



Regeneration of Potassium Poisoned Catalysts for the Selective Catalytic Reduction of NO with NH₃

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ABSTRACT

In this study, we investigated the effect of potassium on the activity and regeneration of potassium-poisoned SCR catalysts. With the addition of potassium species, the NO conversion rate of the catalysts continuously decreased. After washing the poisoned catalysts with an H₂SO₄ solution or doping them with CeO₂, the activity of the catalysts was improved to different extents. Acid washing almost completely removed the surface potassium species, freeing acidic sites to adsorb NH₃, but it also potentially removed some of the active components, such as vanadia. CeO₂ doping, on the other hand, added active components. Combining these two methods, the poisoned catalysts were washed with an H₂SO₄ solution and then doped with 5 wt.% CeO₂. It was found that the level of activity could be restored to that of a fresh catalyst, and a conversion rate of over 90% was observed for NO between 300°C and 450°C, as the added CeO₂ compensated for the active components lost during SCR reactions. Consequently, the above hybrid method shows high potential for regenerating commercial SCR catalysts.

Keywords: Selective catalytic reduction; Potassium; Deactivation; Regeneration; Ceria.

INTRODUCTION

The selective catalytic reduction (SCR) of NO_x with NH₃ has been regarded as an effective method to control NO_x emissions from stationary and mobile sources (Busca *et al.*, 1998). The commercial SCR catalysts consist of TiO₂ as support and V₂O₅-WO₃ or V₂O₅-MoO₃ as active components. They are shaped into honeycomb matrix because of the advantages such as low pressure drop, high geometric surface area, and resistance to deposition of dust (Lei *et al.*, 2009).

The (co-)firing of biomass is a significant way to reduce the net CO₂ emissions. However, high levels of alkali and alkaline earth metals, especially potassium, are present in the fly ash of the biomass fired systems. And potassium has been demonstrated to do harm to the SCR catalysts (Kamata *et al.*, 1999; Moradi *et al.*, 2003; Zheng *et al.*, 2004, 2005; Due-Hansen *et al.*, 2007; Castellino *et al.*, 2009; Klimczak *et al.*, 2010). Doping with alkali and alkaline earth metals results in a strong catalyst deactivation and

the poisoning effect of alkali and alkaline earth metals is related to their basicity. The order is listed as K > Na > Ca > Mg (Klimczak *et al.*, 2010). It is concluded that potassium preferentially coordinates to the Brønsted acid sites, which are responsible for the ammonia adsorption, thus decreasing their number and strength of the Brønsted acid sites. As a result, catalyst activity would be adversely affected. A deactivation of about 1% per day was found over monolith catalysts, which were exposed in a high-dust flue gas produced from straw-fired grate boiler (Zheng *et al.*, 2005).

The cost of the catalysts is a major part of the total expense in an SCR system. Hence, it is important and necessary to regenerate the catalysts (Du *et al.*, 2018; Wang *et al.*, 2018a, b). Regeneration by washing with water followed by sulfation was not an optimal regeneration method due to the insufficient removal of the poison (Zheng *et al.*, 2004). Washing with sulfuric acid can remove potassium accumulated on the surface and recover the catalytic activity (Khodayari and Odenbrand, 2001a, b; Zheng *et al.*, 2004). However, active components such as vanadium and tungsten can also be removed through washing with sulfuric acid. So, it is necessary to compensate the loss of the active components. Recently, ceria-based catalysts have been investigated for SCR reactions because of the high oxygen storage capacity and excellent redox properties of CeO₂ (Li *et al.*, 2012; Hu *et al.*, 2017; Huang

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et al., 2017; Jiang et al., 2017; Li et al., 2017; Yao et al., 2017; Chen et al., 2018; Jiang et al., 2018). We could also add ceria on the catalyst to compensate the loss of the active components.

In this work, potassium ions were doped on the commercial V₂O₅-WO₃/TiO₂ catalysts to simulate the poison effect. Then, a study of the regeneration of K-poisoned catalysts was presented. Specifically, loading different amount of ceria on the deactivated catalysts with or without sulfuric acid and deionized water washing have been investigated to show the commercial potential of ceria-involved regeneration method.

