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One-step synthesized SO_4^{2-} - TiO_2 with exposed (001) facets and its application in selective catalytic reduction of NO by NH_3

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ABSTRACT

A sample of sulfated anatase TiO_2 with high-energy (001) facets (TiO_2 -001) was prepared by a simple one-step hydrothermal route using SO_4^{2-} as a morphology-controlling agent. After doping ceria, Ce/TiO_2 -001 was used as the catalyst for selective catalytic reduction (SCR) of NO with NH_3 . Compared with $\text{Ce}/\text{P25}$ (Degussa P25 TiO_2) and $\text{Ce}/\text{P25-S}$ (sulfated P25) catalysts, Ce/TiO_2 -001 was more suitable for medium- and high-temperature SCR of NO due to the high surface area, sulfation, and the excellent properties of the active-energy (001) facets. All of these facilitated the generation of abundant acidity, chemisorbed oxygen, and activated NO_x -adsorption species, which were the important factors for the SCR reaction.

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1. Introduction

During the past several years, it has been proved that the selective catalytic reduction (SCR) process with NH_3 is one of the most prospective methods of removing NO_x in flue gases [1]. Among various transition-metal oxides (e.g., V_2O_5 , CuO , Fe_2O_3 , Cr_2O_3 , MnO_x , etc.) [2–7], titania-based catalysts have been considered the most suitable catalysts for widespread SCR application due to their thermal stability and better resistance to sulfur dioxide poisoning [8,9]. Recently, TiO_2 doped with ceria has attracted significant attention because of its excellent SCR catalytic performance and environmentally friendly properties [10–12].

At present, many researchers have focused on the anatase TiO_2 micro/nanostructures with (001) high-energy facets, and

their applications in many fields, such as catalysts, photocatalysts, catalyst supports, sensors, photoanodes, etc. [13–18]. The TiO_2 (001) surface exposed all coordinatively unsaturated atoms five-fold Ti (5c-Ti), and this particular surface structure gave rise to an abundant oxygen deficiency and favors the dissociative adsorption for water and other molecules [19,20]. Moreover, other researchers reported that the reactive oxygen atoms on the (001) facets played an important role in high photocatalytic selectivity [21]. It has been reported that TiO_2 -NS with (001) facets showed much better catalytic performance in many cases than TiO_2 -NP with (101) facets due to the more active sites and higher active energy. Liu *et al.* [22] investigated that, upon altering the ratio of (001), (101), and (010) facets, the photocatalytic reactivity would be correspondingly changed. Furthermore, Deng *et al.* [23] studied that

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manganese oxide doped on an anatase TiO_2 with (001) high-energy facets could promote the SCR process. Shi *et al.* [24] studied that octahedral vanadia species was the dominant species on TiO_2 (001) and was very active, while the tetrahedral vanadia species was prone to form on TiO_2 (101) and was inactive.

For restraining the growth of the stable (101) facets, some capping agents could be chosen to cause an exceptional stabilization of the (001) facets in anatase TiO_2 crystals, for instance, HF and SO_4^{2-} [18]. It is well known that SO_4^{2-} species was a very promising promoter of the high reactivity of the SCR reaction without by-products, especially for sulfated TiO_2 [25]. The introduction of sulfation could generate surface acidity, which leads to the enhancement of adsorption and activation of ammonia at high temperature [26]. Moreover, sulfation improves the redox properties of vanadate at the surface because of the strong electronic interaction between vanadia and sulfates on the sulfated V/ TiO_2 catalysts [27]. In addition, it was also reported that catalytic activity was significantly affected by the different sulfation preparation methods [28]. Compared with CeO_2 -S prepared by precipitation methods, the sulfated- CeO_2 prepared by a hydrothermal method with cerium(IV) sulfate as a precursor showed excellent SCR activity and high N_2 selectivity due to the intimate binding between sulfate species and Ce^{4+} [29].

In conclusion, until now, less attention has been paid to the influence of TiO_2 with high-energy (001) facets on catalytic performance, especially for the influence of sulfated TiO_2 with (001) facets. In this paper, sulfated titanium with exposed (001) facets was prepared by a simple one-step hydrothermal route using SO_4^{2-} as a morphology-controlling agent. After doping with ceria, Ce/ TiO_2 -001 was used as the catalyst for NH_3 -SCR of NO, and its catalytic performance was tested. Meanwhile P25 and P25-S (prepared by another sulfation method, i.e., precipitation) were available as a reference. Furthermore, these catalysts were characterized by using various physico-chemical techniques, such as Brunauer-Emmett-Teller (BET) methods, X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD), *in situ* diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS), etc., to discuss the relationship between the surface chemical properties and catalytic performance.

