemed that the production of N_2O was proportional to the NO conversion of the catalyst samples.

2.2. Catalyst sample characterization

The concentrations of Pb, K, Na, Ca and P in fresh and deactivated samples are shown in Fig. 2. As glass fibers are generally added in the commercial SCR catalysts to enhance the mechanical properties, Na and Ca presented higher concentrations among the elements in fresh catalyst (Nova et al., 2001). After the fresh sample was impregnated by the mixed solution, the concentrations of Pb, K, Na, Ca and P in De sample were obviously higher than those for the Fresh one, especially Na, Pb and K. Na or K could react with V-OH to form V-ONa or V-OK, which might inhibit the absorption of NH_3 on the surface of the catalysts, and thus caused the deactivation of catalysts (Kamata et al., 1999; Chen et al., 2011). In addition, Na_2SO_4 and K_2SO_4 would damage the surface pore structure of catalysts, and caused a decrease in specific surface area (Larsson et al., 2007). Pb might react with V=OH and form V-O-Pb-O-V, thus hindering NH_3 absorption on the surface of catalysts (Jiang et al., 2014). P could form vanadyl phosphate,

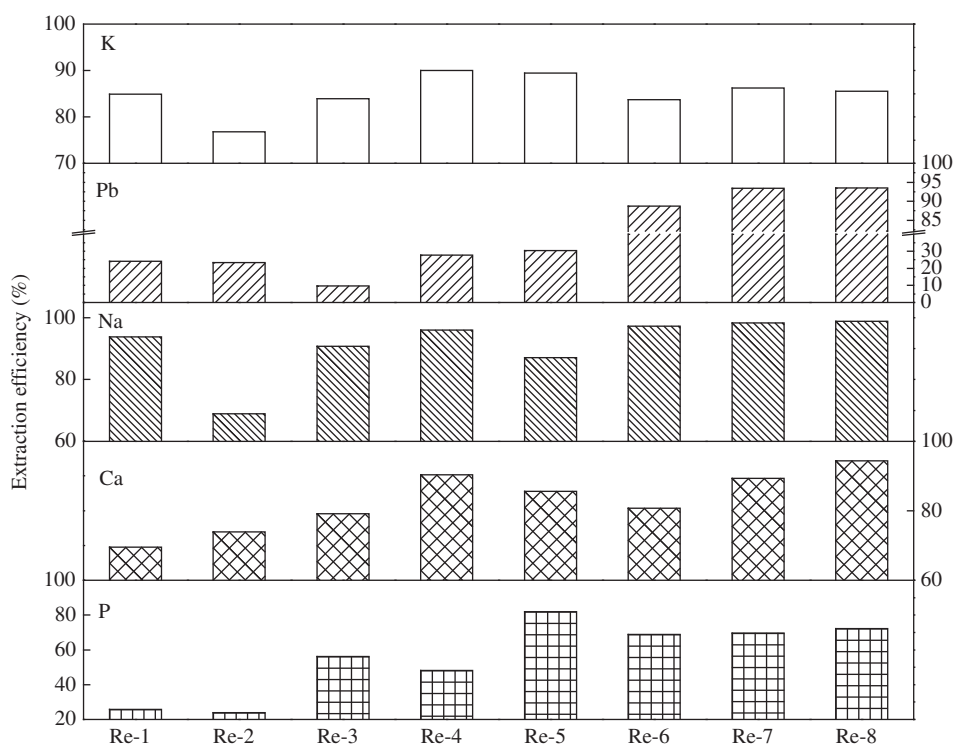


Fig. 3 – The extraction efficiency of K, Pb, Na, Ca and P for different methods.

Table 2 – Concentration of Ti (given as TiO₂), V (V₂O₅), W (WO₃) and S (SO₃) in all samples detected by XRF (%).

