Regeneration of potassium poisoned catalysts for the selective catalytic reduction of NO with NH_3

Shaojun Liu[1,2], Peidong Ji[1], Dong Ye[1], Ruiyang Qu[1], Chenghang Zheng[1], Xiang Gao[1,*]

[1] *State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, China*

[2] *Key Laboratory of Low-grade Energy Utilization Technologies and Systems (Chongqing University), Ministry of Education of China, Chongqing University, Chongqing 400044, China*

[*] Corresponding author. Tel: 1-350-571-1887; Fax: 1-350-571-1887

E-*mail address*: xgao1@zju.edu.cn

Abstract

In this study, we investigated the effect of potassium on the activity of the SCR catalysts and the regeneration of potassium-poisoned SCR catalysts. Given the addition of potassium species, NO conversion of catalysts continuously decreased. After washing with H_2SO_4 solution or addition of CeO_2, activities of poisoned catalysts were improved to different extents. For acid washing, surface potassium species were almost completely removed, which made occupied acidic sites be released for the adsorption of NH_3. However, acid washing may also remove part of active components such as vanadia. For CeO_2 doping, extra active components were added. Combined with these two methods, poisoned catalysts were washed with H_2SO_4 solution and then doped with 5 wt.% CeO_2. It was found that the activity could be restored to the level of the fresh one and over 90% NO conversion could be observed between 300 and 450 ^oC. This is because added CeO_2 compensated the lost active components for the SCR reactions. Consequently, the above hybrid method showed potential application in the regeneration of commercial SCR catalysts.

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

INTRODUCTION

The selective catalytic reduction (SCR) of NO_x with NH_3 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 TiO_2 as support and V_2O_5-WO_3 or V_2O_5-MoO_3 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 CO_2 emissions. However, high levels of alkali and alkali 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 alkaline and alkaline earth metals results in a strong catalyst deactivation and the poisoning effect of alkali and alkali earth 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 a SCR system. Hence, it is important and necessary to regenerate the catalysts. 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, 2001b, a; 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 CeO_2 (Chen et al.; Jiang et al.; Li et al., 2012; Hu et al., 2017; Huang et al., 2017; Jiang et al., 2017; Li et al., 2017; Yao et al., 2017). We could also add ceria on the catalyst to compensate the loss of the active components.

In this work, potassium ions was doped on the commercial V_2O_5-WO_3/TiO_2 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

Catalysts preparation

The commercial honeycomb-type catalysts used in this investigation were obtained from RAGA Technology Co., Ltd. The catalysts contained about 1% V_2O_5 and 5% WO_3 as active phase doped on a TiO_2 support. The catalyst had a wall thickness of 1mm and a channel pitch of 6 mm. The catalysts were cut into 25mm × 20mm × 20mm blocks for poisoning of potassium and regeneration method tests.

Deactivating of catalysts

The catalysts doped with potassium were prepared by wet-impregnation method with aqueous solutions of KNO_3. The prepared monolithic catalysts were immersed into 25ml aqueous solutions with different concentration of KNO_3. Then the samples were first dried at 110 ^oC overnight and then calcined at 500 ^oC for 5 h in a muffle furnace to form potassium oxide.

Regeneration of deactivated catalysts

Several blocks of deactivated catalysts (25mm 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 ^oC. After washing, different contents of CeO_2 were loaded on the catalysts using the same method as potassium doping. Another regeneration method was that CeO_2 was added on the deactivated catalysts without washing process. The catalysts were donated as xK-ySA-$z$$CeO_2$. 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 CeO_2 (wt. %) on the catalysts.

Activity tests

The activity tests for the reduction of NO by NH_3 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 NH_3, 5 vol. % O_2 and N_2 as the balance gas. The total flow rate of the feed gas was 1000 mL/min and the GHSV was 183000 h^{-1}. The catalytic reaction was carried out with temperature ranging from 150 ^oC to 450 ^oC. The concentrations of NO and N_2O before and after reaction were measured by an FTIR gas analyzer Gasmet Dx4000.The NO conversion is defined as

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

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 N_2 adsorption and desorption experiments at liquid nitrogen temperature (-196^oC) 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 Ka radiation. The X-ray tube was operated at 40kV and 40mA.

