The synthesis of titanium dioxide nanoparticles from titanium slag and its use for low temperature SCR catalyst

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Abstract. The titanium dioxide nanoparticles with high purity and specific surface area were synthesized through an alkali-solution and acid-isolation method with titanium slag as raw material. As a catalyst support of V2O5-WO3-MoO3/TiO2 selective catalytic reduction catalyst, the high specific surface area TiO2 nanoparticles can improve the low temperature activity of the catalyst and enhance its resistance to sulfur poisoning.

1. Introduction
As a non-toxic and environmentally benigh inorganic chemicals, titanium dioxide (TiO2) has been widely used as white pigment, paints, coating, ointments, toothpaste, solar cells, self-cleaning, chemical sensors[1-9] etc. Titanium dioxide has three different crystallographic forms: brookite, anatase, and rutile. Rutile is the only stable phase, whereas anatase and brookite are both metastable concern at all temperatures. Both anatase and rutile forms have good pigmentary properties, yet rutile is more thermally stable than anatase.

With the advent of nanotechnology, nanostructured titanium dioxide (spheroidal nanocrystallite, nanoparticles, nanorods, nanowires, nanotubes, nanosheets and nanofibers) has found a great deal of applications, especially in photocatalysis and photovoltaics [10-12]. Nanosized titanium dioxide in the phase of anatase possessed higher photocatalytic performance compared to other phases [11, 13-14]. The high photocatalytic activity can be obtained using the photocatalyst with high surface area per mass [15]. Various synthesis methods, including precipitation, micro emulsion, sol–gel, as well as physical or chemical vapor deposition(CVD) [16-18] have been reported, however, these routes usually involve complicated process, expensive alcoxide-preursors and precise equipment. The complicated preparation process and expensive raw material have astricted the application of nanosized titanium dioxide.

The introduction of selective catalytic reduction (SCR) in commercial denitration in the early 1960s was one of the most significant advances in the history of environmental protection. Titanium dioxide (anatase phase) can serve as an ideal support for SCR catalyst. SCR catalyst with ammonia or urea was regarded as one of the most efficient and developed technologies to reduce the NOx emissions from coal-fired power plants. Commercial SCR catalyst, usually containing 0.5 wt.%–1.5 wt.% V2O5, 5 wt.%–10 wt.% WO3 and TiO2 as carrier [19-20]. V2O5 is considered as the main active component providing acid sites to adsorb and activate NH3. WO3 acts as an important promoter which favors the spreading of vanadia on the catalyst surface and stabilizes the anatase TiO2 phase transition into rutile.
Furthermore, WO₃ increases the surface acidity of catalyst, and improves the poison resistance of catalyst to alkali metals [21].

However, the reaction temperature range of commercial V₂O₅-WO₃/TiO₂ SCR catalyst is usually at 573–693 K [22]. Meanwhile, the catalyst bed must be located upstream of the desulfurizing tower and the particulate control device to avoid flue gas reheating and dust depositing [23]. However, the temperature of the flue gas discharged from the boiler is reduced to 200 °C, since the flue gas cools down when it passes through the boiler economizer and the air preheater. Therefore, it is difficult for the tail end configurations to apply SCR De-NOₓ technologies developed under middle to high temperature conditions in practical situations. Moreover, in coking, refining, glass and other industries, the temperature of flue gas is lower than the commercial V₂O₅-WO₃/TiO₂ SCR catalyst temperature range. Therefore, it is an urgent requirement to develop SCR catalyst that could work effectively in the medium and low temperature range (453-573 K). As a catalyst support of V₂O₅-WO₃/TiO₂ SCR catalyst, nanosized titanium dioxide possessed a higher specific surface area which provided to the high dispersion of vanadium nanoparticles over the TiO₂ support. The highly dispersed vanadia on the support can accelerate the phase transformation by decrease the activation temperatures [24-26]. Therefore, it is expected to resolve the conundrum of low catalytic activity and easily causes SO₂ poisoning at low concentrations using nanosized titanium dioxide as SCR catalyst support.