METHODS

Catalyst Preparation

The commercial honeycomb-type catalysts used in this investigation were obtained from RAGA Technology Co., Ltd. The catalysts contained about 1% V₂O₅ and 5% WO₃ as active phase doped on a TiO₂ support. The catalyst had a wall thickness of 1 mm and a channel pitch of 6 mm. The catalysts were cut into 25 mm × 20 mm × 20 mm blocks for poisoning of potassium and regeneration method tests.

Deactivation of Catalysts

The catalysts doped with potassium were prepared by wet-impregnation method with aqueous solutions of KNO₃. The prepared monolithic catalysts were immersed into 25 mL aqueous solutions with different concentration of KNO₃. Then the samples were first dried at 110°C overnight and then calcined at 500°C for 5 h in a muffle furnace to form potassium oxide.

Regeneration of Deactivated Catalysts

Several blocks of deactivated catalysts (25 mm long monolithic segment) were washed in 1000 mL 0.5 M sulfuric acid (SA) solution for 120 min and then washed in 1000 mL deionized water for 15 min. In some cases, different concentrations of sulfuric acid (0.05 M, 0.1 M, 0.3 M, 0.5 M, 0.7 M) were used to optimize the washing process. The washing process was under continuous stirring. The temperature of the washing solution was kept at 50°C. After washing, different contents of CeO₂ were loaded on the catalysts using the same method as potassium doping. Another regeneration method was that CeO₂ was added on the deactivated catalysts without washing process. The catalysts were donated as xK-ySA-zCeO₂. *x* represents the loading of potassium element (wt.%), *y* represents the concentration of SA (sulfuric acid) used for catalysts washing (M) and *z* represents the loading of CeO₂ (wt.%) on the catalysts.

Activity Tests

The activity tests for the reduction of NO by NH₃ were carried out in a fixed bed quartz micro-reactor (inner diameter: 4 mm) with 0.2 g catalyst power of 250–380 μm in diameter. The feed gas mixture contained 1000 ppm NO, 1000 ppm NH₃, 5 vol.% O₂ and N₂ as the balance gas. The total flow rate of the feed gas was 1000 mL min⁻¹ and

the GHSV was 183,000 h⁻¹. The catalytic reaction was carried out with temperature ranging from 150°C to 450°C. The concentrations of NO and N₂O before and after reaction were measured by an FTIR gas analyzer, the Gaset DX4000. The NO conversion is defined as

$$\text{NO Conversion (\%)} = \frac{\text{NO}_{in} - \text{NO}_{out}}{\text{NO}_{in}} \times 100 \quad (1)$$

where NO_{in} and NO_{out} stand for the NO concentration at the inlet and outlet, respectively.

Catalyst Characterization

The specific surface area and the textural properties (i.e., pore volume and average pore diameter) were measured by N₂ adsorption and desorption experiments at liquid nitrogen temperature (−196°C) with Autosorb-1-C instrument (Quantachrome Instrument Corp.). The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method while the average pore diameter was calculated from the surface area and BET pore volume.

The X-ray diffraction (XRD) patterns were collected using a Panalytical X'pert Pro diffractometer equipped with Cu Kα radiation. The X-ray tube was operated at 40 kV and 40 mA.

The chemical composition of catalyst samples was analyzed by inductively coupled plasma-mass spectroscopy (ICP-MS; 7500a, Agilent) after the catalysts dissolved completely.

NH₃-TPD tests were carried out on an AutoChem 2920 instrument provided by Micromeritics Corporation. NH₃ signal was detected using a Hiden QIC20 mass spectrum instrument. 0.2 g catalyst powder was pretreated in He at 500°C for 30 min. After that, the sample was cooled to 100°C and exposed to a gas mixture of 5% NH₃ in He for 30 min. Then the sample was flushed with pure He until signal was stabilized. The sample was then heated up to 700°C at a rate of 10°C min⁻¹.

H₂-TPR was also carried out in a quartz-tube reactor. 0.10 g catalyst powder was pre-treated at 200°C in N₂ for 30 min. After that, the sample was cooled to room temperature and then heated to 700°C at a rate of 10°C min⁻¹ in a gas mixture of 5 vol.% H₂ and Ar. The consumption of H₂ was detected by a thermal conductivity detector (TCD).