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

NH_3-TPD tests were carried out on an AutoChem 2920 instrument provided by Micromeritics Corporation. NH_3 signal was detected using a Hiden QIC20 mass spectrum instrument. 0.2 g catalyst powder was pretreated in He at 500 ^oC for 30 min. After that, the sample was cooled to 100 ^oC and exposed to a gas mixture of 5% NH_3 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 ^oC at a rate of 10 ^oC/min.

H_2-TPR was also carried out in a quartz-tube reactor. 0.10 g catalyst powder was pre-treated at 200 ^oC in N_2 for 30 min. After that, the sample was cooled to room temperature and then heated to 700 ^oC at a rate of 10 ^oC/min in a gas mixture of 5 vol.% H_2 and Ar. The consumption of H_2 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 ^{o}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 (Chen et al., 2011).

Effect of acid washing

To regenerate the poisoned catalyst, the first step is to remove the accumulated K. Sulphuric acid was used as detergent combined with fresh water rinsing after the process. Different concentrations of sulphuric 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 weaken 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.1s 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 is hard to totally recover the activity of the catalyst. In another 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 ^{o}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 ^{o}C remained almost unchanged. It should be noted that the activity of the regenerated catalyst washed 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 0.5 K-0.5SA-3CeO_2 catalyst is almost the same as that of the 0.5 K-10CeO_2 catalysts below 300 ^{o}C. With temperature increasing, 0.5 K-0.5 SA-3CeO_2 catalyst exhibited a better activity than that of 0.5 K-10CeO_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 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 0.5M H_2SO_4 and deionized water treatment could remove potassium species that interacted with the active sites, and 5 wt. % CeO_2 additives could supply extra active sites to some extent.

Selectivity of regenerated catalysts

In addition to NO conversion, N_2O formation is also an important parameter to evaluate catalyst performance. Fig. 5 displays N_2O formation in the SCR reactions. For the fresh and regenerated catalysts, the N_2O concentration were fairly low (< 5 ppm) below 350 ^oC. As the temperature increased, N_2O concentration of the fresh catalyst rapidly increased up to 47 ppm at 450 ℃, while the N_2O 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 add of Ce, confirmed by Fig.1s and Table 1. Since V_2O_5 has a strong ability to oxidize NH_3 into N_2O at higher temperatures(Chen et al., 2009), decrease of V_2O_5 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 a third with the content of tungsten remaining almost unchanged after the washing process. 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 TiO_2 phase with the absence of V_2O_5 and WO_3 crystallites, indicating that V_2O_5 and WO_3 were amorphous in structure on the TiO_2 support (Lisi et al., 2004; Kustov et al., 2005; Zhang et al., 2009). Given the addition of 3% CeO_2, no cubic CeO_2 phase could be detect. This result indicated that ceria were highly dispersed and existed as an amorphous state. Further increasing the CeO_2 loading amount to 5% or more, cubic CeO_2 phase began to be observed, suggesting that CeO_2 loading was beyond the theoretical monolayer coverage on the TiO_2 support.

NH_3-TPD

According to previous studies, acidity plays an important role in the SCR reactions, since the first step is the adsorption of NH_3 on the surface acidic sites of catalyst (Busca et al., 1998; Forzatti, 2001; Ye et al., 2018). NH_3-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-10CeO_2 catalysts had several NH_3 desorption peaks in the temperature region of 100-350 ^oC, while the other catalysts possessed broad desorption peaks between 100 and 450 ^oC. The peaks near 170 ^oC (peak I) could be assigned to the desorption of physisorbed NH_3, and the peaks around 270 ^oC (peak II) were attributed to NH_3 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 NH_3-TPD is summarized in Table 2. For the 0.5K and 0.5K-10CeO_2 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 NH_3 could be adsorbed on the catalyst surface, reacting with NO. Besides, doping CeO_2 could also in part enhance the acidity of the catalysts, which made 0.5K-0.5SA-5CeO_2 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 CeO_2 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 NH_3 oxidation at high temperatures.

