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Article

Characterization and activity of V_2O_5 - CeO_2 / TiO_2 - ZrO_2 catalysts for NH_3 -selective catalytic reduction of NO_x

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ABSTRACT

A series of V_2O_5 - $xCeO_2$ / TiO_2 - ZrO_2 (Ti-Zr) catalysts with different CeO_2 loadings (x = molar ratio of Ce/Ti -Zr) were prepared, and their catalytic performance for the selective catalytic reduction (SCR) of NO_x by NH_3 was investigated in the presence of SO_2 and H_2O . The physicochemical properties of the catalysts were characterized by N_2 sorption analysis, high-resolution transmission electron microscopy, X-ray diffraction, H_2 -temperature-programmed reduction, NH_3 -temperature-programmed desorption, and in situ diffuse reflectance infrared Fourier transform spectroscopy. The presence of CeO_2 in the catalysts led to higher conversion of NO_x within a wider operating temperature range. V_2O_5 - $xCeO_2$ / Ti -Zr catalyst ($x = 0.2$) exhibited the highest activity. Higher loadings of CeO_2 adversely affected the NO_x conversion at higher temperatures. The characterization results revealed that CeO_2 was amorphous and highly dispersed over the Ti-Zr support. The catalysts featured single-crystal electron diffraction features. The presence of CeO_2 significantly increased the reduction ability of the catalysts, and low V_2O_5 loadings were beneficial to the low-temperature SCR. V_2O_5 / TiO_2 catalyst exhibited medium-to-strong and strong acid desorption of NH_3 , whereas V_2O_5 / Ti -Zr featured weak acid sites onto which desorption of NH_3 occurred. The presence of CeO_2 could increase the amount of both the Brönsted and Lewis acid sites, which were expected to play a key role in the excellent SCR activity. In contrast, the presence of V_2O_5 reduced the amount of Brönsted acid sites. All V_2O_5 - CeO_2 / Ti -Zr catalysts exhibited poor stability and weak resistance to H_2O poisoning but high resistance to SO_2 . However, the original catalytic activity of V_2O_5 - $xCeO_2$ / Ti -Zr ($x = 0.3$) could be fully restored following poisoning with SO_2 and H_2O . For the poisoned catalysts, the formation of $Ce(SO_4)_2$ led to the decreased catalytic performance at the intermediate temperatures, which increased at the higher temperatures because of the presence of V_2O_5 .

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1. Introduction

The selective catalytic reduction (SCR) of nitrogen oxides (NO_x) by NH_3 has developed into a mature and highly efficient technology for coal-fired flue gas denitration [1–4]. The

well-known commercial SCR catalysts for this process are V_2O_5 - WO_3 / TiO_2 and V_2O_5 - MoO_3 / TiO_2 monoliths [1,3]. Because the catalyst generally accounts for more than 80% of the total mass, the use of high-quality and affordable catalysts is desirable. TiO_2 is typically employed as a support of SCR catalysts.

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However, recent studies have shown that TiO_2 may not be ideal owing to its low specific surface area and poor thermal stability. In contrast, Ti-Zr complex oxides typically feature larger surface areas and strong surface acidity. Particularly, it has been demonstrated that the surface area reaches a maximum when the molar ratio of TiO_2 to ZrO_2 is 1:1 [5–7].

Besides the catalyst support, the prominent problems associated with SCR include the narrow operating temperature window (300–400 °C) and high conversion rate of SO_2 into SO_3 [8,9]. Therefore, the development of high-performance catalysts is necessary and has recently been extensively studied.

Recently, as an auxiliary component of NH_3 -SCR catalysts, CeO_2 has attracted much attention owing to its high oxygen storage and release capacity [10]. As demonstrated, Ce-containing mixed oxide catalysts, such as Ce/Ti-Si-Al [11], Mo_2O_3 (Co_2O_3)/Ce-Zr [12], and CeO_2 -CuO [12], have excellent NH_3 -SCR activity. A Ce-W mixed oxide catalyst was studied in 2011, and a NO_x conversion of ~100% could be achieved within a wide operating temperature range of 250–425 °C; the gas hourly space velocity (GHSV) was as high as 500 000 h^{-1} [13]. Moreover, further studies showed that Ti and W doping could afford a higher dispersion degree of Ce species and increase the ratio of $\text{Ce}^{3+}/\text{Ce}^{4+}$, thereby leading to higher SCR activity at lower temperatures [14]. More specifically, the ceria-modified 1 wt% V_2O_5 -10 wt% ZrO_2 / WO_3 - TiO_2 catalyst features more active adsorbed nitrates during the SCR reaction process. However, the catalyst displays poor hydrothermal stability owing to the presence of cerium oxide [15]. Nevertheless, several studies indicated that CeO_2 could enhance the SO_2 durability of NH_3 -SCR catalysts [16,17]. Shu et al. [18] reported that in the presence of 1000 ppm SO_2 , the NO_x conversion over CeO_2 -Fe/WMH catalyst decreased from 97.6% to 90.3% after 50 min of reaction, and decreased further to 88% after 100 h of reaction. After 10% H_2O was added, the conversion rate was maintained at ~70% for 100 h at 250 °C. A related research study investigated CeO_2 - TiO_2 composite as a support for the preparation of V_2O_5 - WO_3 /CeO₂- TiO_2 catalysts, which displayed improved resistance to SO_2 poisoning [19]. Some studies claimed that the strong interaction between CeO_2 and TiO_2 suppressed the adsorption of SO_2 onto the surface of CeO_2 / TiO_2 [20,21], which may contribute to the high resistance of the catalyst to SO_2 . In another study, it was demonstrated that the presence of Zr in Fe-Mn/Ti-Zr (the ratio of Ti/Ti+Zr was 0.05) improved the SO_2 tolerance performance of the catalyst, thus decreasing the SO_2 deactivation rates [22]. Additionally, a Ce-Ti-Zr composite oxide catalyst, which was prepared by the sol-gel method, showed strong resistance to H_2O and SO_2 poisoning [23].