2. Experimental

2.1. Catalyst preparation

The precursors, containing TiOSO_4 (15 wt% solution in dilute sulfuric acid, Sigma Aldrich, USA) and tert-butyl alcohol (molar ratio 1:165), were placed in autoclave at 110 °C for 48 h [30]. The products were filtered and washed with distilled water and ethanol. After being dried and calcined, the required TiO_2 was prepared, and denoted TiO_2 -001.

The other nanoparticle TiO_2 supports used in the present study were commercial P25 and P25-S. To obtain the sulfated P25, the P25 powder was added to the calculated H_2SO_4 solu-

tion (0.0625 mol/L) and stirred. The obtained solids were then dried and calcined.

The introduction of ceria (Ce/Ti molar ratio 1:19) into the supports was conducted by impregnating the titanium support with the required amount of cerium nitrate solution and the mixture stirred for 6 h, and then dried and calcined to give the final metal-oxide-loaded catalysts for further analysis and examination. The catalysts were designated Ce/ TiO_2 -001, Ce/P25, and Ce/P25-S.

2.2. Catalyst characterization

The crystal phases of the samples were analyzed using an X-ray diffractometer (X'Pert3 Powder, PANalytical B.V., The Netherlands). XPS with Al K_{α} X-ray ($h\nu = 1486.6$ eV) radiation operated at 150 W (Thermo ESCALAB 250, USA) was used to investigate the surface properties. The morphology, structure, and grain size of the samples were examined by TEM (FEI F20, ThermoFisher, USA). Specific surface areas were determined by the BET methods on a nitrogen-adsorption apparatus (ASAP 2020, Micromeritics, Inc., USA). NH_3 -TPD and O_2 -TPD experiments were carried out on a custom-made thermal conductivity detector (TCD) setup using 100-mg catalysts. Prior to the experiments, catalysts were pre-treated in pure He at 400 °C for 1 h. For NH_3 -TPD experiments, catalysts were saturated with anhydrous NH_3 (4% in He) at a flow rate of 30 mL/min for approximately 30 min. For O_2 -TPD experiments, catalysts were saturated with anhydrous O_2 (4% in He) at a flow rate of 30 mL/min at 350 °C for approximately 30 min. Desorption of NH_3 or O_2 was carried out by heating the catalyst in He (50 mL/min) with a heating rate of 10 °C/min.

2.3. In situ DRIFTS experiments

In situ DRIFTS spectra were measured on a Fourier-transform infrared (FTIR) spectrometer (TENSOR 27, Bruker Corp., USA) with a mercury-cadmium-telluride (MCT) detector. Prior to each experiment, the sample was pretreated at 450 °C in a flow of He for 60 min and cooled to target temperature to obtain the background spectra. All spectra were recorded from 4000 to 600 cm^{-1} by accumulating 64 scans with a resolution of 4 cm^{-1} .

For the desorption of $\text{NO}+\text{O}_2$ as a function of temperature, the catalysts were saturated by absorbed- NO_x species under a flow of 1000 ppm $\text{NO}+3\%$ O_2 at 30 °C. The desorption process DRIFT spectra were then collected from 30 to 350 °C under a He flow. Then, *in situ* DRIFTS were recorded as a function of time at the reaction temperature of 250 °C, the catalysts were exposed to a flow of 1000 ppm $\text{NO}+3\%$ O_2 for 60 min, and the reaction process was recorded at different periods with a flow of 1000 ppm NH_3 .

2.4. SCR activity measurements

SCR activity measurements were carried out in a fixed-bed reactor at 80–550 °C containing 0.5 g catalyst with a gas hourly space velocity (GHSV) of 100 000 h^{-1} . The typical reactant gas

Fig. 1. XRD patterns of prepared catalysts.

composition was as follows: 600 ppm NO, 600 ppm NH₃, 3.5% O₂, and balance N₂. NO, NO₂, and O₂ concentrations were monitored by a flue-gas analyzer (Testo 335, Testo, Inc., USA).

3. Results and discussion

3.1. Morphology and structure investigation

Based on the XRD patterns shown in Fig. 1, it was confirmed that all of the identified peaks could be perfectly indexed to anatase TiO₂ (JCPDS Card No. 21-1272) for TiO₂-001. The three strong peaks at $2\theta = 25.3^\circ$, 37.8° , and 48.1° were attributed to anatase (101), (004), and (200) diffractions, respectively. P25 was a mixed-phased TiO₂ containing anatase and rutile phases. Few changes have been observed for the sample P25-S, except for the weaker intensity of the diffraction peaks, which indicated that sulfation had little influence on crystal-phase transformation. In addition, for TiO₂-001, the intensity of the diffraction peaks was much weaker and broader than that of P25, suggesting that the synthesized TiO₂ with exposed (001) facets had smaller crystal size. In addition, no diffraction peaks of cerium oxide were found on the catalysts Ce/TiO₂-001, Ce/P25-S, and Ce/P25, which might be due to good dispersion of cerium oxide on the supports.