H_2-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 H_2-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 V^{5+} to V^{3+} (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 consistence with the results of Chen et al (Chen et al., 2011), showing that potassium doping exerted a negative on the catalyst redox properties. After H_2SO_4 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 CeO_2. Moreover, the adding of CeO_2 slightly increased the consumption of H_2, 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.2s confirmed that no obvious change in chemical state of V , W and Ti after acid washing or CeO_2 modification. Combined with aforementioned results, it implied that improved SCR activity after acid washing and CeO_2 adding could be ascribed to optimized acidic sites, which facilitate the low temperature SCR activity and inhibit high temperature NH_3 oxidation.

CONCLUSIONS

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

1. Potassium doping had a negative effect on the activity of the catalysts. The increase in the potassium loading amount continuously decreased the NO conversion of the catalysts. After washing with H_2SO_4 solution and deionized water, SCR activity could be partially restored. Further addition of CeO_2 made the regenerated catalysts possess almost the same activity with the fresh one.

2. After washing with H_2SO_4 solution and deionized water, potassium species could be almost completely removed, making occupied acidic sites be released for adsorption of NH_3. Besides, CeO_2 was added for the compensation of the lost active species. These factors constituted the main reasons for the recovery of the catalyst activity after regeneration.

ACKNOWLEDGMENTS

This work is supported by the National Key Research and Development Program of China (No. 2018YFC0213400), and National Science Foundation of China (NO. U1609212 and NO. 51306079), and Open Fund of Key Laboratory of Ministry of Education of China (No. LLEUTS-201507).

DISCLAIMER

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

REFERENCES

Busca, G., Lietti, L., Ramis, G. and Berti, F. (1998). Chemical and Mechanistic Aspects of the Selective Catalytic Reduction of NOx by Ammonia over Oxide Catalysts: A Review. *Appl. Catal. B-Enviro.* 18: 1-36.

Castellino, F., Jensen, A.D., Johnsson, J.E. and Fehrmann, R. (2009). Influence of Reaction Products of K-Getter Fuel Additives on Commercial Vanadia-Based SCR Catalysts Part I. Potassium Phosphate. *Appl. Catal. B-Enviro.* 86: 196-205.

Chen, L., Li, J. and Ge, M. (2009). Promotional Effect of Ce-Doped V_2O_5-WO_3/TiO_2 with Low Vanadium Loadings for Selective Catalytic Reduction Of NO_x by NH_3. *J. Phys. Chem. C* 113: 21177-21184.

Chen, L., Li, J.H. and Ge, M.F. (2011). The Poisoning Effect of Alkali Metals Doping over Nano V_2O_5-WO_3/TiO_2 Catalysts on Selective Catalytic Reduction of NOx by NH_3. *Chem. Eng. J.* 170: 531-537.

315 Chen, Y., Wang, M., Du, X., Ran, J., Zhang, L. and Tang, D. High Resistance to Na
316 Poisoning of V_2O_5-$Ce(SO_4)_2/TiO_2$ Catalyst for the NO SCR Reaction. *Aerosol Air*
317 *Qual. Res.*, in press.
318 Due-Hansen, J., Boghosian, S., Kustov, A., Fristrup, P., Tsilomelekis, G., Stahl, K.,
319 Christensen, C.H. and Fehrmann, R. (2007). Vanadia-Based SCR Catalysts
320 Supported on Tungstated and Sulfated Zirconia: Influence of Doping with
321 Potassium. *J. Catal.* 251: 459-473.
322 Forzatti, P. (2001). Present Status and Perspectives in De-NOx SCR Catalysis. *Appl.*
323 *Catal. A-Gen.* 222: 221-236.
324 Guan, B., Lin, H., Zhu, L. and Huang, Z. (2011). Selective Catalytic Reduction of
325 NO_x with NH_3 over Mn, Ce Substitution $Ti_{0.9}V_{0.1}O_{2-\delta}$ Nanocomposites Catalysts
326 Prepared by Self-Propagating High-Temperature Synthesis Method. *J. Phys. Chem.*
327 *C* 115: 12850-12863.
328 Hu, W., Zhang, Y., Liu, S., Zheng, C., Gao, X., Nova, I. and Tronconi, E. (2017).
329 Improvement in Activity and Alkali Resistance of a Novel V-$Ce(SO_4)_2$/Ti Catalyst
330 for Selective Catalytic Reduction of NO with NH_3. *Appl. Catal. B-Enviro.* 206:
331 449-460.
332 Huang, X., Ma, Z., Lin, W., Liu, F. and Yang, H. (2017). Activation of Fast Selective
333 Catalytic Reduction of NO by NH_3 at Low Temperature Over TiO_2 Modified
334 CuO_x-CeO_x Composites. *Catal. Commun.* 91: 53-56.