Sample	TiO ₂	V ₂ O ₅	WO ₃	SO ₃
Fresh	85.31	1.36	4.45	1.24
De	83.78	1.31	4.39	0.97
Re-1	83.01	1.15	4.67	0.84
Re-2	85.05	1.05	4.37	0.52
Re-3	85.42	1.12	4.17	0.56
Re-4	84.87	1.11	4.78	0.61
Re-5	85.93	0.99	4.97	0.13
Re-6	85.08	1.13	4.88	0.29
Re-7	84.91	1.09	4.78	0.31
Re-8	84.72	1.09	4.57	0.28

which has been proposed as one of the reasons for deactivation of the catalysts (Kamata et al., 1998). Like Na₂SO₄ and K₂SO₄, CaSO₄ also could lead to a decrease in specific surface area (Crocker et al., 2004). The deposition of a mass of impurities on the surface of the catalyst is likely to be the main reason for the deactivation of the SCR catalysts.

The regeneration methods could eliminate the impurities on the catalyst to some extent, and the extraction efficiency of different methods is shown in Fig. 3. It could be found that all methods could remove K efficiently, and more than 75% of K was eliminated from the deactivated catalysts. However, the extraction efficiency for Pb of the different methods showed clear differences. All single acid solutions presented a low extraction efficiency (<30%). However, the combination of EDTA-2Na and H₂SO₄ solutions resulted in a high extraction efficiency (>85%) and the solution concentration had some influence on the extraction efficiency for Pb. The extraction efficiency of 0.01 mol/L solution was about 87%, but for 0.02 and 0.04 mol/L solution, the extraction efficiency increased to about 93%. The extraction efficiency for Pb followed the order: Re-3 < Re-1 ≈ Re-2 < Re-4 < Re-5 < Re-6 < Re-7 ≈ Re-8, which was very similar to the activity sequence of regenerated samples, suggesting that the elimination of Pb should be the key factor for regeneration of catalysts in this experiment. This might explain the reason of the lower effect of H₂SO₄ solution, which was different from the findings of some

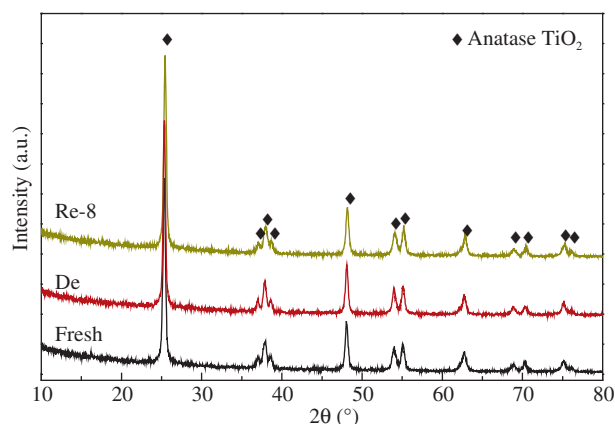


Fig. 4 – XRD patterns obtained over Fresh, De and Re-8 sample.

former studies (Shang et al., 2012; Gao et al., 2014). In other works, alkali elements were found to be the main reason for the deactivation of catalysts (Shang et al., 2012; Gao et al., 2014) and H₂SO₄ solution could remove alkali elements efficiently. But in this experiment, H₂SO₄ solution showed lower ability for elimination of Pb, so the regeneration effect of H₂SO₄ solution was low for the catalyst samples used in this experiment. All methods showed a high extraction efficiency for Na (>84%) except oxalic acid (69%). Among the single acids, it seemed that HNO₃ presented the highest extraction efficiency for Ca (90%), similar to the combination of EDTA-2Na and H₂SO₄. The extraction efficiency for P by

