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Article

Improving the denitration performance and K-poisoning resistance of the $V_2O_5-WO_3/TiO_2$ catalyst by Ce^{4+} and Zr^{4+} co-doping

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ABSTRACT

A series of $V_2O_5-WO_3/TiO_2-ZrO_2$, $V_2O_5-WO_3/TiO_2-CeO_2$, and $V_2O_5-WO_3/TiO_2-CeO_2-ZrO_2$ catalysts were synthesized to improve the selective catalytic reduction (SCR) performance and the K-poisoning resistance of a $V_2O_5-WO_3/TiO_2$ catalyst. The physicochemical properties were investigated by using XRD, BET, NH_3 -TPD, H_2 -TPR, and XPS, and the catalytic performance and K-poisoning resistance were evaluated via a NH_3 -SCR model reaction. Ce^{4+} and Zr^{4+} co-doping were found to enhance the conversion of NO_x , and exhibit the best K-poisoning resistance owing to the largest BET-specific surface area, pore volume, and total acid site concentration, as well as the minimal effects on the surface acidity and redox ability from K poisoning. The $V_2O_5-WO_3/TiO_2-CeO_2-ZrO_2$ catalyst also presents outstanding $H_2O + SO_2$ tolerance. Finally, the *in situ* DRIFTS reveals that the NH_3 -SCR reaction over the $V_2O_5-WO_3/TiO_2-CeO_2-ZrO_2$ catalyst follows an L-H mechanism, and that K poisoning does not change the reaction mechanism.

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1. Introduction

NO_x emissions have caused a series of environmental problems in the recent years, including serious harm to our lives and belongings. Stationary source emissions (such as coal-fired power plants) account for ~60% of the total NO_x emissions. Ammonia-selective catalytic reduction (NH_3 -SCR) is an effective method to eliminate NO_x from stationary sources, and the de-

nitration catalyst is the key unit for this technique [1]. $V_2O_5-WO_3/TiO_2$ is the commercial catalyst for the NH_3 -SCR process; it exhibits excellent denitration performance between 300 and 400 °C [2]. However, this type of catalyst typically suffers from serious deactivation caused by alkali (alkaline-earth) metals, heavy metals, water vapor, and sulfur dioxide during operation [3–5]. For alkali (alkaline-earth) metal poisoning, it has been widely reported that the degree of poisoning was

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positively related to the alkalinity of the metal, *i.e.*, $K > Na > Ca > Mg$ [6,7]. The proportion of medium-alkali coal (alkali metal content 0.3%–0.5%) and high-alkali coal (alkali metal content > 0.5%) in China is ~28.94%; however, the traditional V_2O_5 - WO_3 / TiO_2 catalyst exhibits poor performance resistance to alkali metal poisoning, especially to K poisoning [8]. For example, Kamata et al. [9] reported that the activity of the V_2O_5 - WO_3 / TiO_2 catalyst was lost almost completely at 350 °C, when the mass fraction of K_2O is 1%. Therefore, it is paramount to improve the anti-alkali metal poisoning of the V_2O_5 - WO_3 / TiO_2 catalyst to satisfy applications under a high-alkali metal condition.

The reduction in surface acidity [10,11] and redox ability [7,12] are two major factors in the deactivation of NH_3 -SCR catalysts. Li et al. [13] reported that the mechanism of alkali (alkali-earth) metal poisoning of the V_2O_5 - WO_3 / TiO_2 catalyst involved the passivation of surface acid sites and bulk tungsten species, and the suppression and reducibility of active surface oxygen species. Peng et al. [14] conducted a theoretical study regarding the effects of alkali poisoning on vanadium-based catalysts based on DFT calculations. The results indicated that doping the alkali metal could lower the reducibility of the active component V_2O_5 , and could decrease surface acidity.

Ceria has received considerable attention recently in NH_3 -SCR reactions because of its excellent redox properties. Some researchers have reported Ce^{4+} -modified vanadium-based catalysts for NH_3 -SCR reactions, such as V_2O_5 - $Ce(SO_4)_2$ / TiO_2 , $VO_x/Ce_xZr_{1-x}O_2$, and V_2O_5 - CeO_2 / TiO_2 catalysts [1,15,16]. These researchers suggested that Ce^{4+} addition could not only promote the surface acidity and redox ability of the catalysts, but also enhance their alkali metal resistance.

