



Uniformly active phase loaded selective catalytic reduction catalysts ($V_2O_5/TNTs$) with superior alkaline resistance performance



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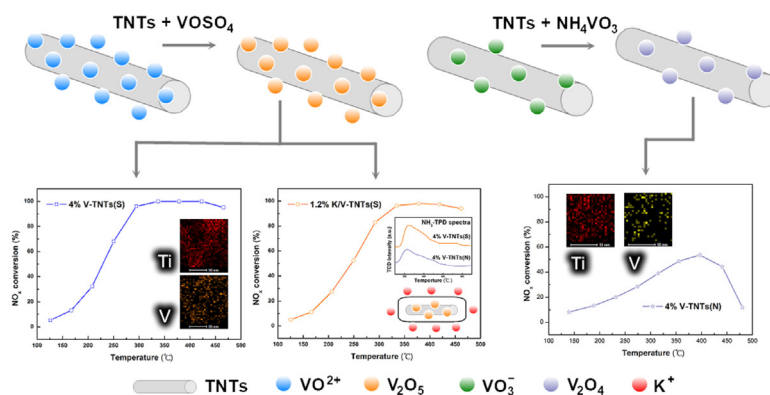
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HIGHLIGHTS

- $VOSO_4$ exhibited better synergistic effect with titanate nanotubes than NH_4VO_3 .
- Ion-exchange reaction occurs between $VOSO_4$ and titanate nanotubes.
- Ion-exchange resulting in uniformly vanadium distribution on titanate nanotubes.
- $VOSO_4$ -based catalyst exhibited impressive SCR activity and alkaline resistance.

GRAPHICAL ABSTRACT

Uniformly active phase loaded SCR catalyst ($V_2O_5/TNTs$) synthesized via ion-exchange mechanism: achieving excellent NO_x removal efficiency and alkali resistance.



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ABSTRACT

In this work, protonated titanate nanotubes was performed as a potential useful support and different vanadium precursors (NH_4VO_3 and $VOSO_4$) were used to synthesize de NO_x catalysts. The results showed that $VOSO_4$ exhibited better synergistic effect with titanate nanotubes than NH_4VO_3 , which was caused by the ion-exchange reaction. Then high loading content of vanadium, uniformly active phase distribution, better dispersion of vanadium, more acid sites, better V^{5+}/V^{4+} redox cycles and superior oxygen mobility were achieved. Besides, $VOSO_4$ -based titanate nanotubes catalysts also showed enhanced alkaline resistance than particles (P25) based catalysts. It was strongly associated with its abundant acid sites, large surface area, flexible redox cycles and oxygen transfer ability. For the loading on protonated titanate nanotubes, active metal with cation groups was better precursors than anion ones. $V_2O_5/TNTs$

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catalyst was a promising substitute for the commercial vanadium catalysts and the work conducted herein provided a useful idea to design uniformly active phase loaded catalyst.

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1. Introduction

Recently, serious hazy weather invaded most areas of China more than once. For the formation of haze, NO_x is one of the main pollutions. With regard to the NO_x emission control, cement plants, steelworks, industrial boilers and power plants are the emphasis targets. Selective catalytic reduction (SCR) of NO_x by NH_3 within O_2 had been reported as a promising technology for these stationary sources and the vanadium based catalysts ($\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ or $\text{V}_2\text{O}_5\text{-MoO}_3/\text{TiO}_2$) are the mostly used commercial SCR catalysts [1–4]. However, many obstacles emerge in practical application of SCR method and the deactivation of vanadium catalysts caused by alkali/alkaline earth metals (hereafter referred to as alkaline poisons) is the especially serious one. Moreover, the NO_x emission from refuse incinerators and glass furnaces are coming to the view of public, where the alkaline poisoning takes place much more seriously [5–7].

Actually, commercial vanadium catalysts in most power plants demand replacement or cleaning within intervals of 2–5 useful years on stream, which is largely resulted from the deactivation by alkaline poisons existed in the exhaust gas [8]. Besides, with the biomass is widely used as an alternative for fossil fuels in power plants, the vanadium catalysts suffer more serious deactivation, which is mainly caused by the presence of high amounts of potassium and sodium (almost up to 2 wt%) [8–10]. Thus, the problem of alkaline deactivation of traditional vanadium catalysts becomes an urgent issue to be solved and more and more attention is being paid to.