335 Jiang, Y., Bao, C., Liu, S., Liang, G., Lu, M., Lai, C., Shi, W. and Ma, S. Enhanced
336 Activity of Nb-modified CeO_2/TiO_2 Catalyst for the Selective Catalytic Reduction
337 of NO with NH_3. *Aerosol Air Qual. Res.* in press.
338 Jiang, Y., Wang, X., Xing, Z., Bao, C. and Liang, G. (2017). Preparation and
339 Characterization of CeO_2-MoO_3/TiO_2 Catalysts for Selective Catalytic Reduction
340 of NO with NH_3. *Aerosol Air Qual. Res.* 17: 465-469.
341 Kamata, H., Takahashi, K. and Odenbrand, C.U.I. (1999). The Role of K_2O in the
342 Selective Reduction of NO with NH_3 over a $V_2O_5(WO_3)/TiO_2$ Commercial
343 Selective Catalytic Reduction Catalyst. *J. Mol. Catal. A-Chem.* 139: 189-198.
344 Khodayari, R. and Odenbrand, C.U.I. (2001a). Regeneration of Commercial SCR
345 Catalysts by Washing and Sulphation: Effect of Sulphate Groups on the Activity.
346 *Appl. Catal. B-Enviro.* 33: 277-291.
347 Khodayari, R. and Odenbrand, C.U.I. (2001b). Regeneration of Commercial
348 TiO_2-V_2O_5-WO_3 SCR Catalysts Used in Bio Fuel Plants. *Appl. Catal. B-Enviro.* 30:
349 87-99.
350 Klimczak, M., Kern, P., Heinzelmann, T., Lucas, M. and Claus, P. (2010).
351 High-Throughput Study of the Effects of Inorganic Additives and Poisons on
352 NH_3-SCR Catalysts Part I: V_2O_5-WO_3/TiO_2 Catalysts. *Appl. Catal. B-Enviro.* 95:
353 39-47.

354 Kustov, A.L., Kustova, M.Y., Fehrmann, R. and Simonsen, P. (2005). Vanadia on
355 Sulphated-ZrO_2, a Promising Catalyst for NO Abatement with Ammonia in Alkali
356 Containing Flue Gases. *Appl. Catal. B-Enviro.* 58: 97-104.
357 Lei, Z.G., Liu, X.Y. and Jia, M.R. (2009). Modeling of Selective Catalytic Reduction
358 (SCR) for NO Removal Using Monolithic Honeycomb Catalyst. *Energy Fuels* 23:
359 6146-6151.
360 Li, L., Zhang, L., Ma, K., Zou, W., Cao, Y., Xiong, Y., Tang, C. and Dong, L. (2017).
361 Ultra-Low Loading of Copper Modified TiO_2/CeO_2 Catalysts for Low-Temperature
362 Selective Catalytic Reduction Of NO by NH_3. *Appl. Catal. B-Enviro.* 207: 366-375.
363 Li, Q., Hou, X., Yang, H., Ma, Z., Zheng, J., Liu, F., Zhang, X. and Yuan, Z. (2012).
364 Promotional Effect of CeO_x for NO Reduction over V_2O_5/TiO_2-Carbon Nanotube
365 Composites. *J. Mol. Catal. A-Chem.* 356: 121-127.
366 Lisi, L., Lasorella, G., Malloggi, S. and Russo, G. (2004). Single and Combined
367 Deactivating Effect of Alkali Metals and HCl on Commercial SCR Catalysts. *Appl.*
368 *Catal. B-Enviro.* 50: 251-258.
369 Moradi, F., Brandin, J., Sohrabi, M., Faghihi, M. and Sanati, M. (2003). Deactivation
370 of Oxidation and SCR Catalysts Used in Flue Gas Cleaning by Exposure to
371 Aerosols of High- and Low Melting Point Salts, Potassium Salts and Zinc Chloride.
372 *Appl. Catal. B-Enviro.* 46: 65-76.