In our previous work, CeO_2 was introduced into the V_2O_5 /Ti-Zr catalyst as a promoter [7]. The Ce-containing catalysts displayed better catalytic activity within a wider temperature range of 220–450 °C than the Ce-free catalyst. The improved catalytic activity was likely due to the higher amount of surface acid and active intermediate sites on the Ce-containing catalysts. The relative content of vanadic oxide was 3 wt%. However, it has been suggested to control the content of V_2O_5 within a range of 0.8%–1.2% because of its high toxicity [24]. In

that study, V_2O_5 was loaded prior to CeO_2 loading, and thus CeO_2 was considered as the active component.

In the present study, the doping sequence of V_2O_5 and CeO_2 was changed so that V_2O_5 was the main active component likewise to traditional catalysts. Furthermore, the loading content of V_2O_5 was reduced to 1 wt%. The role of ZrO_2 was investigated. The influence of CeO_2 on the surface acidity was mainly explored by temperature-programmed desorption of NH_3 (NH_3 -TPD) and in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Subsequently, the catalytic activity of the oxide catalysts was experimentally investigated in the “ $\text{NH}_3+\text{NO}+\text{O}_2+\text{SO}_2+\text{H}_2\text{O}$ ” reaction. Additionally, the specific surface area and NO_x conversion of the poisoned catalysts were determined at different temperatures. N_2 sorption analysis, X-ray diffraction (XRD), and high-resolution transmission electron microscopy (HRTEM) were used to assess the structural properties of the catalysts, and temperature-programmed reduction of H_2 (H_2 -TPR) was used to evaluate the reduction properties of the catalysts. The obtained results were compared with those obtained previously [7] to illustrate any differences.

2. Experimental

2.1. Sample preparation

The TiO_2 - ZrO_2 (molar ratio of 1:1) support (Ti-Zr) was prepared by a co-precipitation method. Equal molar amounts of TiCl_4 solution and ZrOCl_2 solution were dissolved in deionized water, followed by dropwise addition of aqueous ammonia with constant stirring until the pH reached 10. The obtained precipitate was aged for 12 h, washed with deionized water until the supernatant was free from Cl^- , and dried overnight at 110 °C. Finally, the product was calcined at 450 °C for 4 h in a muffle stove.

V_2O_5 - CeO_2 /Ti-Zr samples were prepared by a step-by-step impregnation of Ti-Zr with an aqueous solution containing the desired amount of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, followed by drying at 110 °C for 12 h and calcination at 450 °C for 4 h. Intermediate CeO_2 /Ti-Zr products were then impregnated with a NH_4VO_3 solution. The obtained samples were denoted as V-xCe/Ti-Zr, where x represents the molar ratio of Ce to Ti-Zr support, and the relative content of V_2O_5 was 1 wt%.

A V_2O_5 /Ti-Zr sample with a V_2O_5 loading of 1 wt% was synthesized by impregnating the Ti-Zr support with a NH_4VO_3 solution. The mixture was dried at 110 °C for 12 h, followed by calcination under flowing air at 450 °C for 4 h. The V_2O_5 /Ti-Zr sample is referred to hereafter as V/Ti-Zr.

The V_2O_5 / TiO_2 sample was prepared by the impregnation method. The TiO_2 support was prepared using the same method as that used for the synthesis of the Ti-Zr support. Then, the TiO_2 support was impregnated with a required amount of NH_4VO_3 solution to achieve a V_2O_5 loading of 1 wt%, followed by drying at 110 °C for 12 h and calcination under flowing air at 450 °C for 4 h. The sample is hereafter referred to as V/Ti.

2.2. Catalyst characterization

The BET surface areas and BJH pore size distributions of the prepared samples were determined by N₂ adsorption–desorption analysis at –196 °C on a Micromeritics ASAP 2020 (USA). Before analysis, the samples were evacuated for 2–3 h at 200 °C in the degassing port of the instrument.

XRD patterns were obtained on a Rigaku D-max/RB diffractometer (Japan) using Cu K α (λ = 0.15406 nm) radiation. The data were collected at 2θ = 10°–80° with a step size of 0.02°.

H₂-TPR analysis was carried out in a quartz U-tube reactor (internal diameter = 6 mm) connected to a FINESORB-3010 instrument. For the measurements, 20 mg of sample and H₂-Ar (1% H₂ by volume), as reductant, were used. The samples were heated from room temperature to 800 °C at a rate of 10 °C/min.

NH₃-TPD analysis was conducted in a quartz U-tube reactor (internal diameter = 6 mm) connected to a FINESORB-3010 instrument. For the measurements, 70 mg of sample and NH₃-He, as adsorbent, were used. The samples were heated from room temperature to 700 °C at a rate of 10 °C/min.