From Table 1 and Fig. 2(a), it is obvious that P25 consists of mixed-phased nanoparticles with a surface area of 52.4 m²/g and an average diameter of 20 nm, matching the XRD definition. For P25-S, the average pore size and pore volume increased, and the BET surface areas decreased due to sulfation,

Table 1
Physical properties of prepared samples.

Catalyst	BET surface area (m ² /g)	Pore volume (10 ⁻² cm ³ /g)	Average pore diameter (nm)
TiO ₂ -001	107.4	13.1	4.9
Ce/TiO ₂ -001	94.2	11.9	5.1
P25	52.4	18.8	14.4
Ce/P25	49.5	21.9	17.7
P25-S	43.4	22.1	20.3
Ce/P25-S	40.5	19.3	19.1

Fig. 2. TEM and HRTEM images of P25 (a) and TiO₂-001 (b).

but the influence was slight.

Because of the difference in the preparation method, the sample TiO₂-001 exerted a significant change on the structure and BET surface areas. The low-magnification TEM (left-hand inset of Fig. 2(b)) and nitrogen adsorption-desorption experience (Fig. 3 and Table 1) demonstrates the formation of mesoporous TiO₂ single crystals with a high surface area of 107 m²/g and a uniform pore diameter of 4.9 nm. From the high-resolution TEM (HRTEM) images in Fig. 2(b), it was found that a perpendicular lattice spacing of 0.19 nm was consistent with the (200) and (020) atomic planes of the anatase TiO₂. The corresponding selected-area electron-diffraction (SAED) pattern (right-hand inset of Fig. 2(b)) further confirms that the exposed crystal facet was a (001) facet. This is because of the addition of H₂SO₄ in the precursor solutions [30].

3.2. Elemental analysis

The XPS spectra of S 2p, Ce 3d, and O 1s levels are displayed in Fig. 4. The binding energies of S 2p for the catalysts Ce/TiO₂-001 and Ce/P25-S were 168.6 and 168.2 eV, which suggested the presence of S⁶⁺ and S existing as sulfate [25]. From Table 2, it was found that the surface sulfate content for both catalysts was similar to each other.

The XPS spectra of Ce 3d of all catalysts are shown in Fig. 4(b). The peaks at 916.4, 905.0, 900.0, 896.3, 886.3, and 882.7 eV correspond to the Ce⁴⁺ species, while those at 904, 898,

Fig. 3. Nitrogen adsorption-desorption isotherms of samples.

Fig. 4. XPS spectra of catalysts. (a) S 2p; (b) Ce 3d; (c) O 1s.

885.1, and 879.1 eV correspond to the Ce^{3+} species [31,32]. The curve fittings in the XPS peaks of Ce 3d demonstrate that Ce existed as a mixture of Ce^{4+} and Ce^{3+} . Incorporating XRD investigations confirms that the cerium existed well dispersed on catalysts as an amorphous nature of CeO_2 and Ce_2O_3 for the three catalysts. For the sulfated catalysts Ce/TiO₂-001 and Ce/P25-S, the peaks at binding energies of 885.1, 898, and 904 eV increased compared with Ce/P25, which contributed to the binding energy of Ce^{3+} . Thus, it could be seen that sulfation was beneficial to the formation of Ce^{3+} . It was reported that Ce^{3+} species could lead to the increase of chemisorbed oxygen on the surface, which was very active and played an important role in the reaction [10].

The XPS spectra for O 1s show that there are three peaks for the samples, which could be attributed to O_γ type (527.0–531.5 eV, lattice oxygen), O_β type (529.0–533.0 eV, chemisorbed oxygen) oxygen, and O_α type (530.7–534.7 eV, physically absorption oxygen) on the catalyst surface [11]. As shown in Fig. 4(c) and Table 2, compared with Ce/P25, the O_α concentration of Ce/TiO₂-001 and Ce/P25-S decreased slightly, but that of O_β type increased, which indicates the increase of chemisorbed oxygen. These results are in accord with the status of Ce^{3+} in Fig. 4(b).

3.3. TPD results

In Fig. 5, the feature of NH_3 desorption of Ce/TiO₂-001 was quite different from Ce/P25 and the surface-sulfated Ce/P25-S. From 130 to 500 °C, a wide and large ammonia adsorption peak was observed along with a maximum at 300 °C, suggesting that the Ce/TiO₂-001 catalyst was composed of abundant weak, medium, and strong acid sites, especially the strong ones.