Literatures had reported that protonated titanate nanotubes (TNTs) was a good choice to act as supports for deNO_x catalysts, which was mainly attributed to its large surface area, special nanotubular structure and abundant acid sites [11–13]. Besides, the titanate nanotubes also showed excellent adsorptive ability in the area of wastewater treatment [14,15], superior catalytic properties among thermocatalytic or photocatalytic research area [16–18] and remarkable performance as the materials of solar cells and batteries [19,20]. Moreover, the titanate nanotubes and titanate nanotubes with addition of metals, rare earth and metal oxides were applied as solid catalysts in the homogeneous catalysis process [21]. Our previous work verified that the hollow interlayered tubular structure of titanate nanotubes could protect the CeO_2 inside from the poisoning of Na^+ , K^+ , Ca^{2+} , and also the protons existed in the interlayers of titanate nanotubes could be ion-exchanged with poisoning cations (Na^+ , K^+ , Ca^{2+}) [22]. Otherwise, researchers also declared that the titanate nanotubes was wonderful support for Cu, Mn and other active metals [23–25].

Most recently, different kinds of vanadium-based catalysts with enhanced performance have been well developed by various interesting routes for the $\text{NH}_3\text{-SCR}$ of NO [26–29]. In this study, TNTs-based catalyst with NH_4VO_3 (active metal with anion groups) and VOSO_4 (active metal with cation groups) loaded were both synthesized to investigate the SCR performance. As an inspiring result, the sample used VOSO_4 as precursor exhibited superior NO_x reduction activity than that used NH_4VO_3 , potentially indicating that the VOSO_4 had a special synergistic effect with titanate nanotubes but NH_4VO_3 not. To further investigate the alkaline resistance of VOSO_4 -based catalysts, nano-particle support (TiO_2 , Degussa P25) was applied to prepare the catalyst with granular structure.

It was interesting to find that the combination of titanate nanotubes and VOSO_4 not only achieved excellent SCR performance but also gained remarkable alkaline poisoning resistance. A series of characterization methods, such as XRD, BET, ICP-MS, Zeta Potential, HADDF-STEM, HRTEM-EDX, XPS, $\text{H}_2\text{-TPR}$, $\text{NH}_3\text{-TPD}$, $\text{NO} + \text{O}_2\text{-TPD}$ and $\text{NH}_3\text{-FTIR}$ were conducted to explore this special synergistic effect and the enhanced alkaline resistance. We expect that this meaningful breakthrough could provide a new way to design catalysts with uniformly loading active phase based on ion-exchange mechanism.

2. Experimental

2.1. Catalyst preparation

Titanate nanotubes were prepared via a typical hydrothermal treatment [30–32]. The P25 TiO_2 purchased from Degussa (Germany) was firstly mixed with 10 mol/L NaOH solution and stirred for 6 h, then the mixture were transferred into a teflon-lined autoclave and kept at 130 °C for 24 h. After hydrothermal reaction, the precipitate was firstly washed with 0.1 mol/L HCl solution to pH = 1.6, secondly with deionized water to pH = 7, lastly immersed by excess ethanol solution for 24 h to disperse and then dried at 80 °C for more than 12 h before use.

The deposition of vanadium was carried out as follows: 1) NH_4VO_3 was dissolved in oxalic acid solution and then the TNTs support (4 g) was impregnated in the mixed solution; 2) VOSO_4 was dissolved in deionized water and the TNTs or P25 was added. Then the mixtures were stirred, dried and calcined at 450 °C. The vanadium catalysts synthesized with NH_4VO_3 and VOSO_4 on TNTs or P25 supports were labeled to V-TNTs(N), V-P25(S) and V-TNTs(S), respectively. Besides, a series of V-TNTs(S) catalysts with the weight percent of vanadium oxides varied from 2 wt% to 5 wt% were prepared to optimize the active metal content.

Alkaline poisoner was added as literature reported [33–35]. The vanadium catalysts synthesized with VOSO_4 after potassium deposited were labeled to K/V-P25(S), K/V-TNTs(S), respectively. And the weight percent of potassium oxides was varied from 0.8 wt% to 2.4 wt%.

In the ICP-OES experiments, 4 mg TNTs were immersed into 60 ml NH_4VO_3 + oxalic acid/ VOSO_4 solutions and stirring for 6 h. The concentrations of the vanadium in NH_4VO_3 + oxalic acid/ VOSO_4 solutions before and after TNTs immersing were detected by ICP-OES.

2.2. Catalyst characterization

X-ray diffraction with Cu $\text{K}\alpha$ radiation (model D/max RA, Rigaku Co., Japan) was used to investigate the crystal phases of the samples and the information was obtained with scattering angles (2θ) ranging from 10° to 80° with a step size of 0.02°.

Microscopic morphology, structure and the distribution of active phase were detected by transmission electron microscopy (JEM-2010, Japan).

The specific surface areas, pore size and pore volume were obtained by a nitrogen adsorption-desorption device (JW-BK132F, China) with the Brunauer-Emmett-Teller method. The samples were purified at vacuum state before measurement at 100 °C.

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