Zirconia is an acid-based amphoteric oxide used widely as a support and co-catalyst, *e.g.* WO_3 - ZrO_2 , ZrO_2 - SO_4^{2-} , MnO_x - ZrO_2 , and CeO_2 - ZrO_2 support [17–21]. Additionally, CeO_2 - ZrO_2 is a good support for the NH_3 -SCR reaction. Vuong et al. [16] reported V_2O_5 supported on CeO_2 - ZrO_2 is better than that on pure CeO_2 or ZrO_2 support. This is likely related to the -O-Ce-O-V(=O)-O-Zr-O- moiety, which may benefit oxygen transport. Shen et al. [22] explored the influence of Ce-Zr ratios on Mn/Ce-Zr catalysts, and found that the presence of ZrO_2 in the catalyst enhanced the BET specific surface area and surface acidity efficiently. Furthermore, researchers have demonstrated that Zr^{4+} addition can improve the thermal stability of the catalyst [23,24]. For example, Shi et al. [24] reported that the introduction of Zr^{4+} efficiently increased the high-temperature activity and N_2 selectivity of the V_2O_5 - WO_3 / TiO_2 catalyst, because Zr^{4+} inhibited the shrinking of catalyst surface area and growth of the TiO_2 crystallite size at high temperatures.

To the best of our knowledge, modifying with Ce^{4+} can enhance the tolerance of alkali metals, and adding Zr^{4+} can improve the thermal stability, specific surface area, and oxygen transport performance. However, the V_2O_5 - WO_3 / TiO_2 catalyst modified by co-doping of Ce^{4+} and Zr^{4+} to improve the denitration performance and K-poisoning resistance has not yet been reported. Based on the V_2O_5 - WO_3 / TiO_2 catalyst, herein we successfully synthesized a novel V_2O_5 - WO_3 / TiO_2 - CeO_2 - ZrO_2 cata-

lyst for the selective catalytic reduction of NO_x with NH_3 . It demonstrates good denitration performance and excellent anti-K poisoning performance. Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), temperature-programmed desorption of NH_3 (NH_3 -TPD), and temperature-programmed reduction of H_2 (H_2 -TPR) were used to characterize both fresh and poisoned catalysts. Moreover, the NH_3 -SCR mechanism over these catalysts was explored through *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) technology.

2. Experimental

2.1. Catalyst preparation

The TiO_2 - CeO_2 - ZrO_2 support with a molar ratio of Ti:Ce:Zr = 9:0.5:0.5 was prepared by a co-precipitation method. First, the required amounts of $TiCl_4$, $Ce(NO_3)_3 \cdot 6H_2O$ and $Zr(NO_3)_4 \cdot 5H_2O$ were dissolved with ultrapure water to form a solution at room temperature. Next, excess ammonia was added to the solution with vigorous stirring until pH = 10, and the resulting solution was again stirred for 3 h, followed by aging for 24 h. The precipitate was subsequently filtered and washed several times with ultrapure water until a pH change was not observed (pH = 7, measured by pH test paper) and no Cl^- appeared (detected by the solution of $AgNO_3$); the obtained cakes were dried overnight at 110 °C, and were finally calcined at 450 °C for 5 h.

The V_2O_5 - WO_3 / TiO_2 - CeO_2 - ZrO_2 catalyst was prepared by the impregnation method. The V_2O_5 was 1 wt% and the WO_3 was 5 wt%. Ammonium metavanadate and ammonium tungstate were mixed in the oxalic acid solution in the desired proportion. The appropriate amount of TiO_2 - CeO_2 - ZrO_2 support was impregnated by stirring for 1 h, dried overnight at 110 °C, and subsequently calcined at 450 °C for 5 h. For comparison, the V_2O_5 - WO_3 / TiO_2 , V_2O_5 - WO_3 / TiO_2 - ZrO_2 , and V_2O_5 - WO_3 / TiO_2 - CeO_2 catalysts with a molar ratio of Ti:Ce (or Zr) = 9:1 were synthesized using the same method.

The K-poisoned catalysts were prepared using the wet impregnation method with a KNO_3 solution (K_2O was 1 wt%), subsequently evaporated at 110 °C using an oil bath and calcined at 450 °C for 5 h. Herein, we denoted the V_2O_5 - WO_3 / TiO_2 , V_2O_5 - WO_3 / TiO_2 - ZrO_2 , V_2O_5 - WO_3 / TiO_2 - CeO_2 , and V_2O_5 - WO_3 / TiO_2 - CeO_2 - ZrO_2 catalysts as VWT, VWTZ, VWTC, and VWT CZ, respectively, and the K-poisoning V_2O_5 - WO_3 / TiO_2 , V_2O_5 - WO_3 / TiO_2 - ZrO_2 , V_2O_5 - WO_3 / TiO_2 - CeO_2 , and V_2O_5 - WO_3 / TiO_2 - CeO_2 - ZrO_2 catalysts as KVWT, KVWTZ, KVWTC, and KVWTCZ, respectively, for simplicity.

