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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 Ce/P25 (Degussa P25 TiO_2) and Ce/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.

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 solution (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 NO+O_2 as a function of temperature, the catalysts were saturated by absorbed-NO_x species under a flow of 1000 ppm 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 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