In the present work, we proposed a process which used industrial slag as raw material to manufacture nanoscale titanium dioxide. We investigated the effect of calcination temperature, NaOH–titanium slag mass ratio and sulfuric acid concentration on the physical and chemical properties of the synthesized titanium dioxide nanoparticles. Meanwhile, we prepared honeycomb SCR denitration catalyst (V₂O₅-WO₃-MoO₃/TiO₂) using the titanium dioxide nanoparticles as support to study its performance on catalyst performance.

2. Experimental

2.1. The synthesis of TiO₂ nanoparticles

The synthesis experiments were utilized conventional materials, such as titanium slags, sodium hydroxide, and sulfuric acid. Titanium slags (Panzhihua Steel Group Company) and sodium hydroxide were mixed in certain proportion and calcination at the temperatures between 400 °C and 600 °C for 6 hours. The calcined mixtures washed with deionized water and filtered until the washings close to neutral. The filter residue was dried at the temperatures of 90 °C for 12 hours and acid hydrolysis by sulfuric acid solution. The component of titanium, iron, manganese, magnesium, aluminum and calcium in filter residue could be converted into soluble metatitanate by acid hydrolysis reaction. In our work, 100g filter residue was mixed with 650 ml of 35 wt. % H₂SO₄ solution refluxed at 108 °C (the boiling point) for 4 hours to perform acid hydrolysis. This acid solution was added iron powder to deduct the Fe³⁺ to Fe²⁺, and then sodium hydroxide was added until the pH value approaching to 2.5. The H₂TiO₃ product was precipitated, filtered, and washed with deionized water. The H₂TiO₃ precipitate was dried at 80 °C for 12 hours and calcination at the temperatures of 500 °C for 4 hours to synthesize TiO₂ nanoparticles.

2.2. SCR catalysts preparation

The synthesized anatase TiO₂ nanoparticles were used as the V₂O₅-WO₃-MoO₃/TiO₂ SCR catalyst support and all other reagents in this part were of analytical grade. The V₂O₅-WO₃-MoO₃/TiO₂ SCR catalysts were prepared by wet impregnation of anatase TiO₂ in a vanadium solution. Firstly, a certain amount of oxalic acid was dissolved in deionized water under stirring at 55°C and then a certain amount of ammonium metavanadate (NH₄VO₃), ammonium molybdate ((NH₄)6Mo7O24) and ammonium tungstate ((NH₄)10W12O41.xH₂O) were dissolved in the oxalic acid solution. After ammonium metavanadate, ammonium molybdate and ammonium tungstate was completely dissolved, titanium dioxide nanoparticles was then added, which was impregnated at 85°C for 4 hours and dried later at
110°C for 8 hours. After grinding, the catalyst sample was calcined at 450°C for 4 hours. The nominal mass ratio of V2O5:WO3:MoO3:TiO2 in the catalyst was 1.5:4.5:4:90.

The catalysts powder blend with adhesive (polyethylene oxide), extruding-aid additive (glycerol), pore-enlarging additive (carboxymethyl cellulose), reinforcing agent (fiberglass), lactic acid, NH3.H2O and water to prepared honeycomb SCR catalysts by extrusion technology. After extrusion, the SCR catalysts were dried in humidity controlled chamber for days in order to minimize the formation of cracks and finally calcined at a procedure temperatures for days. The size of the channels in the honeycomb SCR catalyst was 4×4 mm and the thickness of the catalyst layer was 1 mm. The honeycomb SCR catalysts with geometry of cylinder (41.7mm× 39.7mm× 39.7mm) were used for denitration experiments.

2.3. SCR catalysts performance tests

The catalytic tests were carried out in a fixed-bed tubular reactor operating at atmospheric pressure of 250 °C, which is the usual operational pressure and temperature of lower temperature denitration in industry. The reactor tube was located into a tube furnace. The gas flow was controlled by mass flow meters. The reaction temperature was measured by a type K thermocouple inserted into the catalyst bed. The gas mixture containing 0.06% NO, 0.06% NH3, 0.06%SO2, 10% H2O and 5% O2 in N2 was passed through 40.63 g (~51.62ml) catalyst at a total flow rate of 4300 ml.min⁻¹, which corresponded to a gas hourly space velocity (GHSV) of 5000 h⁻¹. The inlet and outlet concentrations of NO, N2O and NO2 were monitored by Wuhan SIFANG Infrared line monitor. The conversion of NOx was obtained by following equations:

\[ \text{NOx conversion} = \frac{[NO_x]_{\text{inlet}} - [NO_x]_{\text{outlet}}}{[NO_x]_{\text{inlet}}} \times 100\% \]

[NOx] means the gross concentration of NO, NO2 and 1/2 N2O.