The particle size and morphology of the samples were analyzed via HRTEM on a JEOL JEM-200CX (Japan) transmission electron microscope. Prior to analysis, the samples were dispersed in ethanol, and the suspension was dropped onto a holey carbon film supported on a copper grid, followed by drying at 110 °C in an oven.

NH₃ adsorption in situ DRIFTS spectroscopy was conducted on a Nicolet 6700 spectrometer (Thermo Electron Corporation; USA) within a scanning range of 400–4000 cm^{–1} at a resolution of 4 cm^{–1} (32 scans were taken for each spectrum). For analysis, the samples were pressed into self-supporting disks for the IR characterization at room temperature and pretreated with N₂ at 400 °C for 1 h. The samples were cooled to 25 °C before each measurement, and then exposed to a stream of NH₃ for 1 h. Subsequently, a temperature ramp of 10 °C/min from 25 to 400 °C was used to record the spectra.

2.3. Catalytic activity tests

SCR activity measurements of the catalysts were carried out in a fixed-bed reactor at 200–450 °C containing 0.3 g of catalyst (40–60 mesh) with a GHSV of 20 000 h^{–1}. A feed stream at a fixed composition was pre-mixed in a gas mixer to obtain the simulated gas comprising 0.08% NO, 0.08% NH₃, 5% O₂ (by volume) and balanced by N₂. Then, the mixed gas was introduced into the reactor. The NO and NO₂ concentrations were continually monitored by a flue gas analyzer (Testo 330-2 LL).

Additionally, the stability of the catalysts against SO₂ (200 ppm) and H₂O (10%) poisoning was investigated at 250 °C. Liquid water was heated at 250 °C and then introduced into the fixed-bed reactor.

3. Results and discussion

3.1. Catalytic performance

The effect of CeO₂ loading on the NO_x conversion was investigated, and the results are shown in Fig. 1. As observed, Ce doping afforded widening of the operating temperature win-

Fig. 1. NO_x conversion rates of the different prepared catalysts.

dow for the SCR reaction as well as considerable improved catalytic performance (200–450 °C) when compared with the Ce-non-doped catalysts. More specifically, the NO_x conversion rate initially increased to a maximum of 92% at 250 °C with increasing CeO₂ loadings to Ce/Ti = 0.2, and then decreased with further increases in CeO₂ loading. Thus, among the catalysts investigated, V-0.2Ce/Ti-Zr showed the best performance and the widest operating temperature window. These results agreed with results of the previous study [7]. However, the higher content of V₂O₅ employed in the previous study resulted in better catalytic activity at a higher temperature of 450 °C. Based on the previous and current studies, it can be deduced that CeO₂ primarily influences the catalytic activity at low reaction temperatures, whereas V₂O₅ determines the catalytic performance at higher temperatures.

3.2. Crystal phase analysis

Figure 2 shows the XRD patterns of all prepared samples. As observed, V/Ti displayed strong peaks that could be indexed to anatase TiO₂ (JCPDS No. 21-1272). Furthermore, the intensity of the peaks was stronger than that displayed by the other catalysts. No distinct diffraction peaks could be detected for Ti-Zr. In contrast, the Ti-Zr sample doped with V₂O₅ displayed diffraction peaks corresponding to ZrTiO₄ mixed oxide (JCPDS No. 80-1783) that suggested the presence of amorphous TiO₂-ZrO₂ in the sample and thermodynamic stability of the sample [25]. As expected, the non-crystalline porous structure featured heterojunctions at the boundary of the two different oxide components, which have different oxygen coordination numbers, i.e., 6 for Ti and 8 for Zr [26]. In contrast, this feature was not observed for literature-reported V/Ti-Zr (V₂O₅ loading of 3 wt%) that may be due to the higher loading of V₂O₅ employed [7] (when compared with the loading amount used in the present study). Following introduction of CeO₂ (Ce/Ti = 0.1) in V/Ti-Zr, the diffraction peaks split, generating anatase-related peaks and weak V₂O₅-related peaks (JCPDS No. 86-2248). More diffraction peaks corresponding to anatase, CeO₂ (JCPDS No. 81-0792), and ZrO₂ (JCPDS No. 88-1007) were apparent within the 2θ region of 40°–80° with increasing CeO₂ loadings. This observation suggested the onset of considerable decrease in

Fig. 2. XRD patterns of the different prepared catalysts.

the degree of dispersion of CeO₂ in the samples. When the loading of CeO₂ increased to Ce/Ti = 0.3, the diffraction profile of the resulting sample became smoother, with weak peaks corresponding to ZrTiO₄ and strong peaks corresponding to ZrTiO₄ and CeO₂. It is worth noting that excess CeO₂ is expected to reduce dispersion of V-xCe/Ti-Zr over the catalysts.