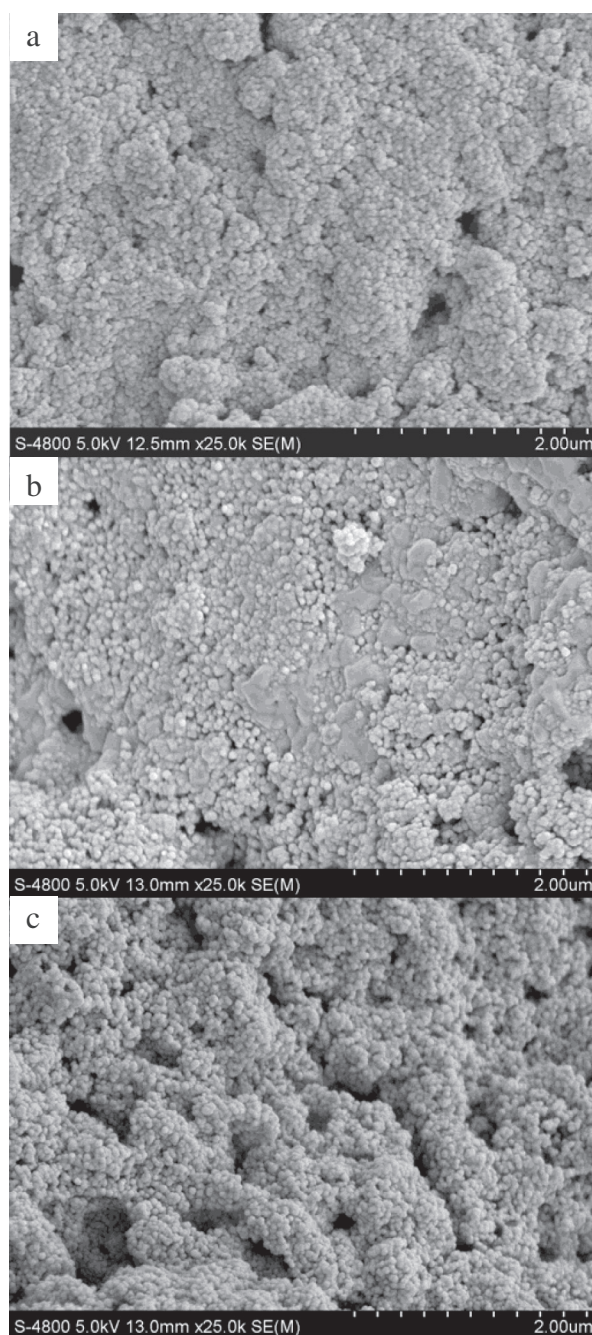


Fig. 5 – SEM photos of (a) Fresh, (b) De and (c) Re-8 sample. SEM: scanning electron microscopy.

different methods varied greatly, and HNO_3 was more effective than other methods. It seemed that among single acids, HNO_3 exhibited the best efficiency for removing impurities other than Pb. In summary, the combination of EDTA-2Na and H_2SO_4 should be considered the best method to remove impurities.

The concentrations of Ti (given as TiO_2), V (given as V_2O_5), W (given as WO_3) and S (given as SO_3) in all samples were measured by XRF and the results are shown in Table 2. Compared with Fresh and De samples, it seemed that the concentrations of TiO_2 and WO_3 showed little variation in the regenerated samples, suggesting that washing did not have an obvious influence on the carrier. However, the concentration of V_2O_5 decreased to some extent during the regeneration process, which was consistent with other research (Yu et al., 2016). After regeneration, the concentration of S (SO_3) decreased greatly, suggesting that sulfate would dissolve in the washing solution.

The XRD results of Fresh, De and Re-8 samples are shown in Fig. 4. Only the diffraction peaks associated with anatase TiO_2 were detected in the Fresh sample. The crystalline phases of V_2O_5 and WO_3 could not be detected in the XRD patterns because the amounts of V_2O_5 (1.36 wt.%) and WO_3 (4.45 wt.%) in the catalyst were too low to give measureable diffraction XRD patterns. After the catalyst was doped with impurities, the patterns still only showed the diffraction peaks associated with anatase, suggesting that the concentrations of impurities were lower than the detection limit. After regeneration, the crystalline structure of the carrier did not change, indicating that the carrier was stable during the regeneration period.