Table 2
Surface composition of catalysts.

Catalyst	at%					
	S	Ce	Ti	O_α/O	O_β/O	O_γ/O
TiO ₂ -001	2.82	—	24.75	—	—	—
Ce/TiO ₂ -001	2.18	2.70	22.71	6.9	18.5	74.6
P25	—	—	25.21	—	—	—
Ce/P25	—	3.61	22.53	13.6	16.8	69.6
P25-S	2.74	—	23.10	—	—	—
Ce/P25-S	2.04	6.02	21.19	7.4	24.14	68.52

First, for Ce/TiO₂-001, the number of total acid sites might be relative to the sulfation and the high surface area, which could carry more acid sites. Sulfation could create abundant Brönsted/Lewis acid sites and strengthen the acidity [33]. However, as we know, half-fivefold- (5c-Ti) and half-sixfold- (6c-Ti) coordinated Ti atoms were present on the (101) ideal surface, while only 5c-Ti atoms were present on the (001) surface. Therefore, the water molecules were energetically favored to be dissociated on the (001) facets compared with (101) facets [20]. Consequently, more hydroxyls were terminally bonded to adjacent Ti sites and favored the formation of acid sites, especially for the medium- and high-strength acid sites. Therefore, it could be concluded that the TiO₂ with exposed (001) facets might affect the type of acid sites for the catalyst Ce/TiO₂-001.

TPD of O_2 is a direct method of measuring the oxygen species. As we know, the peak at 200–600 °C is due to chemisorbed oxygen, which plays an important role for medium- and high-temperature SCR performance [8]. From Fig. 6, the amount of chemisorbed oxygen increased successively as follows: Ce/P25 < Ce/P25-S < Ce/TiO₂-001. The reasons are two-fold. First, the sulfation favored the generation of Ce^{3+} , which was close to the chemisorbed oxygen, already mentioned above. Second, high-energy (001) facets played an important role. The surfaces of the (001) facets were composed of a high density of under-coordinated Ti atoms and very large Ti-O-Ti bond angles, resulting in abundant oxygen deficiency. In addition,

Fig. 5. NH_3 -TPD profiles for Ce/P25, Ce/P25-S, and Ce/TiO₂-001.

Fig. 6. O_2 -TPD profiles for Ce/P25, Ce/P25-S, and Ce/TiO₂-001.

tion, the surface twofold-coordinated O (O_{2c}) atoms on (001) facets were quite different from the state of O_{2c} atoms on (101) facets and were very active [19,21].

3.4. *In situ* DRIFT

In situ DRIFTS experiments of $NO+O_2$ desorption were carried out to investigate the formation and transformation of NO_x species on the catalyst surface. As shown in Fig. 7(a), the adsorbed NO_x species were the gaseous NO_2 at 1614 cm^{-1} , the bidentate nitrates at 1581/1548 cm^{-1} , the linear nitrites at 1488 cm^{-1} , the monodentate nitrates at 1290 cm^{-1} , and the bridged nitrates at 1245 cm^{-1} over Ce/P25 catalyst at 30 °C [34–39]. With increasing temperature, the linear nitrites, monodentate nitrates, and bridged nitrates gradually decreased and vanished at 350 °C, while the gaseous NO_2 and bidentate nitrates were still stable and became the dominant species at high temperature.

In comparison with the *in situ* DRIFT spectra of Ce/P25, two obvious differences appeared in the spectra of Ce/P25-S and Ce/TiO₂-001 (Figs. 7(b) and 7(c)). (1) The main NO_x species were monodentate nitrates and monodentate nitrites on the Ce/P25-S and Ce/TiO₂-001 catalysts at 30 °C, with bands at 1528/1520 cm^{-1} [35] and 1321/1307 cm^{-1} [38]. Additionally, the bands at 1633/1650 cm^{-1} appeared at 30 °C, but disappeared at temperatures higher than 100 °C. Yang *et al.* [40] proposed that this band was to the absorbed H_2O . (2) The

bands of monodentate nitrates/nitrites became weaker with increasing temperature and disappeared at temperatures higher than 150 °C. Meanwhile, for the Ce/P25-S catalyst, the gaseous NO_2 (1603 cm^{-1}) and bidentate nitrates (1573 cm^{-1}) turned into the dominant species, and could be observed even at 350 °C. Moreover, the bands at 1398 and 1380 cm^{-1} assigned to ionic nitrates [36] were also detected at 350 °C over Ce/P25-S. In case of Ce/TiO₂-001 catalyst, the gaseous NO_2 (1610 cm^{-1}) and bidentate nitrates (1575 cm^{-1}) appeared at higher temperature, but only gaseous NO_2 was still obvious at 350 °C. In brief, the evident differences might be related to the acidic properties and the high-energy (001) facet on the catalyst surface.