As the SCR catalyst ages in the flue gas which contains ash, SOx, arsenides and alkali metals, it loses activity and selectivity. SO2 has severely negative effects on vanadia-based SCR catalyst, especially at low temperature, for ammonium sulfates are easily formed by SO2 and NH3 and deposited at the surface of catalyst. The deposition of ammonium sulfates on catalyst could lead to pore plugging and blockage of the active sites [27-29]. The deactivated catalysts were removed ammonium sulfate using heat treatment at 400°C for 6 hours. The catalytic activity of deactivated SCR catalyst can be partially restored after the heat treatment. The catalyst repeats several times of deactivation and regeneration, and tests its performance in denitration.

2.4. Characterization of titanium slags, TiO2 nanoparticles and SCR catalysts

The crystalline phase of titanium slags were characterized by powder X-ray diffraction (XRD) and X-ray fluorescence spectroscopy (XRF) system was used for chemical composition analysis. The microscopic features of the TiO2 nanoparticles were observed in a transmission electron microscope (TEM). The structure of the TiO2 nanoparticles and SCR catalysts were determined by X-ray diffraction (XRD).

The BET specific surface area of the as-prepared nanoparticles was determined from nitrogen adsorption equilibrium isotherms at liquid nitrogen temperature (77 K) using an automated gas sorption system (Quantachrome NovaWin) operating in continuous mode. Prior to the analysis, 0.015-0.020 g of TiO2 was evacuated under helium atmosphere for 2 h at 200°C in the degassing port of the instrument. Specific surface area (SSA) was calculated at 77 K using a six-point N2 adsorption isotherm recorded in a relative partial pressure (p/p0) range of 0.05–0.99, and by taking 0.162 nm² as the molecular area of the nitrogen molecule. Pore volume was calculated at the relative pressure of about 0.99 using a single-point adsorption value. The specific desorption pore volume was assessed by the Barrett–Joyner–Halenda (BJH) method.
3. Results and discussion

3.1. Preparations of TiO<sub>2</sub> nanoparticles

3.1.1. Effects of decomposition temperature and sodium hydroxide-to-titanium slag mass ratio. The detailed chemical composition of titanium slag was examined by X-Ray Fluorescence and the analytic results are listed in Table 1.

| Composition   | CaO | MgO | Al<sub>2</sub>O<sub>3</sub> | Fe<sub>2</sub>O<sub>3</sub> |
|---------------|-----|-----|--------------------------|--------------------------|
| Ratio (mass.%)| 1.51| 6.34| 4.04                     | 7.82                     |

Table 1: Chemical compositions of the titanium slag (mass.%)

The X-ray diffraction (XRD) analysis of the titanium slag (Figure 1) indicates that the main crystalline phase is Fe<sub>2</sub>TiO<sub>5</sub>, TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, Mn<sub>2</sub>O<sub>3</sub> and MgTi<sub>2</sub>O<sub>5</sub>. The mixture of titanium slags and sodium hydroxide could convert into sodium titanate (Na<sub>2</sub>TiO<sub>3</sub>) through calcination [30-31]. Sodium titanate could be dissolved in hydrochloric acid or sulfuric acid solution. In this work, we choose the sulfuric acid as solvent to decompose titanium slag. By calcination, Al<sup>3+</sup> and Si<sup>4+</sup> reacted with NaOH to form soluble sodium metasilicate (Na<sub>2</sub>SiO<sub>3</sub>) and sodium aluminate (NaAlO<sub>2</sub>) which dissolved in the washing liquid during the washing process. Subsequently, the Ca<sup>2+</sup>, Mg<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Mn<sup>2+</sup>, Zr<sup>4+</sup> can be easily dissolved in hot sulfuric acid solution.