3.3. BET surface area and pore volume analysis

Table 1 lists the BET surface areas and pore volumes of the prepared samples. As observed, the Ti-Zr support had a large specific surface area of 255.73 m²/g. In our previous study [7], Zr_{0.5}Ti_{0.5}O₂ was prepared using a co-precipitation method and calcination at 550 and 650 °C. Zr_{0.5}Ti_{0.5}O₂ calcined at 550 °C was amorphous and displayed higher specific surface area and pore volume than Zr_{0.5}Ti_{0.5}O₂ calcined at 650 °C, which displayed distinct zirconium titanate crystalline features that resulted in a lower surface area and pore volume. In contrast, as reported, TiO₂ calcined at 500 °C displayed anatase features, whereas calcination at a higher temperature of 600 °C resulted in rutile TiO₂, with a corresponding decline in surface area, thus demonstrating the poor stability of TiO₂ at high temperatures [27]. In another study, ZrO₂-TiO₂ was prepared and calcined at 500 °C, and Mn-Fe/ZrO₂-TiO₂ catalyst was prepared and calcined at 500 and 800 °C. No anatase TiO₂-related peaks were detected in the Mn-Fe/ZrO₂-TiO₂ catalyst calcined at 500 °C, which displayed low crystalline (amorphous) features. When a higher calcination temperature of 800 °C was used, no rutile TiO₂-related peaks were detected in Mn-Fe/ZrO₂; however,

ZrTiO₄-related peaks were observed. It was further observed that the surface area of the Mn-Fe/ZrO₂-TiO₂ catalyst decreased from 175 to 10.67 m²/g when the calcination temperature increased from 500 to 800 °C [28]. These studies demonstrate that the phase transition of TiO₂ is slower in a TiO₂-ZrO₂ mixed oxide support upon calcination at high temperatures. However, this phenomenon would adversely affect the surface area greatly and would likely result in poor catalytic activity.

In the present study, V/Ti-Zr featured a larger specific surface area than V/Ti. The addition of Ce significantly reduced the surface area and pore volume of the resulting catalysts when compared with that of the Ti-Zr support. With increase in the CeO₂ content, the surface area and pore volume first increased and then decreased. Overall, the specific surface area and pore volume decreased following impregnation of the vanadium and cerium oxide components when compared with that of the Ti-Zr support. This decrease was attributed to the penetration of the deposited active oxides into the pores of the support that led to the narrowing of pores and blocking of some of the microspores [7]. In general, high specific surface areas are indicative of better dispersion of the active ingredient and greater contact area of the reaction gases that are favorable to the conversion of NO_x. The presence of excess CeO₂ led to reduced BET surface area and dispersion of the active ingredient. Therefore, as deduced from the results, the optimum Ce-doping level was Ce/Ti molar ratio of 0.2.

3.4. HRTEM analysis

HRTEM was used to analyze the microstructure of the catalysts (Fig. 3). As observed from Fig. 3(a), V-0.1Ce/Ti-Zr featured an average particle size of 14.52 nm. The calculated interplanar spacing (from the observed lattice fringes) of 0.312 nm could be assigned to the (111) plane of CeO₂ (theoretical interplanar spacing = 0.312 nm). The second calculated interplanar spacing was 0.351 nm, which could be assigned to the (101) plane of TiO₂ (theoretical interplanar spacing = 0.352 nm). V-0.2Ce/Ti-Zr featured an average particle size of 10.75 nm and interplanar spacing of 0.362 nm, corresponding to the (011) plane of ZrTiO₄ (theoretical interplanar spacing = 0.361 nm). Fur-

Table 1

BET surface area and pore volume of the prepared samples.

Sample	S_{BET} (m ² /g)	V_p (mL/g)
V-0.1Ce/Ti-Zr	35.27	0.12
V-0.2Ce/Ti-Zr	54.45	0.14
V-0.3Ce/Ti-Zr	44.91	0.10
V/Ti-Zr	143.77	0.21
Ti-Zr	255.73	0.55
V/Ti	66.10	0.32

Fig. 3. TEM images and associated HRTEM images of V-0.1Ce/Ti-Zr (a) and V-0.2Ce/Ti-Zr (b).

Fig. 4. Selected area electron diffraction patterns of V-0.1Ce/Ti-Zr (a) and V-0.2Ce/Ti-Zr (b).

thermore, as observed from Fig. 3, both V-Ce/Ti-Zr samples featured spherical particles that confirmed that CeO₂ and V₂O₅ were well dispersed on the surface of ZrTiO₄ and also interacted with ZrTiO₄. However, the interaction was weaker in V-0.1Ce/Ti-Zr when compared with that in V-0.2Ce/Ti-Zr. This phenomenon was supported by the presence of more diffraction peaks in V-0.1Ce/Ti-Zr when compared with the number of diffraction peaks featured in the other samples in Fig. 2. The bright spots observed in the selected area electron diffraction patterns in Fig. 4 suggested the existence of single-crystal electron diffraction features in both samples [29].

3.5. Reducible properties of the catalysts

H₂-TPR was performed to assess the availability and amount of reducible species on the catalyst surfaces. Figure 5 shows the H₂-TPR profiles of the different catalysts. The Ti-Zr support exhibited high thermal stability, as deduced from the late appearance of a reduction peak after 700 °C. CeO₂ has strong abilities to store and/or release oxygen via the redox shift between Ce⁴⁺ and Ce³⁺ [30]. More specifically, in CeO₂ nanoparticles, reduction of Ce⁴⁺ first occurs on the surface sites at ~200–430 °C (α peak), and subsequently in the subsurface layers and deeper internal regions of the nanoparticles at 430–600 °C (β peak). The γ peak (>600 °C) is typically related to the reduction of bulk CeO₂ that is dependent on the bulk structure [31,32]. According to the literature [29], the arrangement and size of the grains of the catalyst determine the reduction of the catalyst. In the present study, the interaction between Ti-Zr and ceria led to a better crystal orientation arrangement. Thus, the present catalysts showed stronger reduction abilities and lower reduction temperatures when compared with those typically reported for V-W/Ti. Previous reports demonstrated that the reduction peak observed at low temperatures was associated with the reduction of monomeric species or highly dispersed vanadium species [33–35], whereas that at higher temperatures (above 700 °C) was generally attributed to the reduction of bulk vanadium oxide [36,37].