In order to identify the reactive species in the SCR reactions, the *in situ* DRIFTS spectra of NH_3 reacted with the pre-absorbed $NO+O_2$ species at 250 °C as a function of time were studied. As illustrated in Fig. 8(a), the bands at 1602 and 1570/1548 cm^{-1} attributed to the gaseous NO_2 and bidentate nitrates hardly changed with the introduction of NH_3 in the first 5 min. Afterwards, the band at 1570 cm^{-1} shifted to 1558 cm^{-1} in 10 min. Simultaneously, the bands at 3380/3267/1174 cm^{-1} started to be observed, which were attributed to the accumulation of NH_3 absorbed on the Lewis acid sites [41,42]. However, the intensity of bands ranging from 1610 to 1500 cm^{-1} remained and maintained stability longer. Zhan *et al.* [43] proposed that the bands at 1550 cm^{-1} may be related to the intermediate of oxidation of ammonia. Then, it could be assumed that the gaseous NO_2 and bidentate nitrates were inactive on the Ce/P25 catalyst and not or partially reactive to NH_3 . They might coexist with the intermediate of oxidation of ammonia.

In the case of Ce/P25-S (Fig. 8(b)), the band at 1604 cm^{-1} ascribed to the gaseous NO_2 disappeared in 5 min. In addition, the band ascribed to bidentate nitrates (1573 cm^{-1}) decreased with increasing exposure duration, and then was replaced by the band at 1554 cm^{-1} originating from the intermediate of oxidation of ammonia.

Fig 8(c), in contrast, indicates that the gaseous NO_2 (1612 cm^{-1}) disappeared completely after introducing NH_3 for only 1 min. Then, the bands at 3358/3263/1590/1320 and 1678/1445 cm^{-1} appeared, which were attributed to the accumulation of NH_3 absorbed on the Lewis acid sites and Brønsted acid sites, respectively [41,44–46].

The above results strongly demonstrate that the activity of the same NO_x -adsorption species on different catalysts varies

Fig. 7. *In situ* DRIFTS spectra of $NO+O_2$ desorption on Ce/P25 (a), Ce/P25-S (b), and Ce/TiO₂-001 (c) catalysts.

Fig. 8. *In situ* DRIFTS spectra of transient reactions at 250 °C between NH_3 and pre-adsorbed $\text{NO}+\text{O}_2$ species over Ce/P25 (a), Ce/P25-S (b), and Ce/TiO₂-001 (c) catalysts recorded as a function of time.

widely. The activity of gaseous NO_2 and bidentate nitrates over the three catalysts were as follows: Ce/TiO₂-001 > Ce/P25-S > Ce/P25. The gaseous NO_2 was consumed faster over the Ce/TiO₂-001 catalyst than over the other two catalysts, which could be due to the special structure of the high-energy (001) facet of TiO₂ and the high concentration of surface chemically absorbed oxygen.

3.5. SCR activity

NO conversions for the prepared catalysts are shown in Fig. 9. It was observed that the catalytic activity of pure P25 was quite low, and the maximum value of NO conversion was only 38% at 525 °C. After sulfation, the NO conversion reached 85% at 450 °C for the sample P25-S, due to the abundant acid sites, while a better activity was obtained for TiO₂-001 in the high-temperature range, the NO conversion of which reached up to 99% at 480 °C and was maintained above 85% in the range 420–530 °C.

When introducing ceria, it was clear that a high NO conversion rate was obtained for Ce/TiO₂-001, whose maximum value was up to 99% at 290 °C and remained in the temperature range 290–480 °C. It was found that the SCR activity decreased in the following sequence: Ce/TiO₂-001 > Ce/P25-S > Ce/P25.

Sulfation created abundant acid sites, and the influence of acidity on SCR catalytic performance at high temperature,

Fig. 9. NO conversion of catalysts at different temperatures.

which played an important role in the adsorption and activation of ammonia at high temperature, was discussed in previous studies [26]. In this paper, according to the NO conversion for the P25-S and TiO₂-001 catalysts detailed above, it was further proved that sulfation was directly responsible for the SCR reaction at high temperature.

The high surface area was not only beneficial to the good dispersion of sulfate content and ceria, but could also carry more of these active components, which are crucial for SCR performance. Ceria doped on titania provides redox active sites for oxygen circulation and adsorption/activation of NO [10,26]. Therefore, it was easy to understand the excellent performance for the catalyst Ce/TiO₂-001 with a high surface area 94.2 m²/g, approximately twice as much as that of Ce/P25 and Ce/P25-S.