RESULTS AND DISCUSSION

Activity and Selectivity

Effect of Potassium Poisoning

Fig. 1 shows the activity of the fresh and potassium-loaded catalysts. For the fresh catalyst, the NO conversion increased as the temperature increased, which almost reached 100% at 350°C. Given that potassium was introduced, the NO conversion decreased. With the increase in the doping amount of potassium, catalyst activity continuously decreased. When the potassium loading amount reached 1%, the NO conversion of the catalyst was always below 30%. This is consistent with the result of Chen et al. (2011).

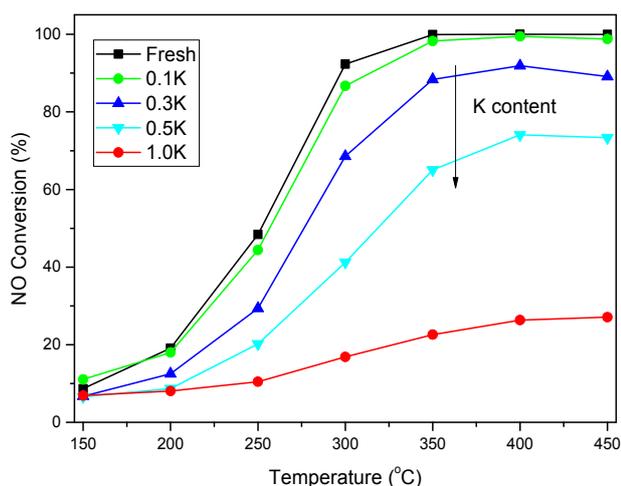


Fig. 1. NO conversion of the catalysts poisoned with different K loading amounts.

Effect of Acid Washing

To regenerate the poisoned catalyst, the first step is to remove the accumulated K. Sulfuric acid was used as detergent combined with fresh water rinsing after the process. Different concentrations of sulfuric acid solutions were chosen and effect on NO conversion is depicted in Fig. 2. It is clear that with concentrated acid, poisoned catalyst is easily recovered, approaching its initial state. However, this effect was gradually weakened when the concentration increased from 0.05 M to 0.5 M. Specially, no obvious difference was observed for the catalysts treated with 0.5 M and 0.7 M H_2SO_4 . As a result, 0.5 M H_2SO_4 was used in later section for acid washing. Moreover, the washing process also contributed to loss of active components, such as V and W. The negative effect of acid washing is shown in Fig. S1 in supporting information. The effect of washing time was also evaluated. It is evident that using diluted acid and short time could remove most of K and reduce the loss of V. However, as shown in Fig. 2, the diluted acid washing couldn't totally recover the activity of the catalyst. On the other hand, after 2 h washing with 0.5 M H_2SO_4 , 40% V of the catalyst was dissolved into the solution, resulting in the reduction of the activity, especially in lower temperatures ($< 350^\circ C$). For this reason, it is necessary to load active components to compensate the loss.

Effect of CeO_2 Loading

The NO conversion of the K-poisoned and regenerated catalysts is presented in Fig. 3. The direct loading of 10% CeO_2 to the deactivated catalyst could improve the activity, which was, however, much lower than that of the fresh catalyst. This is because potassium still remained on the catalyst and exerted a negative effect on the catalyst. Thus, removing potassium species constituted the first step to recover the activity of the deactivated catalyst. After washing with H_2SO_4 solution, an obvious enhancement in the high-temperature activity could be obtained, while the activity below $300^\circ C$ remained almost unchanged. It should be noted that the activity of the regenerated catalyst washed

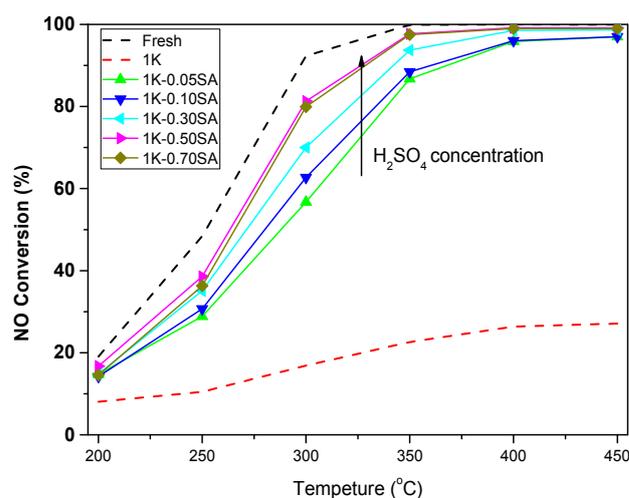


Fig. 2. NO conversion of the catalysts regenerated with different concentrations of H_2SO_4 solution.