373 Putluru, S.S.R., Riisager, A. and Fehrmann, R. (2009). The Effect of Acidic and
374 Redox Properties of V_2O_5/CeO_2-ZrO_2 Catalysts in Selective Catalytic Reduction of
375 NO by NH_3. *Catal. Lett.* 133: 370-375.
376 Shi, Y., Wang, X., Xia, Y., Sun, C., Zhao, C., Li, S. and Li, W. (2017). Promotional
377 Effect of CeO_2 on the Propene Poisoning Resistance of Hbea Zeolite Catalyst for
378 NH_3-SCR of NOx. *Mol. Catal.* 433: 265-273.
379 Tang, F.S., Xu, B.L., Shi, H.H., Qiu, J.H. and Fan, Y.N. (2010). The Poisoning Effect
380 of Na^+ and Ca^{2+} Ions Doped on the V_2O_5/TiO_2 Catalysts for Selective Catalytic
381 Reduction of NO by NH_3. *Appl. Catal. B-Enviro.* 94: 71-76.
382 Topsoe, N.Y. (1994). Mechanism of the Selective Catalytic Reduction of Nitric-Oxide
383 by Ammonia Elucidated by in-Situ Online Fourier-Transform
384 Infrared-Spectroscopy. *Science* 265: 1217-1219.
385 Topsoe, N.Y., Topsoe, H. and Dumesic, J.A. (1995). Vanadia-Titania Catalysts for
386 Selective Catalytic Reduction (SCR) of Nitric-Oxide by Ammonia .1. Combined
387 Temperature-Programmed in-Situ FTIR and Online Mass-Spectroscopy Studies. *J.*
388 *Catal.* 151: 226-240.
389 Wang, X., Shi, Y., Li, S. and Li, W. (2018). Promotional Synergistic Effect of Cu and
390 Nb Doping on a Novel Cu/Ti-Nb Ternary Oxide Catalyst for the Selective Catalytic
391 Reduction of NOx with NH_3. *Appl. Catal. B-Enviro.* 220: 234-250.

392 Yao, X., Zhao, R., Chen, L., Du, J., Tao, C., Yang, F. and Dong, L. (2017). Selective
393 Catalytic Reduction of NO_x by NH_3 over CeO_2 Supported on TiO_2: Comparison of
394 Anatase, Brookite, and Rutile. *Appl. Catal. B-Enviro.* 208: 82-93.
395 Ye, D., Qu, R., Zhang, Y., Wu, W., Liu, S., Zheng, C. and Gao, X. (2018).
396 Investigating the Role of $H_4SiW_{12}O_{40}$ in the Acidity, Oxidability and Activity of
397 $H_4SiW_{12}O_{40}$-Fe_2O_3 Catalysts for the Selective Catalytic Reduction of NO with NH_3.
398 *Mol. Catal.* 448: 177-184.
399 Zhang, X., Li, X.G., Wu, J.S., Yang, R.C. and Zhang, Z.H. (2009). Selective Catalytic
400 Reduction of No by Ammonia on V_2O_5/TiO_2 Catalyst Prepared by Sol-Gel Method.
401 *Catal. Lett.* 130: 235-238.
402 Zheng, Y.J., Jensen, A.D. and Johnsson, J.E. (2004). Laboratory Investigation of
403 Selective Catalytic Reduction Catalysts: Deactivation by Potassium Compounds
404 and Catalyst Regeneration. *Ind. Eng. Chem. Res.* 43: 941-947.
405 Zheng, Y.J., Jensen, A.D. and Johnsson, J.E. (2005). Deactivation of V_2O_5-WO_3-TiO_2
406 SCR Catalyst at a Biomass-Fired Combined Heat and Power Plant. *Appl. Catal.*
407 *B-Enviro.* 60: 253-264.
408
409
410
411

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

Sample	Amount (wt %)				Surface	Total pore	Average pore
	V	W	K	Ce[a]	area(m^2/g)	volume(cm^3/g)	diameter(nm)
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

414 [a] Amount of Ce is from EDS analysis.

415

416 **Table 2.** Quantitative analysis of NH_3-TPD and H_2-TPR over the samples*.