2.2. Catalytic performance test

Activity and H_2O + SO_2 tolerance were measured in a quartz reactor using a 200-mg catalyst (40–60 mesh). The feed gas mixture contained 500 ppm NO , 500 ppm NH_3 , 5% O_2 , 5% H_2O (when used), 100 ppm SO_2 (when used), and N_2 as the balance gas. The gas hourly space velocity was 60000 mL·g⁻¹·h⁻¹. The concentrations of NO_x , NH_3 , and N_2O were detected by a flue gas analyzer, NH_3 analyzer, and N_2O analyzer, respectively. The NO_x

conversion of the catalysts and N₂ selectivity were determined from the following equations:

$$\text{NO}_x \text{ conv. (\%)} = ([\text{NO}_x]_{\text{in}} - [\text{NO}_x]_{\text{out}})/[\text{NO}_x]_{\text{in}} \times 100\% \quad (1)$$

$$\text{N}_2 \text{ selectivity (\%)} = (1 - 2 [\text{N}_2\text{O}]_{\text{out}} / ([\text{NO}_x]_{\text{in}} - [\text{NO}_x]_{\text{out}} + [\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}})) \times 100\% \quad (2)$$

2.3. Catalyst characterization

The XRD patterns of the samples were collected on the Philips X'Pert3 Powder diffractometer between 10° and 90° using a Ni-filtered Cu $K\alpha$ radiation. The scan rate is 10°/min, while the step size is 0.02°. The operating voltage and current of the X-ray tube are 40 kV and 40 mA, respectively.

N₂ adsorption-desorption isotherms were measured with a Belsorp-max analyzer. Prior to each measurement, samples were degassed under vacuum at 300 °C for 4 h. The specific surface areas of the samples were calculated by the BET method.

The temperature-programmed desorption of NH_3 (NH_3 -TPD) and the temperature-programmed reduction of H_2 (H_2 -TPR) were performed using a chemisorption analyzer (TP-5076). For NH_3 -TPD, the sample first was exposed to 1% NH_3 -He gas flow for 1 h at 100 °C, and was flushed under He for 1 h; subsequently, it was desorbed under He gas flow at a rate of 10 °C/min up to 700 °C. For H_2 -TPR, the sample was subjected to a 5% H_2 - N_2 gas flow at a rate of 10 °C/min, up to 900 °C. The gas flow rate was set as 30 mL/min; each sample was pretreated at 300 °C in He for 1 h before testing.

X-ray photoelectron spectroscopy (XPS) was performed using a PHI 5000 VersaProbe system with monochromatic Al K_{α} radiation (1486.6 eV), and an accelerating power of 15 KW. All the binding energies were calibrated by the C 1s peak at 284.6 eV.

The *in situ* DRIFTS experiments were performed on the Nicolet 5700 FT-IR spectrometer. The sample was pretreated with a high-purified N₂ stream at 450 °C for 1 h to remove the absorbed impurities. The sample background of each target temperature was collected during the cooling process. The sample was exposed to a controlled stream-of-reaction atmosphere at a rate of 50 mL/min for 1 h to be saturated at the ambient temperature. Further, the spectra of the adsorbed species, by subtracting the corresponding background reference, were subsequently collected as the sample was heated from room temperature to 450 °C at a rate of 10 °C/min.

3. Results and discussion

3.1. Activity and N_2 selectivity

The NH_3 -SCR performance of various catalysts measured at temperatures ranging from 100 to 500 °C is shown in Fig. 1. The activity of all the catalysts displays a volcano curve with increasing reaction temperature. The activity can be enhanced significantly with the addition of Ce^{4+} and Zr^{4+} , and the reaction temperature window has been expanded. In the temperature range of 300–400 °C, which is the operating temperature window of vanadium-based catalysts, more than 97% of NO_x con-

Fig. 1. The NH_3 -SCR activity and N_2 selectivity of the fresh and K-poisoning catalysts.

version can be achieved. The VWT and VWTZ catalysts are completely inactivated when K is introduced, but the VWTCZ catalyst still exhibits the best activity of approximately 75%, which is also higher than that of the VWTC catalyst. Peng et al. [14] synthesized the V-CeW/Ti catalyst to improve the anti-alkali performance of VW/Ti catalysts. They found that when 1 wt% K was introduced, the V-CeW/Ti catalyst exhibited better catalytic activity than VW/Ti catalyst; however, only approximately 40% NO conversion can be achieved. Shen et al. [25] reported that the addition of SiO₂ can improve the anti-K poisoning performance of the VWT catalyst. When K with a K/V molar ratio of 0.5 was introduced, the anti-K poisoning performance of the VWT catalyst was enhanced after the introduction of SiO₂; however, only 68% of NO can be removed. Compared with these catalysts, the VWTCZ catalyst prepared in the present work exhibits better anti-K poisoning performance, thereby indicating its potential to be used for the denitration of flue gas containing K. One-hundred percent N₂ selectivity is achieved for all the modified catalysts (because KVWT and KVWTZ catalysts are completely inactivated, we no longer discuss their N₂ selectivity and tolerance of H₂O and SO₂ herein). The results above indicate that the co-existence of Ce⁴⁺ and Zr⁴⁺ is crucial for improving the anti-K poisoning performance of the VWT catalyst, and that some synergetic effects occur between them.