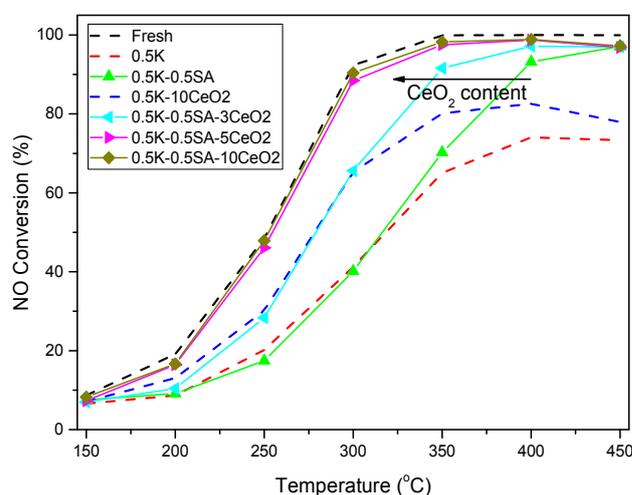


Fig. 3. NO conversion of the catalysts regenerated with different cerium loading amounts.

with H_2SO_4 solution was still lower than that of the fresh one. That might be due to the loss of active components during the H_2SO_4 solution washing process. Therefore, various amounts of CeO_2 were added to the deactivated catalysts after treatment by 0.5 M H_2SO_4 and deionized water. The NO conversion of 0.5K-0.5SA-3 CeO_2 catalyst is almost the same as that of the 0.5K-10 CeO_2 catalysts below $300^\circ C$. With temperature increasing, 0.5K-0.5SA-3 CeO_2 catalyst exhibited a better activity than that of 0.5K-10 CeO_2 catalyst. When the loading amount of CeO_2 exceeded 5 wt.%, the activity of the regenerated catalysts almost restored to the level of the fresh one. Thus, it seems that washing with 0.5 M sulfuric acid solution and deionized water and then doping with 5 wt.% CeO_2 is a good method to regenerate the K-poisoned catalysts.

In order to investigate the adaptability of this regeneration method, catalyst with a higher potassium loading amount were chosen and tested. As illustrated in Fig. 4, it can be concluded that the amount of potassium had no obvious

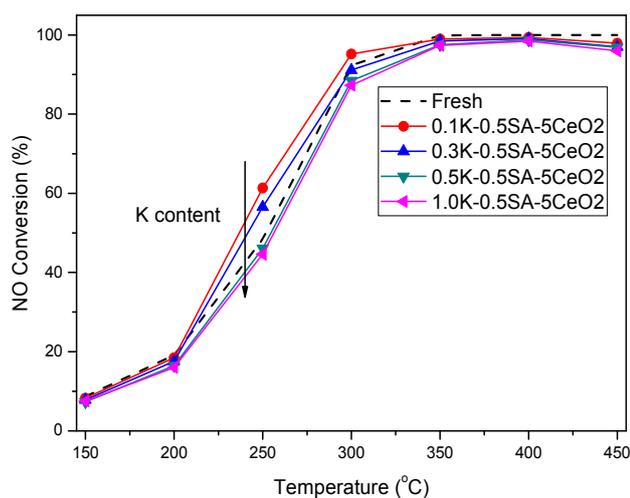


Fig. 4. Effect of K content on the catalysts regenerated by washing and CeO₂ modification.

effect on the activity of the regenerated catalysts in the investigated range and the activity of the regenerated catalysts is almost the same as that of the fresh one. This indicated that 0.5 M H₂SO₄ and deionized water treatment could remove potassium species that interacted with the active sites, and 5 wt.% CeO₂ additives could supply extra active sites to some extent.

Selectivity of Regenerated Catalysts

In addition to NO conversion, N₂O formation is also an important parameter to evaluate catalyst performance. Fig. 5 displays N₂O formation in the SCR reactions. For the fresh and regenerated catalysts, the N₂O concentration were fairly low (< 5 ppm) below 350°C. As the temperature increased, N₂O concentration of the fresh catalyst rapidly increased up to 47 ppm at 450°C, while the N₂O formation of the regenerated catalysts stayed below 17 ppm, suggesting a better selectivity than the fresh one. This phenomenon could be explained by the reduction of V and the addition of Ce, confirmed by Fig. S1 and Table 1. Since V₂O₅ has a strong ability to oxidize NH₃ into N₂O at higher temperatures (Chen *et al.*, 2009), decrease of V₂O₅ could weaken this side reaction and improve the selectivity of SCR reaction.

