



# Morphology-controlled synthesis of 3D flower-like TiO<sub>2</sub> and the superior performance for selective catalytic reduction of NO<sub>x</sub> with NH<sub>3</sub>



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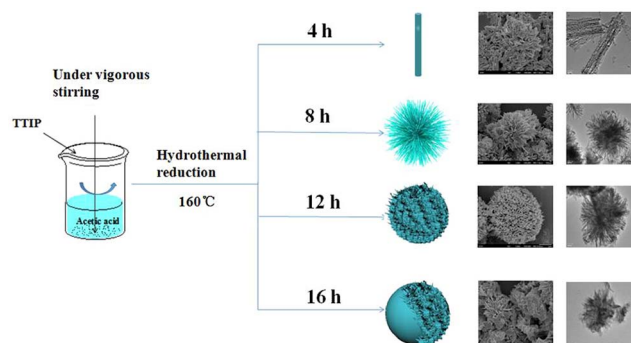
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## HIGHLIGHTS

- Flower-like TiO<sub>2</sub> support was regulated by modulating hydrothermal time.
- Flower-like structure influenced the surface atomic ration of Ce<sup>3+</sup> / (Ce<sup>3+</sup> + Ce<sup>4+</sup>).
- The surface atomic ration of Ce<sup>3+</sup> / (Ce<sup>3+</sup> + Ce<sup>4+</sup>) influenced the SCR performance.
- The catalysts showed satisfactory water-resistance and certain SO<sub>2</sub> tolerance.

## GRAPHICAL ABSTRACT

In this paper, the morphology of 3D TiO<sub>2</sub> support was regulated by modulating the hydrothermal time, and CeO<sub>2</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalysts catalyst was synthesized by impregnation method and used for selective catalytic reduction of NO<sub>x</sub> with NH<sub>3</sub>. The whole formation process of flower-like TiO<sub>2</sub> might be influenced by the changed of the hydrothermal time and also be made.



## ARTICLE INFO

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CeO<sub>2</sub>-WO<sub>3</sub>/TiO<sub>2</sub>

Ce<sup>3+</sup>/(Ce<sup>3+</sup> + Ce<sup>4+</sup>)

## ABSTRACT

Morphology of 3D TiO<sub>2</sub> support was regulated by modulating the hydrothermal time. Notably, the increase of hydrothermal time could greatly promote the transformation of rod-like TiO<sub>2</sub> to flower-like TiO<sub>2</sub>, while the continuous increase of hydrothermal time damaged the integrity of flower-like TiO<sub>2</sub> and led to the appearance of large TiO<sub>2</sub> particles. After that, a series of CeO<sub>2</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalysts were prepared by a typical impregnation method. The catalytic performance of these CeO<sub>2</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalysts for the selective catalytic reduction of nitrogen oxides (NH<sub>3</sub>-SCR) verified that NO<sub>x</sub> conversion was greatly related to morphological integrity of flower-like TiO<sub>2</sub>. Prominently, activity of CeO<sub>2</sub>-WO<sub>3</sub>/TiO<sub>2</sub>-8 catalyst was still excellent after introducing H<sub>2</sub>O and SO<sub>2</sub>, and thus the combined CeO<sub>2</sub>-WO<sub>3</sub>/TiO<sub>2</sub>-8 catalyst showed high catalytic activity and good resistance to H<sub>2</sub>O and SO<sub>2</sub>. Various characterizations indicated that the integrity of flower-like structure could evidently alter the surface atomic ratio of Ce<sup>3+</sup>/(Ce<sup>3+</sup> + Ce<sup>4+</sup>) as well as acid sites. With the increase of surface atomic ratio of Ce<sup>3+</sup>/(Ce<sup>3+</sup> + Ce<sup>4+</sup>), the SCR performance of the catalysts was obviously improved. In short, the superior catalytic performance of CeO<sub>2</sub>-WO<sub>3</sub>/TiO<sub>2</sub> for the SCR of NO<sub>x</sub> was related to the morphology of TiO<sub>2</sub> support, the highly dispersed active species, the valence of Ce, acid sites and lots of surface adsorbed oxygen.