Samples	Peak temperature(^oC)		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

417 *Normalized by the values of the fresh catalyst

418

419

Figure Captions

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

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.

Fig. 4. Effect of K contents on the catalysts regenerated by washing and CeO_2 modification.

Fig. 5. N_2O formation of the catalysts regenerated by washing and CeO_2 modification.

Fig. 6. XRD patterns of the (a): Fresh; (b): 0.5K; (c): 0.5K-0.5SA; (d): 0.5K-10CeO_2; (e): 0.5K-0.5SA-3CeO_2;(f): 0.5K-0.5SA-5CeO_2; (g): 0.5K-0.5SA-10CeO_2.

Fig. 7. NH_3-TPD curves of the (a): Fresh; (b): 0.5K; (c): 0.5K-0.5SA; (d): 0.5K-10CeO_2; (e): 0.5K-0.5SA-3CeO_2;(f): 0.5K-0.5SA-5CeO_2; (g): 0.5K-0.5SA-10CeO_2.

Fig. 8. H_2-TPR profiles of the (a): Fresh; (b): 0.5K; (c): 0.5K-0.5SA; (d): 0.5K-10CeO_2; (e): 0.5K-0.5SA-3CeO_2;(f): 0.5K-0.5SA-5CeO_2; (g): 0.5K-0.5SA-10CeO_2.

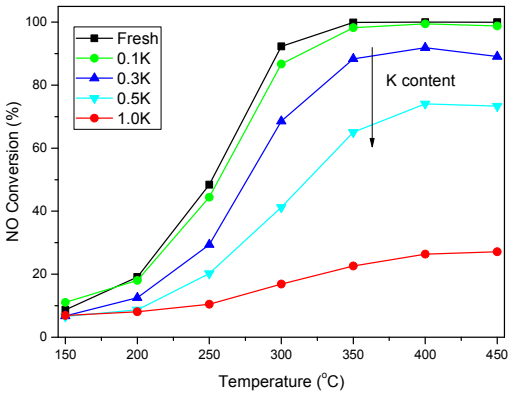
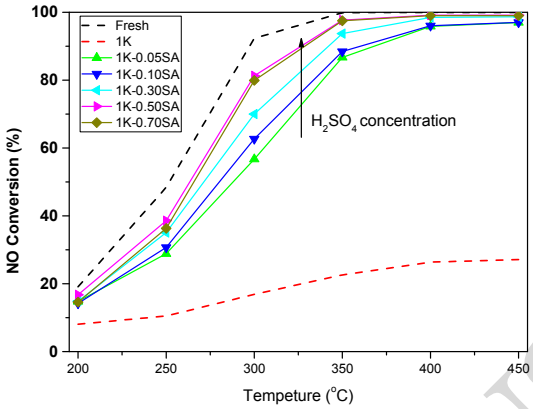


Fig. 1. NO conversion of the catalysts poisoned with different K loading amounts.

449

450



451

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

453 solution.

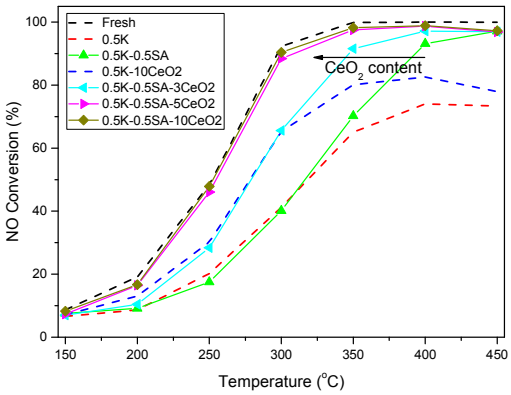
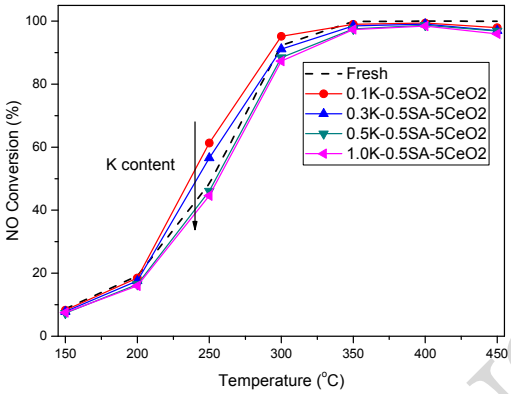


Fig. 3. NO conversion of the catalysts regenerated with different cerium loading amounts.