![Fig. 1 XRD pattern of titanium slag](image)

The effect of sodium hydroxide-to-titanium slag mass ratio on the extraction of titanium slags was investigated at various temperatures with reaction time as shown in Fig. 2. The results in Fig. 2 indicate that the titanium extraction ratio increases with the increase of reaction temperature, and simultaneously improved with the increase of sodium hydroxide-to-titanium slag mass ratio, while little increase is appeared between the ratio of 1.6:1 and 1.8:1. The ratio of 1.8:1 and the temperature of 600℃ is therefore recommended, which the titanium extraction ratio of 97.9% could be achieved.
3.1.2. Effect of sulfuric acid concentration. After acid hydrolysis, the titanium should be separate from the solution. The precipitation of titanium hydroxide, iron hydroxide, manganese hydroxide, magnesium hydroxide, aluminum hydroxide and calcium hydroxide began to emerge of the pH were shown in table 2[32]. Adding iron powder into the solution, the Fe$^{3+}$ is reduced to Fe$^{2+}$, which avoids the adverse impact of Fe$^{3+}$ in the process of extraction titanium. Using NaOH to adjust the pH of the solution to 2.5-3.0, which made of titanium in the form of H$_2$TiO$_3$ precipitation, while the rest of the metals in the form of ions in solution. The H$_2$TiO$_3$ product was filtered and washed with deionized water, dried at 80 °C for 12 h and calcination at the temperatures of 500°C for 4 hours to synthesize TiO$_2$ nanoparticles.

The concentration of H$_2$SO$_4$ solution influences the yield and quality of the product directly. When the mass ration of H$_2$SO$_4$ was lower than 28%, filter residue was could not dissolve completely and yellow colors of the products will be significantly. When the concentration of H$_2$SO$_4$ solution was less than 24 wt. %, no reaction with sulfuric acid happened.

| hydroxide      | The pH value of the precipitation merge |
|----------------|----------------------------------------|
| Ti(OH)$_3$     | 2.5–3                                  |
| Ti(OH)$_4$     | 0.47–1                                 |
| Cr(OH)$_3$     | 4.5–5.6                                |
| Ce(OH)$_4$     | 0.8–1.2                                |
| Fe(OH)$_2$     | 4.5–7                                  |
| Fe(OH)$_3$     | 2–3                                    |
| Mn(OH)$_2$     | 8.6–10.8                               |
| Co(OH)$_2$     | 7.2–8.7                                |
3.2. The characterizations of titanium dioxide nanoparticles and SCR catalysts

![XRD pattern of TiO2 and SCR catalyst](image)

The crystalline XRD pattern of titanium dioxide nanoparticles matches well with that of the anatase TiO$_2$ (JCPDS NO.89-4921), while no signature diffraction peaks from rutile TiO$_2$ (JCPDS NO.21-1276) (Fig.3a). The crystallite size of the prepared TiO$_2$ nanoparticles estimated by Scherrer’s equation was 6.3 nm. This result is consistent with the TEM (Fig.4). The XRD patterns of the SCR catalyst exhibit only the characteristic peaks of anatase titanium dioxide (JCPDS NO.89-4921) (Fig.3b). The absence of diffraction peaks of WO$_3$ (JCPDS NO.87-2385), MoO$_3$ (JCPDS NO. 76-1003) and V$_2$O$_5$ (JCPDS NO.89-0612) attribute to the formation of uniformly spread oxotungsten, oxomolybdenum and amorphous state of vanadia.

The Brunauer–Emmett–Teller (BET) surface areas of the prepared TiO$_2$ nanoparticles were determined by the nitrogen sorption isotherms to be 212 m$^2$/g.