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## 1. Introduction

The emission of nitrogen oxides (NO and NO<sub>2</sub>) from coal fired power plants and automobiles is becoming more and more serious. More importantly, nitrogen oxides can also cause the haze, photochemical smog, acid rain and make a secondary particulate matter [1–3]. Therefore, the removal of these nitrogen oxides is vitally important for ameliorating and protecting the environment. Notably, the selective catalytic reduction of nitrogen oxides with NH<sub>3</sub> (NH<sub>3</sub>-SCR) has been widely used for the removal of nitrogen oxides [4–6]. It was reported that V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> is the most promising NH<sub>3</sub>-SCR catalyst according to lots of literatures [7,8]. However, V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst still exists various disadvantages, such as poor thermal stability, narrow operating temperature window, toxicity of vanadium species, high activity for the oxidation of SO<sub>2</sub> to SO<sub>3</sub> and the alkali metal poison [9]. In addition, V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst could also result in the unselective oxidation of NH<sub>3</sub>. Unfortunately, in this unselective oxidation of NH<sub>3</sub>, some ozone-depleting, greenhouse gas and N<sub>2</sub>O would be generated, which could destroy the balance of the environment [10,11]. Due to these disadvantages, no vanadium catalyst arise great attention [12].

For replacing the vanadium, cerium has been considered as an excellent constituent, which could be additives and carriers. However, cerium-based catalyst has some advantages contrasting with the vanadium catalyst [13–15]. Generally, cerium-based catalyst exist Ce<sup>4+</sup> and Ce<sup>3+</sup> species. Especially, Ce<sup>3+</sup> species is the main existence, which is beneficial for the NH<sub>3</sub>-SCR. Generally, Ce<sup>4+</sup> and Ce<sup>3+</sup> species in cerium-based catalysts could convert into each other during the catalytic reaction. In this process, some active oxygen would be released and promoted the NH<sub>3</sub>-SCR reaction [16–18]. On the other hand, cerium-based catalysts also have some disadvantages, such as their sulfur tolerance. When SO<sub>2</sub> was pumped into the reaction, Ce<sup>3+</sup> would react with the SO<sub>2</sub> to form Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and the decrease of active cerium species [19]. Thus, the sulfur tolerance of catalysts could be improved through various means.

Fortunately, there are two means to improve and avoid the above disadvantages. On one hand, the addition of assistant could avoid the reaction of cerium and SO<sub>2</sub>. On the other hand, the modulation of surface properties of support materials is vitally important for elevating the activity and stability of catalysts [20–23]. Various literatures [24–27] reported that the morphology and surface area of catalyst could alter the surface composition, the valence of element, the defect sites and acid-based sites of catalysts. For example, flower-like support material is very promising because of the special morphology and the big surface area. Li et al. [28] synthesized 3D flower-like NiMnFe mixed oxides as monolith catalysts for NH<sub>3</sub>-SCR and found that the structure of 3D flower-like NiMnFe mixed oxides could enhance evidently performance for the NH<sub>3</sub>-SCR. Ma et al. [29] synthesized a series of MoS<sub>2</sub>@TiO<sub>2</sub> nanohybrids for catalytic hydrogen evolution via simple hydrothermal processes using MOF as precursor for the first time. Besides, Khalid et al. [30] synthesized TiO<sub>2</sub> nano-flowers by hydrothermal method and found that the particles size of flower-like structure increased as the increasing of hydrothermal time. Wang et al. [31] also synthesized 3D flower-like TiO<sub>2</sub> microsphere/composite through a polyvinyl pyrrolidone (PVP) assisted one-step hydrothermal method by using the titanium (IV) isopropoxide (TTIP) and graphene oxide (GO) as precursors. Thus, it can be concluded that hydrothermal method is a usual strategy for the synthesis of flower-like TiO<sub>2</sub>. Although many researchers have successfully synthesized 3D flower-like TiO<sub>2</sub>, some of them only considered how to synthesize and rarely considered how to use the advantages of 3D flower-like in NH<sub>3</sub>-SCR, such as large specific surface area, high dispersion. Thus those advantages were carefully considered in our work so that further promoted the SCR performance and the ability of catalysts.