Characterization of the Catalysts

Chemical Composition and BET Analysis

Table 1 shows the ICP-MS and BET results of the fresh and regenerated catalysts. It seems that no obvious variations could be observed in these catalysts, partly ruling out the possibility that physical properties mainly determined the activity of the catalysts. Instead, the variations in the chemical properties including acidity and redox constituted the main reason for enhanced activity of the catalysts after regeneration.

The ICP-MS results showed that the washing process could drastically remove potassium species over catalyst surface. At the same time, vanadia, as the active component, was also removed by a third with the content of tungsten remaining almost unchanged after the washing process.

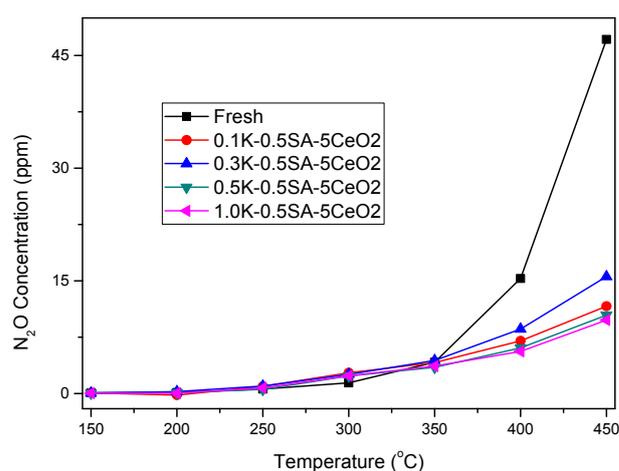


Fig. 5. N₂O formation of the catalysts regenerated by washing and CeO₂ modification.

Additionally, the measured Ce content was lower than the calculated value. This meant that there was loss of Ce during impregnation process.

XRD Analysis

XRD patterns of the series catalysts are shown in Fig. 6. All the catalysts presented anatase TiO₂ phase with the absence of V₂O₅ and WO₃ crystallites, indicating that V₂O₅ and WO₃ were amorphous in structure on the TiO₂ support (Lisi *et al.*, 2004; Kustov *et al.*, 2005; Zhang *et al.*, 2009). Given the addition of 3% CeO₂, no cubic CeO₂ phase could be detect. This result indicated that ceria were highly dispersed and existed as an amorphous state. Further increasing the CeO₂ loading amount to 5% or more, cubic CeO₂ phase began to be observed, suggesting that CeO₂ loading was beyond the theoretical monolayer coverage on the TiO₂ support.

NH₃-TPD

According to previous studies, acidity plays an important role in the SCR reactions, since the first step is the adsorption of NH₃ on the surface acidic sites of catalyst (Busca *et al.*, 1998; Forzatti, 2001; Ye *et al.*, 2018). NH₃-TPD tests were carried out to investigate surface acidity of the series samples, and the results of which are illustrated in Fig. 7. The 0.5K and 0.5K-10CeO₂ catalysts had several NH₃ desorption peaks in the temperature region of 100–350°C, while the other catalysts possessed broad desorption peaks between 100°C and 450°C. The peaks near 170°C (Peak I) could be assigned to the desorption of physisorbed NH₃, and the peaks around 270°C (Peak II) were attributed to NH₃ on weakly acidic sites, while the peaks centering at 610°C (Peak III) linked to the strongly acidic sites (Guan *et al.*, 2011; Li *et al.*, 2012; Li *et al.*, 2017; Yao *et al.*, 2017). The quantity analysis of NH₃-TPD is summarized in Table 2. For the 0.5K and 0.5K-10CeO₂ catalysts, the presence of potassium caused the reduction of Peak II, which correlated with acidic sites, responsible for SCR activity (Forzatti, 2001). After washing process, abundant acidic sites were present, and NH₃ could be adsorbed on

Table 1. Chemical composition, BET surface area, total pore volume, and average pore diameter of different samples.