It was obvious that the (001) facets were also responsible for TiO₂-001 catalyst activity, except for the acidity and high surface area, which affected the formation of the medium- and high-strength acid sites, active chemisorbed oxygen, and activated NO_x -adsorption species.

In short, the catalytic performance for SCR of NO on the catalyst Ce/TiO₂-001 was obviously superior to Ce/P25 and Ce/P25-S because of the high surface area, sulfation, and excellent properties of active-energy (001) facets.

4. Conclusions

For a series of samples, NO reduction activity followed the trend Ce/TiO₂-001 > Ce/P25-S > Ce/P25. The use of Ce/TiO₂-001 revealed an excellent catalytic reaction for the SCR of NO by NH_3 at medium and high temperature, which was discussed from three main aspects. First, there was no doubt that high surface area was an important factor influencing its catalytic performance, which facilitated the dispersion and amount of the sulfate SO_4^{2-} and active-site ceria. Second, sulfation was an important factor that provided abundant acid sites for the good SCR reaction at high temperature and modulated the valence state of ceria. Third, the superior properties of high-energy (001) facets should not be ignored because of the specific surface reconstruction and abundant oxygen deficiency.

References

- [1] S. M. Lee, S. S. Kim, S. C. Hong, *Chem. Eng. Sci.*, **2012**, 79, 177–185.

Graphical Abstract

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One-step synthesized SO_4^{2-} - TiO_2 with exposed (001) facets and its application in selective catalytic reduction of NO by NH_3

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One-step synthesis of SO_4^{2-} - TiO_2 with exposed (001) facet promoted the formation of abundant acid sites, high concentration of chemically absorbed oxygen, and activated NO_x -absorption species, which were responsible for the SCR reaction.