In this work, we synthesized a series of TiO<sub>2</sub> with different morphology by hydrothermal method. It was discovered that hydrothermal time played a key role in determining the morphology and structure of

TiO<sub>2</sub>. In further detail, the active components Ce and W were doped and anchored in these TiO<sub>2</sub> with special morphology to obtain a series of CeO<sub>2</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalysts. Furthermore, the influence of hydrothermal time in the morphology of TiO<sub>2</sub>, the formation process of flower-like TiO<sub>2</sub>, the SCR performance as well as the tolerance to H<sub>2</sub>O and SO<sub>2</sub> of the CeO<sub>2</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalysts were investigated by various characterizations. It was discovered that CeO<sub>2</sub>-WO<sub>3</sub>/TiO<sub>2</sub>-8 catalyst had the superior activity and stability.

## 2. Experimental

### 2.1. Preparation of support materials

In this study, we prepared support materials (TiO<sub>2</sub>) by hydrothermal method and synthesized different support materials by changing the hydrothermal time. In detail, 0.7 g titanium (IV) isopropoxide (TTIP) was added into 75 mL acetic acid with vigorous stirring for 30 min. After that, the solution was transferred into 100 mL stainless steel autoclave and treated at 160 °C for 12 h. The suspension cooled at room temperature. The obtained filter cake was washed with deionized water and ethanol for three times, after that it was dried in an electricity heat drum wind drying oven at 100 °C for 6 h. The dried yellow powder was calcined at 500 °C for 1 h in air with a rate of 1 °C min<sup>-1</sup>. At last, the support material TiO<sub>2</sub> was obtained. Due to the hydrothermal time were 12 h, thus this support material TiO<sub>2</sub> was named as TiO<sub>2</sub>-12. In addition, we also prepared the TiO<sub>2</sub> under the hydrothermal time were 4 h, 8 h and 16 h, and also named those TiO<sub>2</sub> as TiO<sub>2</sub>-4, TiO<sub>2</sub>-8 and TiO<sub>2</sub>-16.

### 2.2. Preparation of CeO<sub>2</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst

The CeO<sub>2</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalysts were prepared by impregnation method. In our study, the loadings of tungsten were 5 wt% and that of cerium were 10 wt%. In detail, 0.08 g of ammonium metatungstate ((NH<sub>4</sub>)<sub>6</sub>H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>·XH<sub>2</sub>O) and 0.37 g of cerium nitrate (Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O) were dissolved in 1.5 mL (15 wt%) oxalic acid solution for 30 min, and then TiO<sub>2</sub> powder was slowly added into the above solution under vigorous stirring for 24 h. After that, the mixture was dried at 100 °C for 6 h. The dried yellow powder was calcined at 550 °C for 5 h in air at a rate of 1 °C min<sup>-1</sup>. Hereafter, they are denoted as CeO<sub>2</sub>-WO<sub>3</sub>/TiO<sub>2</sub>-x, where x represents the hydrothermal time. As a contrast, industrial titanium dioxide was used as support instead of TiO<sub>2</sub>-x for synthesis CeO<sub>2</sub>-WO<sub>3</sub>/TiO<sub>2</sub>-IT catalyst by same method, where IT was the abbreviation of industrial titanium dioxide.

### 2.3. NH<sub>3</sub>-SCR catalytic test

The NH<sub>3</sub>-SCR activity measurement was carried out in a fixed bed reactor operating in a steady state flow mode. 0.40 g of the catalysts were sieved with a 20–40 mesh and used in each test. The reaction conditions were exhibited as follows: 500 ppm of NO, 500 ppm of NH<sub>3</sub>, 3 vol% of O<sub>2</sub> and balance N<sub>2</sub>. The total flow rate was 200 mL min<sup>-1</sup> and a gas hourly space velocity (GHSV) of 30,000 h<sup>-1</sup> was obtained. The temperature increased from 200 to 480 °C. At each temperature step, the data were recorded after steady state. The concentration of NO<sub>x</sub> in the inlet and outlet gas was measured by a KM9106 flue gas analyzer. In here, NO<sub>x</sub> meant the NO and NO<sub>2</sub>. The NO<sub>x</sub> conversion was calculated according to the following expression:

$$\text{NO}_x \text{ conversion (\%)} = \frac{[\text{NO}_x]_{\text{in}} - [\text{NO}_x]_{\text{out}}}{[\text{NO}_x]_{\text{in}}} \times 100\%$$

### 2.4. Characterization of the catalysts

The morphology of the catalysts was obtained by using a scanning electron microscope (SEM). The SEM images were recorded on a JSM-

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