Fig. 5. H₂-TPR profiles of the different prepared samples.

Herein, V/Ti displayed a two-peak reduction pattern. The peak centered at 422 °C was assigned to the reduction of vanadia from V⁵⁺ to V⁴⁺ and the second peak centered at 560 °C was ascribed to the reduction of V⁴⁺ to V³⁺ [38]. In contrast, V/Ti-Zr displayed broadened H₂-consumption peaks. Furthermore, the first reduction peak was shifted to a lower temperature upon introduction of ZrO₂. Presumably, the vanadium species were well dispersed on the Ti-Zr support.

As observed, the overall intensity of the profiles of the V-*x*Ce/Ti-Zr samples was stronger. More specifically, the first reduction peak shifted to lower temperatures, and the intensity of the peaks grew stronger with increasing CeO₂ loadings. These results were attributed to the surface (α) reduction processes of CeO₂. Furthermore, V-0.2Ce/Ti-Zr displayed an additional α peak at 416 °C, indicative of an improved reduction ability at lower temperatures. In accordance with the BET results, the improved reduction ability was attributed to appropriate level of Ce doping and better dispersion. The subsurface layers and deeper regions of the catalyst nanoparticles (with increasing CeO₂ loadings) were reduced at 486, 507, and 489 °C, respectively. The reduction of V⁵⁺ to V³⁺ occurred at respectively 635, 582, and 605 °C on the catalysts with increasing CeO₂ loadings. Ti-Zr and bulk ceria were reduced at $T_{\max}$, which corresponds to the maximum reduction temperature in the H₂-TPR profiles. Low contents of V₂O₅ shifted the reduction peak to lower temperatures.

To further understand the modification role of CeO₂ and ZrO₂, the H₂-TPR peaks were integrated (Table 2), and the

Table 2

Peak information from the H₂-TPR analysis.

Sample	V ₂ O ₅ peak area					CeO ₂ peak area				H ₂ /CeO ₂ (mol/mol)	At $T_{\max}$		Total area
	Peak 1	Peak 2	Peak 3	Peak 4	Ratio	Peak 1	Peak 2	Peak 3	Ratio		Peak	Ratio	
V/Ti-Zr	410	1442	—	—	89%	—	—	—	—	—	239	11%	2091
V-0.1Ce/Ti-Zr	—	—	977	—	37%	244	848	—	42%	4.11	540	21%	2609
V-0.2Ce/Ti-Zr	—	—	—	1639	36%	313	558	1627	55%	5.07	383	9%	4520
V-0.3Ce/Ti-Zr	—	—	3108	—	52%	436	1920	—	39%	3.42	556	9%	6020

overlapping peaks were deconvoluted using the Gaussian function. The peak area of vanadium decreased in the order V-0.3Ce/Ti-Zr (605 °C) > V-0.2Ce/Ti-Zr (582 °C) > V-0.1Ce/Ti-Zr (635 °C). This trend was consistent with the catalytic results that showed that V-0.3Ce/Ti-Zr displayed a better activity than V-0.2Ce/Ti-Zr after poisoning. The peak area trend at $T_{\max}$ was as follows: V-0.3Ce/Ti-Zr (739 °C) > V-0.1Ce/Ti-Zr (735 °C) > V-0.2Ce/Ti-Zr (734 °C) > V/Ti-Zr (713 °C), suggesting that the γ peak appeared over 700 °C and the H_2 consumption increased. Such observations confirmed the strong interaction between CeO_2 and the Ti-Zr support. Additionally, the main redox processes could be correlated to the α and β peaks. Particularly, the consumption of hydrogen per mole of CeO_2 was the largest for V-0.2Ce/Ti-Zr. Hence, different extents of reducibility may indicate that CeO_2 on the catalysts was dispersed with varying degrees and excess doping would decrease the reduction ability of the catalysts.

3.6. NH_3 -TPD

The acidity of a catalyst directly determines the adsorption of NH_3 and the ability of V_2O_5 - $xCeO_2$ /TiO₂-ZrO₂ to participate in chemical reactions in SCR. All the prepared samples were subjected to NH_3 -TPD analysis to investigate the effect of Ce doping on the surface acidity of V/Ti-Zr, and the results are shown in Fig. 6. The temperature of desorption peak can be used as a measure of the acid strength of the catalyst [39].

V/Ti exhibited relatively high desorption temperatures of 271 and 558 °C, indicating the presence of medium-to-strong and strong acid sites, respectively. In contrast, the other catalysts displayed desorption peaks at ~100 °C that can be associated with the presence of weak acid sites [40]. Evidently, the loading of V_2O_5 and CeO_2 led to a reduced desorption of acid that may be due to the reduced specific surface area of the catalysts (Table 1). Higher CeO_2 loadings resulted in the gradual rise in the concentration of the acid sites and reduction of the desorption temperature. Thus, it could be deduced that the SCR reaction mainly occurred on the weak acid sites of the V- x Ce/Ti-Zr catalysts.