3.2. Effects of H_2O and SO_2

The flue gas contains H_2O and SO_2 , which are known to suppress NO_x conversion. We explored the $\text{H}_2\text{O} + \text{SO}_2$ tolerance of those catalysts at 350°C , and the results are as shown in Fig. 2. The NO_x conversion of these catalysts is highly stable within 120 min before the introduction of H_2O and SO_2 , revealing that the $\text{NH}_3\text{-SCR}$ reaction reaches a steady state. The activity decreases by approximately 20% from 120 to 600 min with the introduction of H_2O and SO_2 ; this result is caused by the competitive adsorption between the reactants and $\text{H}_2\text{O} + \text{SO}_2$, the generation of surface hydroxyl groups, and the deposition of sulfates [26–28]. Finally, the NO_x conversion recovers partially

Fig. 2. H₂O + SO₂ tolerance of the fresh and K-poisoning catalysts at 350 °C.

after eliminating H₂O and SO₂ in the last 120 min, thus suggesting that the deactivation of these catalysts suffers from reversible and irreversible deactivations. Interestingly, the activity of the VWTcZ catalyst is still as high as 75% (15% higher than the VWT catalyst), providing evidence that the catalyst co-doped by Ce⁴⁺ and Zr⁴⁺ demonstrates outstanding resistance toward water and sulfur.

3.3. Structural and textural properties

The XRD results of the obtained samples are shown in Figs. 3 and 4. As shown in Fig. 3, only the diffraction peaks assigned to anatase TiO₂ can be observed in the XRD patterns of all the supports [PDF-ICDD 21-1272]. We observed that the peaks of all supports slightly shifted to a low-angle direction when compared with pure TiO₂ (as shown in the partial enlarged view in Fig. 3), thus providing evidence that Ce⁴⁺ and Zr⁴⁺ are incorporated into the lattice of TiO₂. This further causes lattice expansion owing to the radius of Ce⁴⁺ (0.92 Å) and Zr⁴⁺ (0.86 Å), which is larger than that of Ti⁴⁺ (0.68 Å) [29,30]. It is noteworthy that an obvious decrease in the intensity of the diffrac-

Fig. 3. XRD patterns of the supports.

Fig. 4. XRD patterns of the fresh (a) and K-poisoning (b) catalysts.

tion peaks occurred in the modified supports when compared with pure TiO₂. Moreover, the full-widths at half maximum height of the TiO₂-ZrO₂, TiO₂-CeO₂, and TiO₂-CeO₂-ZrO₂ supports are 0.458, 0.604, and 0.563, respectively (calculated from the strongest diffraction peak around $2\theta = 25.3^\circ$), and are larger than that of pure TiO₂ (0.399). These results demonstrate that the doping of Ce⁴⁺ and Zr⁴⁺ can inhibit the growth of TiO₂ grains effectively. The decrease in the grain size leads to an increase in the specific surface area, thus promoting the dispersion of the active species and enhancing the catalyst activity. No new crystal phases are detected when V₂O₅, WO₃, and K₂O are introduced (Fig. 4), thereby indicating that V₂O₅, WO₃, and K₂O are distributed in an amorphous state and/or a highly dispersed state on the surface of these supports.

The textural properties of these supports were measured by BET, and the corresponding results are displayed in Table 1. The specific surface area and the total pore volume of the supports are increased after Ce⁴⁺ and Zr⁴⁺ doping, and the catalyst co-doped by Ce⁴⁺ and Zr⁴⁺ has the largest specific surface area and total pore volume, which is consistent with the XRD results. The larger specific surface area is conducive to the dispersion of the active species, and the increase in the total pore volume assists with the full contact of the reactant molecules with the catalyst, as well as the diffusion of reactant molecules and product molecules, thus resulting in excellent catalytic performance.

3.4. Surface acidity

The surface acidity of the catalysts was tested by NH₃-TPD,

Table 1

BET specific surface area, mean pore diameter and total pore volume of the supports.