- [2] O. Kroecker, M. Elsener, *Appl. Catal. B*, **2008**, 77, 215–227.
- [3] H. Z. Chang, J. H. Li, X. Y. Chen, L. Ma, S. J. Yang, J. W. Schwank, J. M. Hao, *Catal. Commun.*, **2012**, 27, 54–57.
- [4] J. Ochonska, D. McClymont, P. J. Jodlowski, A. Knapik, B. Gil, W. Makowski, W. Lasocha, A. Kolodziej, S. T. Kolaczowski, J. Lojewska, *Catal. Today*, **2012**, 191, 6–11.
- [5] L. K. Boudali, A. Ghorbel, P. Grange, *CR. Chim.*, **2009**, 12, 779–786.
- [6] G. Ramis, M. A. Larrubia, *J. Mol. Catal. A*, **2004**, 215, 161–167.
- [7] F. Ayari, M. Mhamdi, G. Delahay, A. Ghorbel, *J. Porous. Mater.*, **2010**, 17, 265–274.
- [8] Z. Y. An, Y. Q. Zhuo, C. Xu, C. H. Chen, *Chin. J. Catal.*, **2014**, 35, 120–126.
- [9] S. L. Zhang, Q. Zhong, *J. Mol. Catal. A*, **2013**, 373, 108–113.
- [10] S. M. Lee, H. H. Lee, S. C. Hong, *Appl. Catal. A*, **2014**, 470, 189–198.
- [11] T. T. Gu, Y. Liu, X. L. Weng, H. Q. Wang, Z. B. Wu, *Catal. Commun.*, **2010**, 12, 310–313.
- [12] H. Q. Wang, X. B. Chen, X. L. Weng, Y. Liu, S. Gao, Z. B. Wu, *Catal. Commun.*, **2011**, 12, 1042–1045.
- [13] H. M. Zhang, Y. Wang, P. Liu, Y. H. Han, X. D. Yao, J. Zou, H. M. Cheng, H. J. Zhao, *ACS Appl. Mater. Interfaces*, **2011**, 3, 2472–2478.
- [14] S. W. Liu, J. G. Yu, M. Jaroniec, *Chem. Mater.*, **2011**, 23, 4085–4093.
- [15] X. H. Yang, Z. Li, C. H. Sun, H. G. Yang, C. Z. Li, *Chem. Mater.*, **2011**, 23, 3486–3494.
- [16] J. S. Chen, Y. L. Tan, C. M. Li, Y. L. Cheah, D. Luan, S. Madhavi, F. Y. C. Boey, L. A. Archer, X. W. Lou, *J. Am. Chem. Soc.*, **2010**, 132, 6124–6130.
- [17] J. G. Yu, J. J. Fan, K. L. Lv, *Nanoscale*, **2010**, 2, 2144–2149.
- [18] H. G. Yang, C. H. Sun, S. Z. Qiao, J. Zou, G. Liu, S. C. Smith, H. M. Cheng, G. Q. Lu, *Nature*, **2008**, 453, 638–642.
- [19] X. Q. Gong, A. Selloni, *J. Phys. Chem. B*, **2005**, 109, 19560–19562.
- [20] A. Vittadini, A. Selloni, F. P. Rotzinger, M. Gratzel, *Phys. Rev. Lett.*, **1998**, 81, 2954–2957.
- [21] J. Zhang, W. K. Chen, J. H. Xi, Z. G. Ji, *Mater. Lett.*, **2012**, 79, 259–262.
- [22] G. Liu, J. C. Yu, G. Q. Lu, H. M. Cheng, *Chem. Commun.*, **2011**, 47, 6763–6783.
- [23] S. C. Deng, T. T. Meng, B. L. Xu, F. Gao, Y. H. Ding, L. Yu, Y. N. Fan, *ACS Catal.*, **2016**, 6, 5807–5815.
- [24] Q. Q. Shi, Y. Li, Y. Zhou, S. Miao, N. Ta, E. S. Zhan, J. Y. Liu, W. J. Shen, *J. Mater. Chem. A*, **2015**, 3, 14409–14415.
- [25] L. Baraket, A. Ghorbel, P. Grange, *Appl. Catal. B*, **2007**, 72, 37–43.
- [26] S. M. Jung, P. Grange, *Catal. Today*, **2000**, 59, 305–312.
- [27] H. Y. Zhao, S. Bennici, J. Y. Shen, A. Auroux, *J. Catal.*, **2010**, 272, 176–189.
- [28] H. Q. Guo, C. B. Chen, Y. Xiao, J. G. Wang, Z. H. Fan, D. B. Li, Y. H. Sun, *Fuel Process. Technol.*, **2013**, 106, 77–83.
- [29] H. Z. Chang, L. Ma, S. J. Yang, J. H. Li, L. Chen, W. Wang, J. M. Hao, *J. Hazard. Mater.*, **2013**, 262, 782–788.
- [30] Z. F. Bian, J. Zhu, J. Wen, F. L. Cao, Y. N. Huo, X. F. Qian, Y. Cao, M. Q. Shen, H. X. Li, Y. F. Lu, *Angew. Chem. Int. Ed.*, **2011**, 50, 1105–1108.
- [31] H. He, H. X. Dai, C. T. Au, *Catal. Today*, **2004**, 90, 245–254.
- [32] S. Cao, H. Q. Wang, F. X. Yu, M. P. Shi, S. Chen, X. L. Weng, Y. Liu, Z. B. Wu, *J. Colloid. Interf. Sci.*, **2016**, 463, 233–241.
- [33] S. Gao, P. L. Wang, X. B. Chen, H. Q. Wang, Z. B. Wu, Y. Liu, X. L. Weng, *Catal. Commun.*, **2014**, 43, 223–226.
- [34] W. S. Hu, Y. H. Zhang, S. J. Liu, C. H. Zheng, X. Gao, I. Nova, E. Tronconi, *Appl. Catal. B*, **2017**, 206, 449–460.
- [35] L. Zhang, L. Y. Shi, L. Huang, J. P. Zhang, R. H. Gao, D. S. Zhang, *ACS Catal.*, **2014**, 4, 1753–1763.
- [36] B. Azambre, I. Atribak, A. Bueno-López, A. García-García, *J. Phys. Chem. C*, **2010**, 114, 13300–13312.
- [37] M. A. Larrubia, G. Ramis, G. Busca, *Appl. Catal. B*, **2001**, 30, 101–110.
- [38] L. Huang, K. W. Zha, S. Namuangruk, A. Junkaew, X. Zhao, H. R. Li, L. Y. Shi, D. S. Zhang, *Catal. Sci. Technol.*, **2016**, 6, 8516–8524.
- [39] G. Gao, J. W. Shi, C. Liu, C. Gao, Z. Y. Fan, C. M. Niu, *Appl. Surf. Sci.*, **2017**, 411, 338–346.
- [40] S. J. Yang, Y. W. Fu, Y. Liao, S. C. Xiong, Z. Qu, N. Q. Yan, J. H. Li, *Catal.*