SEM photos showing the morphology of Fresh, De and Re-8 samples are shown in Fig. 5. As the figure illustrates, the Fresh sample presented a coarse surface and the particles on the surface were homogeneous. By contrast, the surface of the De sample was significantly different from that of the Fresh one, where some agglomerations appeared, which could be associated with new impurities deposited on the surface of the catalyst. After regeneration by the combination of EDTA-2Na and H_2SO_4 solutions, the impurities on the surface of the deactivated catalyst were removed and the surface was similar to that of the Fresh sample, suggesting that the combination of EDTA-2Na and H_2SO_4 solutions was

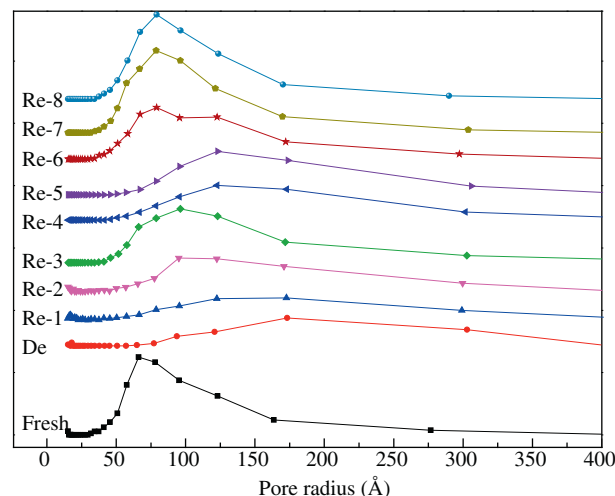


Fig. 6 – Distribution of pore size for fresh, deactivated and regenerated samples.

an effective method to remove impurities on the surface of catalysts.

The specific surface area (S_{BET}), total pore volume (V_p) and average pore radius (r_A) of samples are shown in Table 3. The specific surface area of the Fresh sample was $50.2 \text{ m}^2/\text{g}$ with a mean pore radius of 11.3 nm. After the catalyst samples were impregnated by the mixed solution, the specific surface area decreased significantly. The specific surface area of De was only 42.4% that of the Fresh sample, indicating that the impurities had a damaging effect on the pore structure of the catalyst. Because a high specific surface area supplies more active sites, the specific surface area is an important factor in catalyst activity. The significant decrease of specific surface area should be an important reason for deactivation of catalysts. After regeneration with different methods, the specific surface area increased greatly and varied for different methods. The combination of EDTA-2Na and H_2SO_4 solutions showed the best efficiency with the highest specific surface area, $45.8 \text{ m}^2/\text{g}$, about 2.3 times that of the De sample and 90%

Table 3 – Specific surface areas, total pore volume and average pore diameter of samples.

Sample	S_{BET} (m^2/g)	V_p^a (cm^3/g)	r_A (nm)
Fresh	50.2	0.2833	11.3
De	21.3	0.2518	23.6
Re-1	26.7	0.2142	16.1
Re-2	28.1	0.2373	16.9
Re-3	27.1	0.2431	18.0
Re-4	29.3	0.2518	17.2
Re-5	30.1	0.2685	17.8
Re-6	41.9	0.2578	12.3
Re-7	45.8	0.2818	12.3
Re-8	44.9	0.2815	12.5

^a Obtained at relative pressure of $P/P_0 = 0.99$.

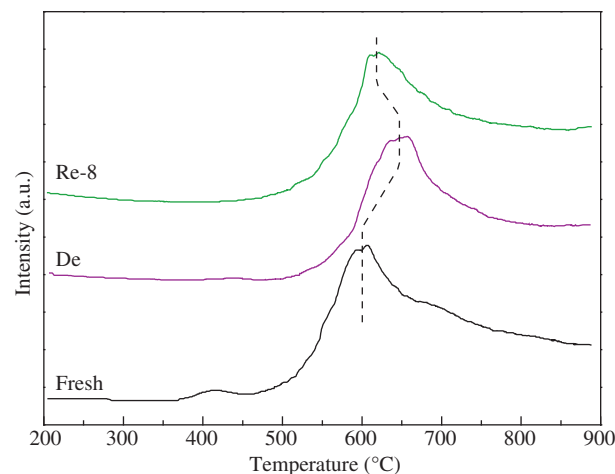


Fig. 7 – The results of H_2 -TPR for Fresh, De and Re-8 sample. H_2 -TPR: H_2 -temperature programmed reduction.