Sample	BET specific surface area (m ² /g)	Mean pore diameter (nm)	Total pore volume (cm ³ /g)
TiO ₂	51	13.1	0.17
TiO ₂ -ZrO ₂	195	7.7	0.38
TiO ₂ -CeO ₂	181	8.8	0.41
TiO ₂ -CeO ₂ -ZrO ₂	214	8.2	0.44

Fig. 5. NH_3 -TPD profiles of the fresh (a) and K-poisoning (b) catalysts.

which is recognized as a key factor for the NH_3 -SCR reaction [28]. Fig. 5 exhibits the NH_3 -TPD curves of the fresh and K-poisoning catalysts. Three desorption peaks (*i.e.*, I, II, and III) for the VWT catalyst appeared, resulting from the desorption of physisorbed NH_3 and from the desorption of chemisorbed NH_3 on weak and medium-strong acid sites, respectively [30]. A new peak is detected when Ce^{4+} and Zr^{4+} are co-doped, and is related to the strong acid (labeled as IV). Moreover, the amount of chemisorbed NH_3 is increased significantly. There is an obvious decrease after K addition, especially for the VWT and VWTZ catalysts, which is primarily owing to the combination of K with vanadium to form a V-O-K species that reduces surface acidity by hindering the adsorption of NH_3 on Lewis or Brønsted acid sites. Notably, the acid amount of the VWTCZ catalyst is best retained after K poisoning, and the retention is 59%, which is much higher than that of other catalysts (Table 2). Peng et al. [14] reported that the contact between the K species and the CeO_2 surface is bonded easily to form a Ce-O-K structure, thereby reducing the adsorption of K on the active V species, based on the DFT study. It is well known that Zr^{4+} can increase the thermal stability of Ce^{4+} , which is beneficial in providing more Ce^{4+} to combine with the K species. Therefore, the active V species can be protected better by the co-doping of Ce^{4+} and Zr^{4+} . Consequently, the results of the NH_3 -TPD indicate that the addition of Ce^{4+} and Zr^{4+} could not only increase the surface acidity of the VWT catalyst, but also effectively reduce the impact of K poisoning.

Table 2

Quantitative data of NH_3 -TPD profiles over the fresh and K-poisoning catalysts.

Sample	Acid amount (a.u.)				Total acid amount (a.u.) $S_{\text{II}} + S_{\text{III}} + S_{\text{IV}}$	Retention (%)
	S_{I}	S_{II}	S_{III}	S_{IV}		
VWT	336	385	427	/	812	/
VWTZ	601	1235	1234	/	2669	/
VWTC	600	1298	1006	707	3011	/
VWTCZ	550	1667	1045	460	3172	/
KVWT	280	90	/	/	90	11
KVWTZ	327	313	/	/	313	12
KVWTC	451	500	372	368	1240	41
KVWTCZ	410	892	547	423	1862	59

3.5. Reduction behavior

The redox properties of various catalysts were detected by H_2 -TPR, which is another important factor for the NH_3 -SCR reaction [26]. As shown in Fig. 6, two primary reduction peaks are observed for all the catalysts at 400–650 °C. For the VWT catalyst, the peak centered at 480 °C can be ascribed to the reduction of $\text{V}^{5+} \rightarrow \text{V}^{3+}$; the peak centered at 548 °C can be assigned to the reduction of $\text{W}^{6+} \rightarrow \text{W}^{4+}$ [31–33]. The stronger reduction peaks of the VWTCZ catalyst is caused by the good dispersion of V_2O_5 and WO_3 species on the surface of TCZ support, as well as the overlapped reduction of surface Ce^{4+} to Ce^{3+} [34]. According to literature [35–37], we found that the improvement in the redox properties for catalysts is beneficial to oxygen migration, such as the transfer of lattice oxygen to form surface oxygen in CeO_2 , and that the surface oxygen can be easily reduced to generate oxygen vacancy, thereby promoting the formation of surface-chemisorbed oxygen species. As is known, the surface chemisorbed oxygen species can oxidize NO to NO_2 effectively, thereby improving the catalytic performance through a “fast NH_3 -SCR” route. With the addition of K, we found that the reduction peaks shift to higher temperatures, thereby demonstrating that K poisoning lessens the reducibility of the primary active species (V and W oxides). However, regarding the Ce^{4+} and Zr^{4+} co-doped catalysts, the effect of K poisoning on the peak temperature is the smallest (29 and 13 °C, respectively). Furthermore, we calculated the H_2 consumption of these catalysts before and after K poisoning. It is found that the H_2 consumption of VWTCZ is greater than that of the VWT catalyst, and the retention of the KVWTCZ is the largest (Table 3). These results suggest that the redox ability can be protected more effectively by co-doping with Ce^{4+} and Zr^{4+} . In summary, Ce^{4+} and Zr^{4+} co-doping can enhance the redox property of the VWT catalyst, and inhibit the decrease caused by K poisoning effectively.

3.6. Surface analysis

XPS measurements were performed to better understand the chemical state of vanadium on the surface of these V-based catalysts, and the results are presented in Fig. 7. According to

Fig. 6. H_2 -TPR profiles of the fresh (a) and K-poisoning (b) catalysts.