![TEM images of TiO2 nanoparticles](image)

3.3. Performance of the synthesized TiO$_2$ nanoparticles as the support of SCR catalyst: Removal of NOx

Catalytic activity tests were performed in a steel tube reactor of 43 mm internal diameter. NO$_x$, O$_2$ and SO$_2$ concentration were simultaneously measured by a Wuhan SIFANG Infrared line monitor. At steady state, a gas N$_2$ mixture containing 600 ppm NO, 600 ppm NH$_3$, 5% O$_2$, 600 ppm SO$_2$ and 10% H$_2$O was introduced into the reactor. The water vapor was adding by an injection pump and an evaporator. In all the tests, the total flow rate was fixed at 4300 ml.min$^{-1}$, which corresponding to a gas hourly space velocity (GHSV) of 5000 h$^{-1}$. 
All catalysts activity tests were carried out at the temperature of 250°C. In order to avoid the impact of gas adsorption on the catalyst samples, we recorded the test data after the reactions had been kept in stable states for 2 h. Further, prior to the activity tests, the catalyst sample was pretreated in a flow of 3% O2/N2 at 1500 ml min⁻¹ for 1 h and then cooled to room temperature.

As shown in figure 6, NO conversion can reach up to 100% in the packed catalyst bed, which showed that the honeycomb SCR catalyst has indeed high low-temperature activity. NO conversion was sharply decreased to 75% after 70 hours of continuous reaction, which attribute to the deposition of (NH₄)₂SO₄ and NH₄HSO₄ on the surface of SCR catalyst and plugging of the pores.

Exhaust gases from stationary sources always contain SO₂, arsenide, alkali oxides and salts which could strongly poison the catalysts. If the temperature of flue gas was lower than 280°C, (NH₄)₂SO₄ and NH₄HSO₄ are easily formed via the SO₂ oxidation to SO₃ and subsequent reactions with NH₃. The sticky (NH₄)₂SO₄ and NH₄HSO₄ are deposited on the surface of SCR catalyst and plugging of the pores, leading to deactivation of the SCR catalyst. To wit, sulfur poisoning was the strongest poisons for low-temperature SCR catalysts.

After 300 hours of continuous reaction, however, NO conversion was still above 75% in spite of undulation. It is demonstrated that the honeycomb SCR catalyst has excellent sulfur resistance.

The regeneration of deactivated catalysts was the most effective approach to recover its catalytic activity. Water or acid solutions (e.g., sulfuric acid and citric acid) washing of the catalysts may remove alkali metals from active sites, while the heat treatment could promote the decomposition of ammonium sulfate.[33-36].

![Fig. 6 The de-NOx activities over the V₂O₅-WO₃-MoO₃/TiO₂ catalysts](image-url)
In our work, the SCR catalyst was operated at a severely reaction condition which the feed gas contains 2500 ppm SO₂. The other reaction condition was same to part 2.3. The deactivate reaction was continuous running for 48 hours. Then, the deactivated catalysts were removed ammonium sulfate using heat treatment at 400 °C for 6 hours. The catalyst repeats several times of deactivation and regeneration, and tests its performance for denitrification.

Fig. 7 shows that, the fresh catalyst was highly active, and the NO conversions were above than 95% at the temperature of 250 °C. The deactivated sample presented a poor activity which lower than 55% at the same temperature after running 48 h. After regeneration, the activity increased significantly which was approaching even more activity than fresh catalyst. The results demonstrated that the regeneration by heat treatment could be efficiently recovering the activity of the deactivated SCR catalyst. Therefore, SCR catalyst with the support of TiO₂ nanoparticles has superior catalytic activity and also excellent sulfur resistance and regeneration properties.

4. Conclusion
In this study, the TiO₂ nanoparticles were prepared through decomposition of titanium slag. Key influencing factors, including decomposition temperature, sodium hydroxide-to-titanium slag mass ratio, and the concentration of sulfuric acid on the titanium extraction were studied. Approximately 97.9% titanium in the titanium slag could be extracted in the optimal conditions of calcined temperature 600 °C, and sodium hydroxide-to-titanium slag mass ratio 1.8:1. The titanium dioxide nanoparticles used as SCR catalyst support performs excellent catalytic activity, which may attribute to its large surface areas provide high dispersion of vanadium over the catalyst supporter. In addition, the SCR catalyst also exhibits outstanding sulfur resistance and regeneration properties.

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