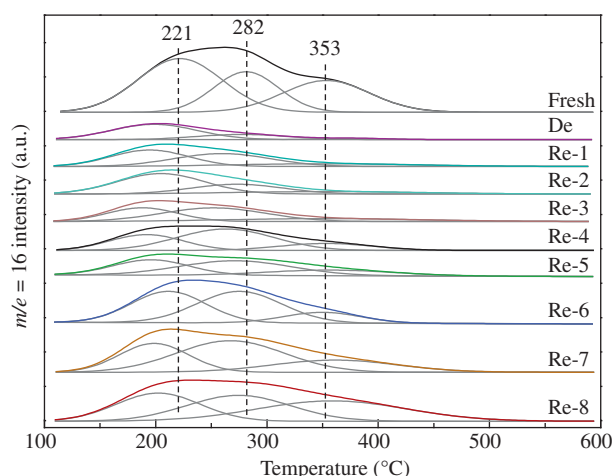


Fig. 8 – NH₃-TPD profiles of all samples. NH₃-TPD: NH₃-temperature programmed reduction.

of the Fresh sample value. The distribution of pore size for each sample is shown in Fig. 6. The Fresh sample presented only a peak at about 6.0 nm; however, the position of the peak shifted to about 17.5 nm for the De sample. After the De sample was washed by different solutions, the distribution of pore size was improved and the Re-6, Re-7 and Re-8 samples presented results similar to the Fresh sample. It could be concluded that the washing process could remove the impurities and recover the pore structure of deactivated catalysts to some extent.

A typical NH₃-SCR reaction is considered to include two cycles: one involving acid sites and one on redox sites (Topsøe, 1994). The reducibility of vanadium species on the catalyst has a great impact on the activity of the catalyst (Paganini et al., 1997; Chen et al., 2011). But in the previous works, most researchers focused on the differences in acid sites between the fresh and deactivated catalyst, and attention to the reducibility of vanadium species on the deactivated catalyst was limited. The surface reducibility of the Fresh, De and Re-8 samples was characterized by H₂-TPR and the results are shown in Fig. 7. All samples presented a dominant

reduction peak in the experimental temperature range. The dominant reduction of the Fresh sample peaked around 600°C, mainly due to the reduction of V species. The temperature location of the reduction peak was higher than that reported in other studies (Chen et al., 2011), which might due to the impurity elements (K, Na and so on) in the glass fibers added into the commercial SCR catalyst, as discussed above. Compared with the Fresh sample, the position of the main peak in De shifted significantly. The shifting of the reduction peak should mainly be attributed to the deposition of alkali metals and alkali earth metals. Previous studies have found that the alkali metals and alkali earth metals could hinder the reducibility of SCR catalysts and shift the reduction of V species to a higher temperature window (Chen et al., 2011; Machli and Lemonidou, 2005). The impurity elements decreased the reducibility of vanadium species, and this should have an adverse impact on the activity of the catalyst. After regeneration by combining EDTA-2Na and H₂SO₄ solutions, the reduction peak shifted toward lower temperature significantly, suggested that washing removed the impurities partially and promoted the reducibility of the deactivated catalyst.