Fig. 6. NH_3 -TPD patterns of the different prepared samples. (1) V/Ti; (2) V/Ti-Zr; (3) V-0.1Ce/Ti-Zr; (4) V-0.2Ce/Ti-Zr; (5) V-0.3Ce/Ti-Zr.

3.7. Effect of SO_2 and H_2O on the NO_x reduction performance

Figure 7 shows the influence of H_2O and SO_2 on the NO_x reduction performance with NH_3 . Before adding H_2O or SO_2 , the SCR reaction was stabilized for 1 h at 250 °C. The NO_x conversion rates over both V-0.2Ce/Ti-Zr and V-0.3Ce/Ti-Zr remained stable for 1 h, whereas that over V-0.1Ce/Ti-Zr decreased within 40 min of reaction. Upon addition of 200 ppm SO_2 to the feed stream, the NO_x conversion rates over V-0.1Ce/Ti-Zr and V-0.2Ce/Ti-Zr decreased by ~5% within the next 2 h of reaction (Fig. 7(a)). When the supply of SO_2 was stopped, the catalytic activity of V-0.1Ce/Ti-Zr decreased further, whereas that of V-0.2Ce/Ti-Zr and V-0.3Ce/Ti-Zr remained mostly unchanged. However, it is worth noting that the NO_x conversion rate over V-0.2Ce/Ti-Zr was the most stable throughout the entire reaction.

To further explore the poisoning mechanism of the catalysts, 10% H_2O was separately added to the feed stream. The NO_x conversion rate of all samples declined sharply regardless of the co-presence of SO_2 in the feed gas (Fig. 7(b) and (c)). When the supply of H_2O was interrupted, the activity of the

Fig. 7. Effect of (a) 200 ppm SO_2 , (b) 10% H_2O , and (c) 200 ppm SO_2 and 10% H_2O on SCR catalytic activity. (1) Ti-Zr; (2) V/Ti-Zr; (3) V-0.1Ce/Ti-Zr; (4) V-0.2Ce/Ti-Zr; (5) V-0.3Ce/Ti-Zr.

catalysts was recovered, but not fully restored. Specifically, 67% of the original activity of V-0.2Ce/Ti-Zr was restored, whereas 84% of the original activity of V-0.3Ce/Ti-Zr was restored. Furthermore, following interruption of the supply of both 200 ppm SO₂ and 10% H₂O, the catalytic performance of V-0.3Ce/Ti-Zr could be fully restored; in contrast, only 68% of the original activity of V-0.2Ce/Ti-Zr was restored. Therefore, it can be deduced that V-0.2Ce/Ti-Zr shows promising resistance to water vapor and SO₂ poisoning.

The above mentioned test indicated that SO₃ escaped upon addition of H₂O. However, if the flue gas contained both SO₂ and H₂O, ammonium sulfate and ammonium sulfite formed, which blocked the pores of the catalyst and subsequently partly damaged the pores upon interruption of the SO₂ and H₂O feed supply. The content of ceria significantly influenced the SCR activity of V-*x*Ce/Ti-Zr catalysts in the presence of SO₂ and H₂O. Further studies toward improving the resistance of catalysts to H₂O and SO₂ poisoning would be beneficial.

Additionally, the NO_x conversion at 200–450 °C over SO₂- and H₂O-poisoned catalysts was examined, as shown in Fig. 8. As observed, overall, the activity of the poisoned V-0.2Ce/Ti-Zr and V-0.3Ce/Ti-Zr catalysts increased within a temperature range of 300–450 °C. It was previously demonstrated that the formation of Ce(SO₄)₂ adversely affected the activity of catalysts in the intermediate temperature range [41]. However, among the prepared catalysts, this phenomenon was the least significant for V-0.3Ce/Ti-Zr owing to the presence of excess CeO₂. Taking into account the H₂-TPR results, it can be deduced that V₂O₅ acts as the active component after 300 °C. Relative to the surface areas of V-0.2Ce/Ti-Zr and V-0.3Ce/Ti-Zr, the surface areas of the corresponding poisoned catalysts decreased to 21.71 and 26.25 m²/g, respectively, but the pore volume of the poisoned catalysts remained mostly unchanged (0.11 mL/g).

3.8. In situ DRIFTS spectroscopy of NH₃ adsorption

Figure 9 shows in situ DRIFTS spectra of NH₃ adsorbed onto the catalysts for 1 h, followed by flushing with N₂ at 50 °C. The (strong) band at 1180 cm⁻¹ was associated with the symmetrical deformation mode of NH₃ coordinatively bound to Lewis acid sites; the intensity of the peak was weakened upon Ce doping. Literature studies confirmed that bands at 1450 and

Fig. 9. Ammonia adsorption DRIFTS spectra of the different prepared catalysts at 50 °C.