Table 3

Quantitative analysis for H₂-TPR profiles of the fresh and K-poisoning catalysts.

Sample	Peak temperature (°C)		H ₂ consumption (μmol/g)			Retention (%)
	<i>T</i> ₁	<i>T</i> ₂	<i>S</i> ₁	<i>S</i> ₂	<i>S</i> ₁ + <i>S</i> ₂	
VWT	480	548	136	144	280	/
VWTZ	526	590	136	84	220	/
VWTC	508	564	267	333	600	/
VWTCZ	552	607	212	108	320	/
KVWT	531	586	20	48	68	24
KVWTZ	574	613	68	46	132	60
KVWTC	560	628	252	252	504	84
KVWTCZ	581	620	156	156	312	98

literature, the binding energies of V⁵⁺, V⁴⁺, and V³⁺ are in the ranges of 516.4–517.2, 515.7–516.2, and 515.2–515.7 eV, respectively [38,39]. The ratio of V⁵⁺ is 38.0% (Table 4) for the VWTCZ catalyst, which is higher than that of the VWT catalyst. When K is introduced, the V⁵⁺ ratio of the catalysts decreases, especially in the VWT catalyst (decrease from 36.8% to 20.0% in Table 4). Topsoe et al. [40] reported that the decrease in V⁵⁺ caused the deterioration in the redox properties of the catalyst. Therefore, the addition of K leads to decreased activity. However, the reduction in the VWTCZ catalyst is slight (decrease from 38.0% to 34.4%, as shown in Table 4), indicating that the co-doping of Ce⁴⁺ and Zr⁴⁺ could effectively reduce the effect of K on the redox properties of the catalyst. This result is consistent with the results of H₂-TPR.

3.7. In situ DRIFTS studies

We performed *in situ* DRIFTS experiments to explore the further interaction between the catalyst and the reaction mol-

Table 4

Surface composition (%) and atomic ratio (%) of the fresh and K-poisoning catalysts.

Sample	O	V	Ti	W	Ce	Zr	K	V ⁵⁺ ratio
VWT	68.92	1.76	24.86	4.46	/	/	/	36.5
VWTCZ	65.94	0.77	23.70	4.75	1.36	3.48	/	38.0
KVWT	68.26	1.54	23.27	4.23	/	/	2.70	20.0
KVWTCZ	69.18	0.70	21.66	3.03	1.65	2.24	1.54	34.4

ecules, as well as the influence of Ce⁴⁺ and Zr⁴⁺ co-doping and K poisoning. Finally, an NH₃-SCR reaction mechanism on the VWTCZ catalyst was proposed.

3.7.1. Adsorption of NH₃

The *in situ* DRIFT spectra of NH₃ adsorption over the fresh and K-poisoning catalysts as a function of temperature are given in Fig. 8. For the VWT catalyst, the bands at 1683, 1605, and 1193 cm⁻¹ at room temperature (25 °C) can be attributed to the asymmetric bending vibration of N-H in coordinated NH₃ that is adsorbed on Lewis acid sites (labeled as L acid) [41–43]. The band at 1459 cm⁻¹ can be assigned to a symmetric bending vibration of the NH₄⁺ species on Brønsted acid sites (labeled as B acid) [44]. With the increased temperature, the bands from the B acid disappear completely at 200 °C; however, the bands of L acid remain, even at 450 °C. This result demonstrates that the L acid is more stable than the B acid. A new band is detected at 1428 cm⁻¹ at 200 °C, which is related to the adsorbed -NH₂ species [42].

The band at 1622 cm⁻¹ can be related to the surface O-H stretching vibration modes when Ce⁴⁺ and Zr⁴⁺ are introduced [45]. The band at 1156 cm⁻¹ can be attributed to the L acid, and

Fig. 7. V 2p_{3/2} XPS results of different catalysts.

Fig. 8. NH_3 adsorption *in situ* DRIFTS spectra of VWT (a), VWTCZ (b), KVWT (c) and KVWTCZ (d) catalysts.

a new band for the adsorption of NH_3 on the L acid sites appears at 1560 cm^{-1} [42]. The intensity of the B acid and L acid over the VWTCZ catalyst are stronger than that of the VWT catalyst at all temperatures. After the K addition, the intensity of the L acid and B acid over the KVWT catalyst are weakened; however, the KVWTCZ catalyst is maintained effectively. These observations demonstrate that the co-doping of Ce^{4+} and Zr^{4+} , as well as the amounts of acid sites on the catalyst surface, can increase the strengths of the L acid and B acid; K poisoning will reduce the surface acidity of the catalyst and affect the adsorption of NH_3 , while Ce^{4+} and Zr^{4+} co-doping can effectively reduce the effect of K on the surface acidity of the catalyst. The results are in good agreement with those of NH_3 -TPD.