Much attention has been paid by most researchers on the fact that surface acid sites play an important role in NH₃-SCR on vanadium-based catalysts (Chen et al., 2011; Yu et al., 2014). The adsorption of NH₃ on the surface is the key step for the NH₃-SCR reaction. Thus, NH₃-TPD was used to investigate the surface acidity of different samples and the results are shown in Fig. 8; the detailed information on acid sites can be found in Table 4. The Fresh sample showed a broad signal from about 120 to 450°C, consisting of three NH₃ desorption peaks at 222, 281 and 353°C, which could be assigned to weak acid sites, medium strong acid sites and strong acid sites, respectively. After being impregnated by the mixed solution, the intensity of the signal decreased greatly. According to the areas of the peaks, the amount of weak acid sites was about 29% of that of the Fresh sample. However, the proportions were only 18% and 3% for medium strong acid sites and strong acid sites, suggesting that the impurities neutralized acid sites, especially the medium strong and strong acid sites on the catalysts. According to other researchers, the medium strong and strong acid sites had a large influence on the

Table 4 – Detailed information of acid sites on surface of samples.

Sample	Area of Mass spectrum (MS) signal ^a	Weak acid sites		Medium acid sites		Strong acid sites	
		Location (°C)	Ratio ^b (%)	Location (°C)	Ratio ^b (%)	Location (°C)	Ratio ^b (%)
Fresh	100.0	222	45.7	281	26.5	353	27.8
De	18.7	198	70.5	278	25.1	378	4.4
Re-1	30.8	195	41.9	260	41.1	351	16.9
Re-2	31.8	204	56.8	273	28.7	351	14.6
Re-3	30.0	188	38.5	252	47.9	350	13.6
Re-4	35.6	192	29.9	263	53.2	353	16.9
Re-5	39.6	196	33.2	271	46.5	357	20.4
Re-6	59.0	211	40.1	275	45.8	350	14.1
Re-7	69.0	198	28.8	267	49.2	361	22.0
Re-8	73.7	202	32.2	274	33.2	358	34.6

^a Area of MS signal for Fresh sample as 100.0.

^b Ratio for the area of the corresponding peak to the total area.

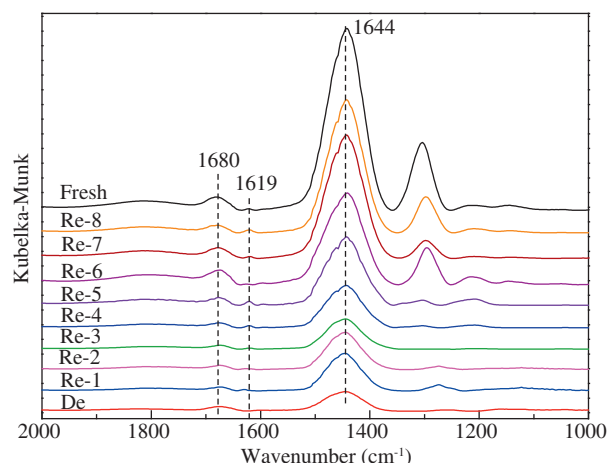


Fig. 9 – DRIFTS spectra of the fresh, deactivated and regenerated samples: NH_3 was adsorbed in 3000 ppm NH_3/N_2 and then purged by N_2 for 15 min at 50°C .

activity of catalysts, and the disappearance of medium strong and strong acid sites should lead to the deactivation of catalysts (Chen et al., 2011). After regeneration, the intensity of the signal increased significantly, especially for the method combining EDTA-2Na and H_2SO_4 , which not only increased the amount of acid sites but also recovered the medium strong and strong acid sites efficiently. The total amount of acid sites for Re-8 was 73.7% of that for the Fresh sample, while the medium acid sites and strong acid sites were almost 90% of the values for the Fresh sample. The increase of acid sites, especially the recovery of the medium strong and strong acid sites, should be the main reason for the effective regeneration of deactivated catalysts.