1660 cm⁻¹ correspond to the asymmetric and symmetric deformation of NH₄⁺ bound to Brönsted acid sites [7,42,43], respectively. Herein, the intensity of these bands was the highest for V-0.2Ce/Ti-Zr among those displayed by all prepared samples. There were abundant Brönsted acid sites as well as Lewis acid sites on the surface of the samples. However, xCe-3%V/Ti-Zr did not exhibit Brönsted acid sites (corresponding to peak at 1627 cm⁻¹) until the molar ratio (*x*) of Ce was 0.2 [7]. It was believed that V₂O₅ inhibited the adsorption of NH₃ on Brönsted acid sites, and the higher CeO₂ content played a greater role in promoting the increase of acid sites. A weak band at 1540 cm⁻¹ was also observed, revealing the appearance of new Lewis acid sites that implied the formation of new Ce species on the surface of V-0.2Ce/Ti-Zr and V-0.3Ce/Ti-Zr catalysts. By integrating the total area of the peaks of the three Ce-containing samples, it could be deduced that V-0.2Ce/Ti-Zr possessed the greatest amount of surface acid sites, which are well known to be important in catalyzing NO_x reduction.

To further compare the acid sites on the prepared samples (V/Ti-Zr, V-*x*Ce/Ti-Zr), the in situ NH₃-adsorbed DRIFTS spectra at different temperatures were recorded and presented in Fig. 10. As observed, the content of Lewis acid sites decreased

Fig. 8. NO_x conversion rates of SO₂- and H₂O-poisoned catalysts.

Fig. 10. In situ NH_3 adsorption DRIFTS spectra of the different prepared catalysts recorded at increasing temperatures from 50 to 400 °C at a heating rate of 10 °C/min. (a) V/Ti-Zr; (b) V-0.1Ce/Ti-Zr; (c) V-0.2Ce/Ti-Zr; (d) V-0.3Ce/Ti-Zr.

slowly and the intensity of the bands associated with adsorbed ammonia on Brönsted acid sites diminished gradually with increasing temperatures to 400 °C. These results suggest that the adsorption capacity of NH_3 on Lewis acid sites was higher than that on Brönsted acid sites. Furthermore, the intensity of the peaks reduced rapidly upon Ce doping.

In particular, V-0.3Ce/Ti-Zr displayed a new weak band at 1598 cm^{-1} above 250 °C, corresponding to adsorbed NH_3 on Lewis acid sites. NH_3 on Brönsted acid sites desorbed mostly at 150 °C. In contrast, no obvious NH_3 desorption from Lewis acid sites, as indicated by the weak band at 1180 cm^{-1} , was observed below 150 °C. This result suggested that this type of Lewis site could re-adsorb the NH_3 molecules that were desorbed from Brönsted acid sites, therefore hindering the decomposition of ammonia at Brönsted acid sites. Another weak peak at 1495 cm^{-1} appeared above 100 °C that was indicative of the presence of an amide (NH_2) species on the surface.

V/Ti-Zr displayed a weak peak at 1555 cm^{-1} above 300 °C that indicated the formation of intermediate species ($-\text{NH}_2$). Additionally, the extent of NH_3 adsorption onto Brönsted acid sites (1450 and 1670 cm^{-1}) decreased rapidly, which was indicative of the formation of new species during the decomposition process.

V-0.1Ce/Ti-Zr displayed a new weak band at 1525 cm^{-1} above 300 °C. It is known that amide species display character-

istic peaks at 1535 cm^{-1} [44] and NH_2 deformation modes are observed within 1505–1580 cm^{-1} [45]. Accordingly, the band at 1525 cm^{-1} was ascribed to NH_2 species. The results demonstrated that Brönsted acid sites played a dominant role in the SCR reaction.

Fig. 10(c) shows that the modified catalyst containing 0.2 mol CeO_2 featured more active intermediates for the NH_3 oxidation reaction that could explain the higher catalytic activity of the catalyst when compared with that of the other modified catalysts with different CeO_2 contents.

4. Conclusions

The present BET, XRD, and HRTEM results demonstrated that the high specific surface area of the amorphous Ti-Zr support decreased following impregnation with V_2O_5 and CeO_2 . The prepared catalysts displayed single-crystal electron diffraction features. H_2 -TPR analysis indicated that CeO_2 promoted the interaction of the metal oxide components that was beneficial to attaining higher catalytic activities. NH_3 -TPD analysis revealed that the addition of ZrO_2 altered desorption acid sites of NH_3 . NH_3 adsorption DRIFTS spectroscopy confirmed that CeO_2 considerably influenced the amount of Brönsted acid sites and Lewis acid sites. Brönsted acid sites played a dominant role in the SCR reaction. Furthermore, the NO_x conversion rates on

catalysts poisoned with SO₂ and H₂O were examined. It was determined that the likely formation and deposition of ammonium bisulfate or ammonium sulfate on the catalyst surface, following formation of Ce(SO₄)₂, adversely affected the NO_x conversion rate and specific surface area. However, the performance of the catalysts in the presence of SO₂ and H₂O increased with increasing CeO₂ loadings in the catalysts. In summary, among all the catalysts investigated, V-0.2Ce/Ti-Zr exhibited the best performance and featured a wider operating temperature window.

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Graphical Abstract

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Characterization and activity of V₂O₅-CeO₂/TiO₂-ZrO₂ catalysts for NH₃-selective catalytic reduction of NO_x

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With increasing CeO₂ contents, the catalytic activity, reduction ability, resistance to H₂O and SO₂, and amount of Brønsted and Lewis sites on the Ce-containing catalysts increased. CeO₂ was highly dispersed on the amorphous ZrTiO₄ support.