3.7.2. Co-adsorption of $\text{NO} + \text{O}_2$

Fig. 9 displays the *in situ* DRIFT spectra of surface-adsorbed species resulting from the co-adsorption of $\text{NO} + \text{O}_2$ at different temperatures over the fresh and K-poisoning catalysts. For the VWT catalyst, the bands at 1632 and 1292 cm^{-1} can be attributed to the adsorbed NO_2 molecules and linear nitrites [41,42]. When Ce^{4+} and Zr^{4+} are doped, the intensity of the adsorbed NO_2 molecules and linear nitrites are strengthened. At the same time, two new bands appeared at 1581 and 1233 cm^{-1} , which are related to the bidentate nitrates and the chelating bidentate nitrates [42,46]; this result is caused by the oxidation of NO to NO_2 . Several new bands are observed at 1598 , 1511 and 1380 cm^{-1} when K is introduced, and they are assigned to the monodentate nitrates, bidentate nitrates and $\text{cis-N}_2\text{O}_2^{2-}$ species, respectively [42,47,48]. However, the bands at 1632 and 1233 cm^{-1} are weakened. This result shows that the addition of K reduces the ability of the catalysts to oxidize

NO to NO_2 , while NO_2 is the key factor for the “fast NH_3 -SCR” route. These phenomena indicate that the doping of Ce^{4+} and Zr^{4+} can enhance the adsorption and oxidation of NO to form different types of nitrates; K poisoning increases the adsorption of NO but reduces the redox properties of the catalysts and attenuates the oxidation of NO to NO_2 . However, the addition of Ce^{4+} and Zr^{4+} can reduce this effect effectively, and the results are consistent with those of H_2 -TPR.

3.7.3. Co-adsorption of $\text{NO} + \text{O}_2 + \text{NH}_3$

The VWTCZ catalyst demonstrates excellent physicochemical properties, good $\text{H}_2\text{O} + \text{SO}_2$ tolerance, outstanding catalytic performance, and optimal anti-K-poisoning performance. $\text{NO} + \text{O}_2 + \text{NH}_3$ co-adsorption was measured by *in situ* DRIFTS to reveal the reaction mechanism, and the results are presented in Fig. 10. The bands of bridging nitrates (1638 and 1216 cm^{-1}), bidentate nitrates (1600 cm^{-1}), L acid (1683 cm^{-1}), and B acid (1442 cm^{-1}) are observed when the VWTCZ catalyst is exposed to the mixed gases [41,42,44,45]. These results demonstrate that both NO and NH_3 are absorbed simultaneously on the surface of the VWTCZ catalyst, thereby revealing that the selective catalytic reduction of NO by NH_3 over the catalyst follows the Langmuir-Hinshelwood (L-H) mechanism. Furthermore, compared with the *in situ* DRIFTS results of NH_3 adsorption, the bands of the L acid and B acid are stronger in the mixture gases because the presence of $\text{NO} + \text{O}_2$ increases the intensity of acid sites on the surface of the catalyst. The bands of the adsorbed NO_x and adsorbed NH_3 species still appeared at the corresponding positions for the KVWTCZ catalyst, thus suggesting that K poisoning does not change the reaction mechanism. However, the intensity of these bands is weakened slightly

Fig. 9. NO + O₂ co-adsorption *in situ* DRIFTS of VWT (a), VWT CZ (b), KVWT (c) and KVWT CZ (d) catalysts.

Fig. 10. NO + O₂ + NH₃ co-adsorption *in situ* DRIFTS of VWT CZ (a) and KVWT CZ (b) catalysts.

owing to K poisoning.

4. Conclusions

In this work, a novel V₂O₅-WO₃/TiO₂-CeO₂-ZrO₂ catalyst was synthesized, and exhibited outstanding catalytic performance and excellent anti-K poisoning performance at 300–400 °C. By exploring the effects of Ce⁴⁺ and Zr⁴⁺ co-doping as well as

K-poisoning on the physicochemical properties of V₂O₅-WO₃/TiO₂ catalyst, several conclusions were obtained, as follows: (1) Ce⁴⁺ and Zr⁴⁺ species could be doped into the lattice of TiO₂ to inhibit the grain growth. This led to the increase in the BET specific surface area and total pore volume. (2) For Ce⁴⁺ and Zr⁴⁺ co-doping, the surface acidity and redox properties were enhanced, and the effect of K-poisoning on the surface acidity and the redox properties of the catalyst were reduced

effectively. This may be due to the combination of Ce^{4+} with K to form Ce-O-K, while Zr^{4+} could increase its thermal stability, allowing more Ce^{4+} to bind with K, thus protecting the active V^{5+} species. (3) NO , O_2 , and NH_3 could interact with the VWTCZ catalyst simultaneously, indicating that the NH_3 -SCR reaction over VWTCZ catalyst followed an L-H mechanism. Furthermore, K-poisoning did not change the reaction mechanism.