Sample	Amount (wt %)				Surface area (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹)	Average pore diameter (nm)
	V	W	K	Ce ^a			
Fresh	0.67	3.72	0.03	0.00	63.3	0.312	19.71
0.5K	0.73	4.16	0.34	-	66.7	0.309	18.55
0.5K-0.5SA	0.44	3.90	0.05	-	62.7	0.346	22.06
0.5K-10CeO ₂	0.61	3.35	0.25	9.54	65.1	0.301	18.48
0.5K-0.5SA-3CeO ₂	0.44	3.90	0.04	1.37	67.5	0.353	20.91
0.5K-0.5SA-5CeO ₂	0.41	3.76	0.04	2.36	65.4	0.330	20.21
0.5K-0.5SA-10CeO ₂	0.39	3.45	0.04	9.24	60.5	0.274	18.09

^a Amount of Ce is from EDS analysis.

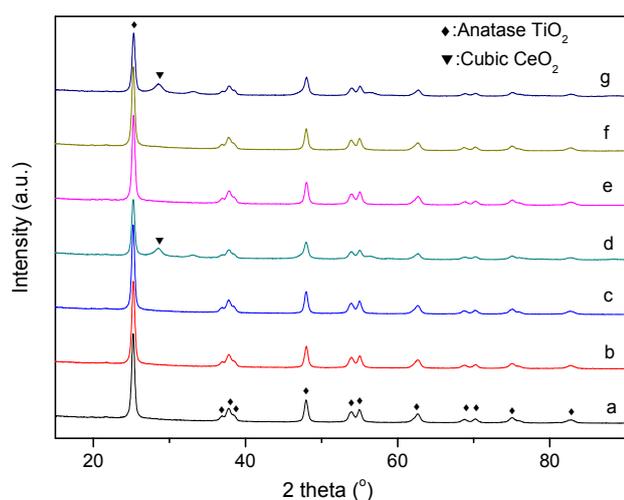


Fig. 6. XRD patterns of the (a) fresh; (b) 0.5K; (c) 0.5K-0.5SA; (d) 0.5K-10CeO₂; (e) 0.5K-0.5SA-3CeO₂; (f) 0.5K-0.5SA-5CeO₂; (g) 0.5K-0.5SA-10CeO₂.

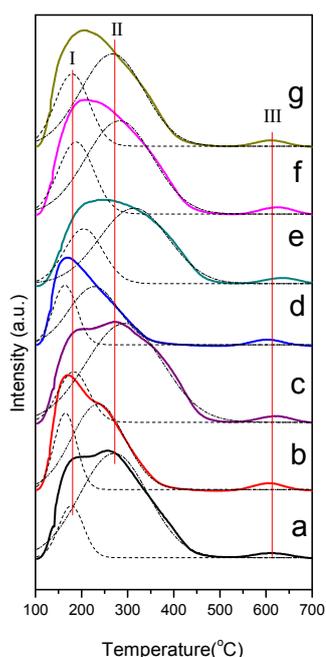


Fig. 7. NH₃-TPD curves of the (a) fresh; (b) 0.5K; (c) 0.5K-0.5SA; (d) 0.5K-10CeO₂; (e) 0.5K-0.5SA-3CeO₂; (f) 0.5K-0.5SA-5CeO₂; (g) 0.5K-0.5SA-10CeO₂.

the catalyst surface, reacting with NO. Besides, doping CeO₂ could also in part enhance the acidity of the catalysts, which made 0.5K-0.5SA-5CeO₂ catalyst had the same activity with the fresh one (Shi *et al.*, 2017). That is consistent with SCR activity results in Fig. 3. Note that after washing and CeO₂ modification, Peak I increased almost up to two times while Peak II reached about 80% of that of the fresh catalyst. It may be related to promoted SCR activity at low temperatures and inhibited NH₃ oxidation at high temperatures.