There are two sorts of acid sites on the surface of catalysts: Brønsted and Lewis acid sites. NH_3 adsorbed on Brønsted acid sites (main as V-OH) is thought to be more active in the NH_3 -SCR reaction over vanadium-based catalysts (Topsøe, 1994). In this study, DRIFTS spectra of NH_3 adsorption were employed to investigate the influence of regeneration methods on the acid sites of the catalyst, and the results are shown in Fig. 9. Several bands at 1444, 1619 and 1680 cm^{-1} were detected for the Fresh sample. The bands at 1444 and

1680 cm^{-1} could be associated with NH_4^+ species chemisorbed on Brønsted acid sites, while the band at 1619 cm^{-1} may be assigned to NH_3 adsorbed on Lewis acid sites (Kamata et al., 1999; Yu et al., 2014). The intensity of the bands at 1444 cm^{-1} for the De sample decreased significantly compared with that of the Fresh sample, suggesting that the amount of Brønsted acid sites on the De sample decreased remarkably. As discussed above, the impurities could poison the Brønsted acid sites (mainly as V-OH). The decrease in number of Brønsted acid sites should be a main reason for the deactivation of the catalyst. After regeneration, it could be found that the intensity of the band at 1444 cm^{-1} increased, especially for the combination of EDTA-2Na and H_2SO_4 , suggesting that the washing treatment recovered the Brønsted acid sites to some extent and thus increased the activity of the deactivated catalyst.

The combination of EDTA-2Na and H_2SO_4 solutions showed a high removal of impurities and greatly recovered the specific surface area and acid sites of the catalyst, and thus significantly promoted the activity of the deactivated sample. The mechanism of regeneration might be described by the scheme shown in Fig. 10: first, EDTA-2Na was an effective chelating agent, and most of the impurities were removed by the dilute solution of EDTA-2Na; however, some Na ions might have deposited on the surface of the catalyst. Then, most of the Na and other residual impurities were removed by the dilute H_2SO_4 solution. Because most of the impurities were removed, the activity of the catalyst recovered significantly.

3. Conclusions

The deposition of impurities could lead to lower specific surface area, fewer Brønsted acid sites and lower surface reducibility, thus causing the deactivation of SCR catalysts. Regeneration by solution washing could increase the activity of the deactivated catalyst, and the regeneration effect followed the order: combination of EDTA-2Na and H_2SO_4 > HNO_3 > EDTA > oxalic acid > H_2SO_4 > acetic acid. The removal of Pb was an important factor in the regeneration effect. Single acid solution washing could remove some impurities, but the extraction efficiency for Pb was limited. The combination of EDTA-2Na and H_2SO_4 solutions showed

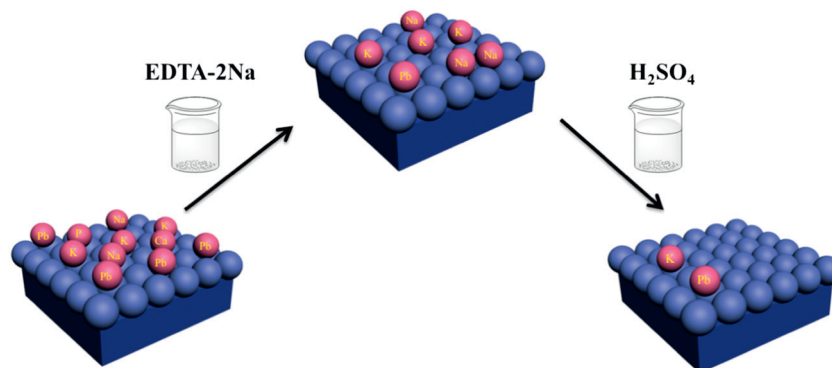


Fig. 10 – The mechanism of regeneration by combination of Ethylenediaminetetraacetic acid disodium salt (EDTA-2Na) and H_2SO_4 solutions.

excellent removal of Pb and other impurities. After being regenerated by a combination of EDTA-2Na and H₂SO₄ solutions, most of the deposited impurities were removed; at the same time, the specific surface area and number of Brønsted acid sites increased greatly, and the surface reducibility was also promoted. Thus, the activity of the deactivated catalyst recovered significantly, becoming similar to the activity of the fresh catalyst at 380°C. The combination of EDTA-2Na and H₂SO₄ solutions might be a potential regeneration method for use in actual operation.

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