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Graphical Abstract

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Improving the denitration performance and K-poisoning resistance of the $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalyst by Ce^{4+} and Zr^{4+} co-doping

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Co-doping of Ce^{4+} and Zr^{4+} enhances the denitration performance and K-poisoning resistance of $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalyst because more K atoms can be combined with Ce^{4+} to yield the better protection of active vanadium species.

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Ce⁴⁺, Zr⁴⁺共掺杂提高V₂O₅-WO₃/TiO₂催化剂脱硝性能及抗K中毒能力

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摘要: 近年来, NO_x的排放造成了严重的环境污染. 氨选择性催化还原技术(NH₃-SCR)是目前消除NO_x最有效的手段之一. V₂O₅-WO₃/TiO₂催化剂在300–400 °C范围内表现出优异的脱硝性能, 因此被广泛用于NH₃-SCR反应. 然而该催化剂抗碱(土)金属中毒性能较差, 且碱(土)金属碱性越强对催化剂的毒害越大(即K > Na > Ca > Mg). 已有研究显示, 当K₂O质量分数达1%时, 催化剂将完全失活, 所以对传统的V₂O₅-WO₃/TiO₂催化剂进行改性以提高其抗K中毒性能具有十分重要的意义.

最近, CeO₂由于具有优异的氧化还原性能和储/释氧能力, 在NH₃-SCR反应得到了广泛的关注. 研究显示, CeO₂的改性可提高钒基催化剂脱硝活性及抗碱金属中毒性能, 这主要是由于CeO₂的掺杂可以有效提高催化剂表面酸性及氧化还原能力. ZrO₂是一种酸碱两性氧化物, 常被用作载体或者助剂. 研究显示, ZrO₂的引入可以提高催化剂热稳定性, 增大比表面积以及提高氧迁移能力. 基于此, 我们制备了一系列的V₂O₅-WO₃/TiO₂-ZrO₂, V₂O₅-WO₃/TiO₂-CeO₂以及V₂O₅-WO₃/TiO₂-CeO₂-ZrO₂催化剂, 以期提高V₂O₅-WO₃/TiO₂催化剂脱硝性能及抗K中毒能力.

研究发现, Ce⁴⁺, Zr⁴⁺共掺杂可以有效提高V₂O₅-WO₃/TiO₂催化活性, 拓宽反应温度窗口, 增强抗K中毒能力. 进一步借助X射线衍射、比表面积测定、氨气-程序升温脱附、氨气-程序升温还原和X射线光电子能谱等表征对催化剂进行全面分析. 结果显示, Ce⁴⁺, Zr⁴⁺共掺杂对V₂O₅-WO₃/TiO₂催化剂物理化学性质的影响与其脱硝性能及抗K中毒能力有着密不可分的关系. 首先, Ce⁴⁺, Zr⁴⁺可以掺杂进入TiO₂晶格, 抑制TiO₂晶粒的生长, 从而导致比表面积以及总孔体积的增加; 比表面积的增加有利于活性物种的分散, 而总孔体积的增加有利于反应物分子与催化剂充分接触. 其次, Ce⁴⁺, Zr⁴⁺共掺杂可以提高催化剂表面酸性和氧化还原性能, 表面酸性的增加有利于催化剂吸附与活化反应物种NH₃, 氧化还原性能的提高有利于NO氧化为NO₂, 进而通过“快速NH₃-SCR”反应提高催化剂活性; 同时, Ce⁴⁺, Zr⁴⁺共掺杂还可以有效降低K中毒对表面酸性和氧化还原性能的影响, 这主要是由于Ce⁴⁺可以与K原子结合形成Ce-O-K物种, 而Zr⁴⁺的引入可以增加Ce⁴⁺的热稳定性, 使得更多的Ce⁴⁺与K结合, 避免了K与活性钒物种结合形成V-O-K物种, 使得活性V⁵⁺得到了有效的保护. 原位红外实验揭示了V₂O₅-WO₃/TiO₂-CeO₂-ZrO₂催化反应遵循L-H机理, 且K中毒并未改变其反应机理. 最后, 该催化剂在H₂O和SO₂存在的条件下仍具有最佳的脱硝性能, 因而有望用于实际高K含量的燃煤烟气脱硝.

关键词: V₂O₅-WO₃/TiO₂-CeO₂-ZrO₂催化剂; 共掺杂; 钾中毒; 氨-选择性催化还原; 反应机理

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