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V₂O₅-CeO₂/TiO₂-ZrO₂催化剂表征及NH₃还原NO_x性能

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摘要: 商业选择性催化还原(SCR)催化剂V₂O₅-WO₃(MoO₃)/TiO₂存在反应温度窗口窄(300–400 °C)和SO₃转化率高缺点, 同时占催化剂总质量80%以上的载体TiO₂比表面积小, 热稳定性差。已有研究发现TiO₂-ZrO₂固溶体具有较大的比表面积和较强的表面酸性, TiO₂与ZrO₂的摩尔比为1:1时其比表面积达到最大。CeO₂作为SCR催化剂的组成部分, 由于其优良的储氧和放氧能力受到广泛关注。研究表明, CeO₂-CuO, Ce/Ti-Si-Al和Mo₂O₃ (Co₂O₃)/Ce-Zr等催化剂具有优良的SCR脱硝活性, 同时对V₂O₅-WO₃/TiO₂催化剂进行CeO₂改性, 可提高催化剂的抗SO₂中毒能力。实际烟气组分中同时存在SO₂和H₂O, 必定会导致催化剂硫酸盐中毒, 而目前对含Ce催化剂的硫酸盐中毒情况研究较少, 因此开发新型高效脱硝催化剂十分必要。

前期我们研究了xCeO₂-3%V₂O₅/TiO₂-ZrO₂催化剂, 发现CeO₂可以显著拓宽脱硝温度窗口, 同时增强催化剂酸性位点, 但是V₂O₅含量较高时对环境及人体健康均有较大危害。本文采用共沉淀法制备摩尔比为1:1的TiO₂-ZrO₂固溶体, 用浸渍法负载不同摩尔比的CeO₂和1%的V₂O₅, 得到一系列V-xCe/Ti-Zr催化剂, 结合X射线衍射(XRD)、比表面积测试(BET)、高分辨透射电镜(HRTEM)、程序升温还原(H₂-TPR)、原位漫反射红外光谱(in situ DRIFTS)和程序升温脱附(NH₃-TPD)等手段分析催化剂的晶相、活性物质分散程度、氧化还原性质及表面酸性, 在200–450 °C范围内考察Ce掺杂催化剂选择性催化还原NO_x的脱硝活性, 并在250 °C测试催化剂在NH₃+NO+O₂+SO₂+H₂O气氛中的脱硝活性, 研究催化剂抗硫酸盐中毒能力。

研究发现, CeO₂掺杂可以拓宽脱硝反应活性窗口, V-0.2Ce/Ti-Zr (摩尔比Ce:Ti = 0.2)表现出最优的脱硝性能, 在250–350 °C范围内脱硝效率均在92%以上, 同时与前期研究结果对比发现CeO₂含量较高时会导致高温段NO_x转化率下降。XRD和HRTEM结果表明, ZrO₂的添加可以显著降低载体TiO₂的结晶度, 复合氧化物TiO₂-ZrO₂呈无定形态, CeO₂高度分散于载体之上, 并且催化剂以单晶形式存在。H₂-TPR结果表明, CeO₂能显著提高催化剂的还原能力, 主要的还原反应发生在CeO₂的α(200–430 °C)和β(430–600 °C)还原峰上, 总体而言, V-0.2Ce/Ti-Zr表现出最大的氢气消耗量, 即其还原性最强。低V₂O₅负载有利于较低温度SCR反应, V-0.3Ce/Ti-Zr的钒氧化物还原峰强度最大, 其次是V-0.2Ce/Ti-Zr。NH₃-TPD测试发现V₂O₅/TiO₂主要存在中强酸及强酸, 而V₂O₅/TiO₂-ZrO₂主要是弱酸, CeO₂负载后随着其含量提高, 弱酸强度增加。结合氨气原位漫反射红外光谱发现, CeO₂可以增加催化剂Brönsted和Lewis酸位数量, 同时出现反应中间物–NH₂, V₂O₅的负载量较高会抑制1660 cm⁻¹处Brönsted酸吸收峰的出现。BET结果发现, TiO₂-ZrO₂和V₂O₅/Ti-ZrO₂比表面积分别可达255.73和 143.77 m²/g, V₂O₅/TiO₂仅为66.1 m²/g, 表明ZrO₂的添加可以显著增大催化剂比表面积, 进而有利于SCR反应进行, 沉积的氧化物进入载体孔道导致催化剂比表面积降低。

V₂O₅-xCeO₂/TiO₂-ZrO₂表现出较强的抗SO₂中毒能力, 但是在H₂O存在条件下脱硝活性较差, 可能是生成的硫酸铵盐及亚硫酸盐阻塞催化剂孔道所致。SO₂和H₂O停止通入后, V₂O₅-0.3CeO₂/TiO₂-ZrO₂活性恢复至原有水平, V₂O₅-0.2CeO₂/TiO₂-ZrO₂恢复至最初的84%。对中毒催化剂进行不同反应温度下的活性测试, 发现V₂O₅-0.2CeO₂/TiO₂-ZrO₂在中温段反应活性显著降低, 可能是由于Ce(SO₄)₂的形成所致, 由于V₂O₅-0.3CeO₂/TiO₂-ZrO₂的Ce含量较高, 其在此温度范围内活性依旧较高。两者在高温段NO_x转化率均较高, 推测是V₂O₅开始发挥活性组分作用的缘故。

关键词: 二氧化钒; 钛-锆; 酸性位; 氮氧化物; 选择性催化还原; 中毒

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