H₂-TPR

The redox properties of the catalysts play an important role in the catalytic cycle of the SCR reactions (Topsoe, 1994; Topsoe *et al.*, 1995; Putluru *et al.*, 2009; Wang *et al.*, 2018). The H₂-TPR profiles and quantity analysis are shown in Fig. 8 and Table 2, respectively. The fresh catalyst showed a reduction peak located at 500°C, while the 0.5K sample presented a peak at 523°C. These peaks could be explained by the reduction of V⁵⁺ to V³⁺ (Tang *et al.*, 2010; Chen *et al.*, 2011; Guan *et al.*, 2011). And it should be noted that the reduction peak shifted to higher temperatures after doping potassium, which is consistent with the results of Chen *et al.* (2011), showing that potassium doping exerted a negative effect on the catalyst redox properties. After H₂SO₄ washing process, a reduction peak at 485°C came out. This meant that washing with sulfuric acid solution and deionized water could remove potassium species and recover the redox ability of the catalysts. The reduction peaks shifted to higher temperature with the increasing loading amount of CeO₂. Moreover, the adding of CeO₂ slightly increased the consumption of H₂, compared to 0.5K-0.5SA. This indicated that loading more Ce had a negative effect on the catalyst reducibility. Besides, XPS results shown in Fig. S2 confirmed that no obvious change in chemical state of V, W and Ti after acid washing or CeO₂ modification. Combined with aforementioned results, it implied that improved SCR activity after acid washing and CeO₂ adding could be ascribed to optimized acidic sites, which facilitate the low temperature SCR activity and inhibit high temperature NH₃ oxidation.

CONCLUSIONS

In this study, a new SCR catalyst regeneration method has been developed. Some conclusions are listed below.

Table 2. Quantitative analysis of NH₃-TPD and H₂-TPR over the samples*.

Samples	Peak temperature (°C)		NH ₃ desorption (a.u.)		Total NH ₃ desorption (a.u.)	Total H ₂ consumption (a.u.)
	T _I	T _{II}	S _I	S _{II}	S _I + S _{II}	
Fresh	178	270	1.00	1.00	1.00	1.00
0.5K	165	236	1.34	0.63	0.74	0.93
0.5K-0.5SA	183	293	1.22	1.05	1.08	0.63
0.5K-10CeO ₂	164	227	1.11	0.40	0.51	1.38
0.5K-0.5SA-3CeO ₂	205	314	1.64	0.73	0.86	0.67
0.5K-0.5SA-5CeO ₂	188	282	2.00	0.87	1.04	0.87
0.5K-0.5SA-10CeO ₂	180	267	1.92	0.81	0.98	0.76

*Normalized by the values of the fresh catalyst.

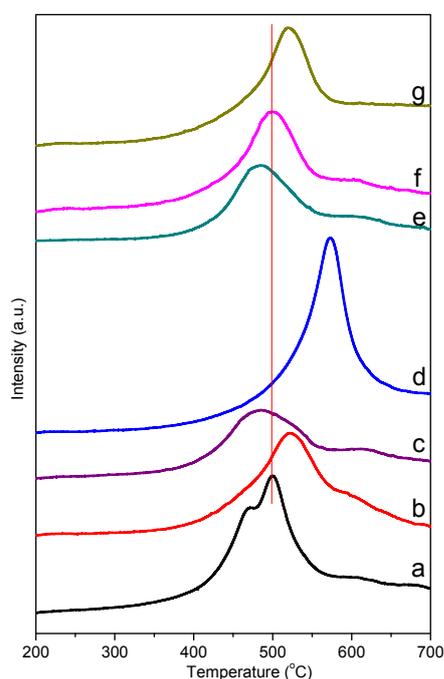


Fig. 8. H₂-TPR profiles of the (a) fresh; (b) 0.5K; (c) 0.5K-0.5SA; (d) 0.5K-10CeO₂; (e) 0.5K-0.5SA-3CeO₂; (f) 0.5K-0.5SA-5CeO₂; (g) 0.5K-0.5SA-10CeO₂.

- Potassium doping had a negative effect on the activity of the catalysts. The increase in the potassium loading amount continuously decreased the NO conversion rate of the catalysts. After washing the catalysts with an H₂SO₄ solution and deionized water, the SCR activity was partially restored. The further addition of CeO₂ caused the regenerated catalysts to exhibit almost as much activity as the fresh ones.
- After washing the catalysts with an H₂SO₄ solution and deionized water, the potassium species were almost completely removed, beneficial to NH₃ adsorption. CeO₂ was then added to compensate for the lost active species. These factors were primarily responsible for the recovery of the catalyst activity after regeneration.

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DISCLAIMER

Reference to any companies or specific commercial products does not constitute.

SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

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