459

460



461

462

463 **Fig. 4.** Effect of K contents on the catalysts regenerated by washing and CeO_2 modification.

464

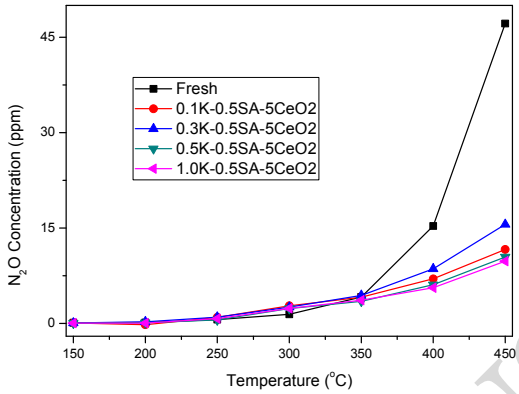


Fig. 5. N_2O formation of the catalysts regenerated by washing and CeO_2 modification.

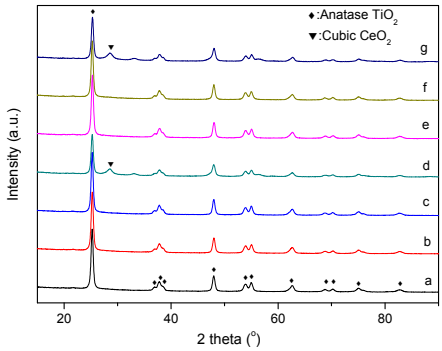


Fig. 6. XRD patterns of the (a): Fresh; (b): 0.5K; (c): 0.5K-0.5SA; (d): 0.5K-10CeO_2; (e): 0.5K-0.5SA-3CeO_2;(f): 0.5K-0.5SA-5CeO_2; (g): 0.5K-0.5SA-10CeO_2.

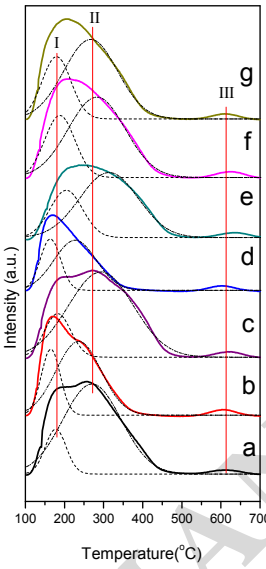
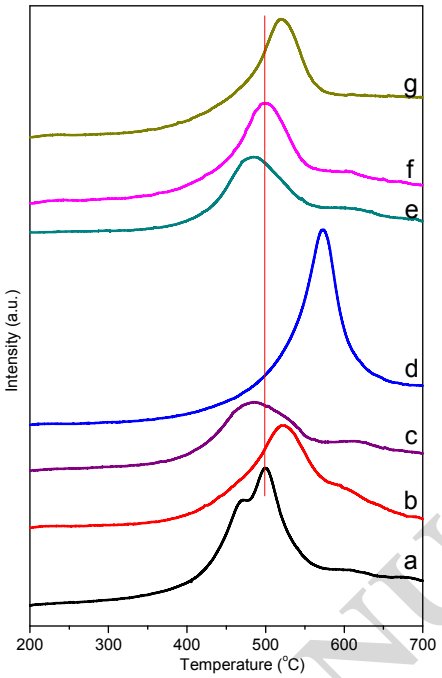


Fig. 7. NH_3-TPD curves of the (a): Fresh; (b): 0.5K; (c): 0.5K-0.5SA; (d): 0.5K-10CeO_2; (e): 0.5K-0.5SA-3CeO_2;(f): 0.5K-0.5SA-5CeO_2; (g): 0.5K-0.5SA-10CeO_2.



483

484 **Fig. 8.** H_2-TPR profiles of the (a): Fresh; (b): 0.5K; (c): 0.5K-0.5SA; (d): 0.5K-10CeO_2; (e):

485 0.5K-0.5SA-3CeO_2;(f): 0.5K-0.5SA-5CeO_2; (g): 0.5K-0.5SA-10CeO_2.

486

487