- Sci. Technol.*, **2014**, 4, 224–232.
- [41] Z. H. Lian, F. D. Liu, H. He, X. Y. Shi, J. S. Mo, Z. B. Wu, *Chem. Eng. J.*, **2014**, 250, 390–398.
- [42] L. Chen, J. H. Li, M. F. Ge, *Environ. Sci. Technol.*, **2010**, 44, 9590–9596.
- [43] S. H. Zhan, M. Y. Qiu, S. S. Yang, D. D. Zhu, H. B. Yu, Y. Li, *J. Mater. Chem. A*, **2014**, 2, 20486–20493.
- [44] C. Gao, J. W. Shi, Z. Y. Fan, Y. K. Yu, J. S. Chen, Z. H. Li, C. M. Niu, *Fuel Process. Technol.*, **2017**, 167, 322–333.
- [45] D. Wang, Y. Peng, S. C. Xiong, B. Li, L. N. Gan, C. M. Lu, J. J. Chen, Y. L. Ma, J. H. Li, *Appl. Catal. B*, **2018**, 221, 556–564.
- [46] X. X. Wang, Y. Shi, S. J. Li, W. Li, *Appl. Catal. B*, **2018**, 220, 234–250.

一步水热法合成具有 (001) 高能晶面的 SO_4^{2-} - TiO_2 及其 NH_3 -SCR 脱硝性能

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摘要: 氮氧化物 (NO_x) 是当今大气环境中的主要污染物之一, 氨法选择性催化脱硝技术 (NH_3 -SCR) 是最有前景的烟气脱硝技术之一. 在众多的 NH_3 -SCR 催化剂中, 钛基催化剂由于其较好的热稳定性、抗硫性和环境友好性成为近年来研究的热点.

本文以 SO_4^{2-} 离子作为晶面导向剂, 采用一步水热法合成了具有 (001) 高能晶面的 SO_4^{2-} - TiO_2 , 负载氧化铈后用于 SCR 反应, 并以 Ce/P25 和 Ce/P25-S (浸渍法硫酸化) 作为参照对比. 研究发现, Ce/ TiO_2 -001 更适合于中、高温 NH_3 -SCR 反应, 在 290 °C 时 NO 转化率已达 99%, 并且在 290–480 °C 范围内均保持 99% 的脱硝效率.

利用 X 射线衍射、 N_2 吸附脱附、透射电子显微镜、X 射线光电子能谱 (XPS)、 NH_3/O_2 程序升温脱附 (TPD)、傅里叶原位红外光谱等技术研究了上述催化剂的表面物化性质与脱硝性能的关系. 相比于 Ce/P25 和 Ce/P25-S, Ce/ TiO_2 -001 具有更高的比表面积 (107 m^2/g), 形成了介孔 TiO_2 单晶, 且晶粒尺寸更小. XPS 和 NH_3 -TPD 结果表明, Ce/ TiO_2 -001 表面具有丰富的酸性位. 硫酸化可以增加催化剂表面的 Brönsted/Lewis 酸性位; 同时, (001) 高能晶面有利于水分子的解离, 从而促进酸性位的产生. O_2 -TPD 表明, Ce/ TiO_2 -001 催化剂表面存在大量化学吸附氧, 这与其一步合成中的硫酸化和 (001) 高能晶面密切相关, 而化学吸附氧在中高温 SCR 反应中起着重要的作用.

通过原位红外分析可得, 不同催化剂表面所形成的 NO_x 吸附物种有所差异, 在 30 °C 时, Ce/P25 的 NO_x 吸附物种比较丰富, 存在气相 NO_2 、双齿硝酸盐、线性硝酸盐、单齿硝酸盐和桥式硝酸盐, 而 Ce/P25-S 和 Ce/ TiO_2 -001 上的 NO_x 吸附物种则以单齿硝酸盐/亚硝酸盐为主. 随着温度的升高, 以上催化剂表面的 NO_x 吸附物种逐渐变为以气相 NO_2 和双齿硝酸盐为主. 但同种 NO_x 吸附物种 (气相 NO_2 、双齿硝酸盐) 在不同催化剂上的反应活性也有所不同, 在 250 °C 时, 其顺序为: Ce/ TiO_2 -001 > Ce/P25-S > Ce/P25, 与脱硝性能相符. 由此可推测, 催化剂表面硫酸化和 (001) 高能晶面的存在有利于提高 NO_x 中间产物的反应活性, 增加反应速率, 从而提高脱硝性能.

综上所述, 硫酸化、高比表面积和 (001) 高能晶面是 Ce/ TiO_2 -001 具有很好脱硝活性的重要原因. 硫酸化可以提供丰富的酸性位, 增强氨的吸附性能; 高比表面积不仅可以负载更多的活性组分, 而且有利于活性组分的均匀分散, 对降低活性中心的尺寸、防止活性组分烧结团聚有积极作用. 而 (001) 高能晶面则可以促进中、强酸和化学吸附氧的形成, 活化 NO_x 吸附物种, 从而提高 SCR 催化活性.

关键词: 锐钛矿 TiO_2 ; 硫酸化; (001) 晶面; 铈; 选择性催化还原

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