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A Compact V₂O₅-WO₃/TiO₂ Monolith Catalyst for Vessel De-NO_x Application

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RESEARCH ARTICLE

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ABSTRACT

Using a corrugated paper as the substrate, a novel compact monolith catalyst assigned as V₂O₅-WO₃/TiO₂ for vessel De-NO_x application was prepared by wash coating method. The prepared corrugated paper catalyst exhibited comparable NO conversion but lower SO₂/SO₃ conversion than that of commercial catalyst at low temperature of 200 and 250 °C.

INTRODUCTION

In order to meet the requirement of International Maritime Organization (IMO) announced NO_x Tier III regulations on vessels, the selective catalytic reduction (SCR) with NH₃ at low temperature <250 °C has been widely studied over various catalysts^[1-2]. Among those catalysts, the V₂O₅-WO₃/TiO₂ is the most representative catalyst^[3].

For mobile vessel NH₃-SCR system, it is obvious that, not only the good reactivity but also compact property like low bulk density is required for the catalyst. However, surprisingly, to our knowledge, most literatures focused only the catalysts reactivity performance, but neglecting the compact issue of the catalysts system. In light of these, a commercial corrugated paper is applied here as the substrate to prepare V₂O₅-WO₃/TiO₂ catalyst by wash-coating method. The catalyst performance was evaluated at both 200 and 250 °C to investigate its application possibility for the vessel NH₃-SCR process.

EXPERIMENTAL

Catalysts Preparation

A commercial corrugated paper (Dongguan Chunhing paper Co., Ltd) was used as a substrate in **Figure 1(a)**. This corrugated paper has a 790 m²/m³ contact area per volume, which is comparable to commercial honeycomb catalyst, whereas the bulk density is only 60% of the commercial honeycomb catalyst value. The composition of this material is SiO₂, Al₂O₃, MgO and CaO. A wash-coating method with the slurry containing commercial WO₃-TiO₂ and Ammonium vanadium oxide was employed to prepare catalysts in this study. The V₂O₅ loading was controlled at 3.8 wt. %. The prepared sample was calcined at 450 °C for 5 h.

As a control sample, a commercial $V_2O_5-WO_3/TiO_2$ honeycomb catalyst with 3.8 wt. % V_2O_5 loading shown in **Figure 1(b)** was provided by Jiangsu Longyuan Catalyst Co., Ltd.

Catalysts Characterization

The elemental composition was determined by the AES-ICP in a Thermo-Electron model 3580 instrument. The XRD was recorded on a Bruker D8 Advanced A25 diffractometer. SEM images were taken by the FEI Quanta 200. The XPS analyses were conducted on a MultiLab ESCA 2000 X-ray photoelectron spectrometer with Mg-K α radiation at 300 W.

Catalysts Reactivity

The catalysts evaluation was performed over a fixed bed reactor. A 57.6 mL prepared corrugated paper catalyst or commercial honeycomb catalyst was loaded into a reactor with O.D.60.5 mm and I.D. 52.9 mm. The catalyst performance is evaluated with both NO conversion and SO_2/SO_3 conversion. For the De-NO_x activity test, a stimulated gas composed of 180 ppm NH_3 , 180 ppm NO, 7% O_2 , 10% H_2O with N_2 balance was applied at SV 28125 h^{-1} . For the SO_2/SO_3 oxidation test, 500 ppm SO_2 , 4% O_2 , 10% H_2O with N_2 balance gas was applied at SV 7734 h^{-1} .

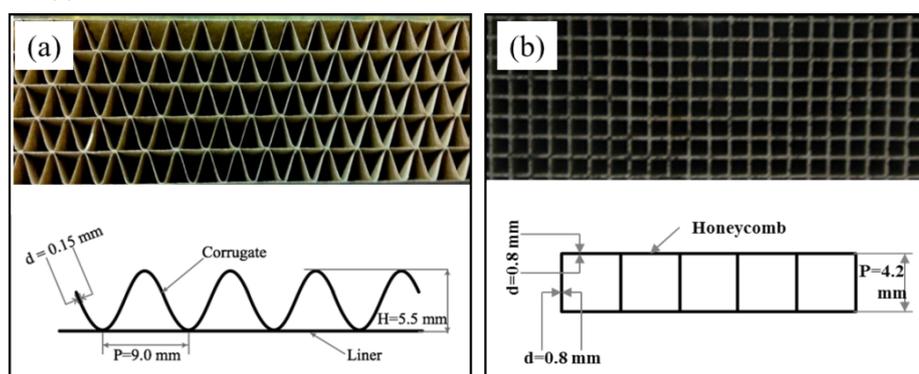


Figure 1. Image and size profile (a) Paper corrugated support; (b) Honeycomb catalysts.

The rate constant K_{NO} is used here to compare prepared corrugated paper catalyst and commercial honeycomb catalyst ^[4]:

$$K_{NO} = -\frac{SV}{A_p} \times \ln\left(1 - \frac{\eta}{100}\right) \quad (1)$$

Where, A_p is the contact area per volume, η is the NO conversion, SV is the space velocity.

RESULTS AND DISCUSSION

Characterization of the Fresh Catalyst

The prepared catalyst in **Figure 2(a)** showed the similar XRD pattern as that of commercial WO_3-TiO_2 powder in **Figure 2(b)**, while negligible V_2O_5 peak could be detected. This implied that the vanadium oxides are well dispersed. The WO_3 refraction peak was only shown after calcining the commercial WO_3-TiO_2 powder at $1100^\circ C$ to transform the anatase TiO_2 to rutile TiO_2 in **Figure 2(c)**.

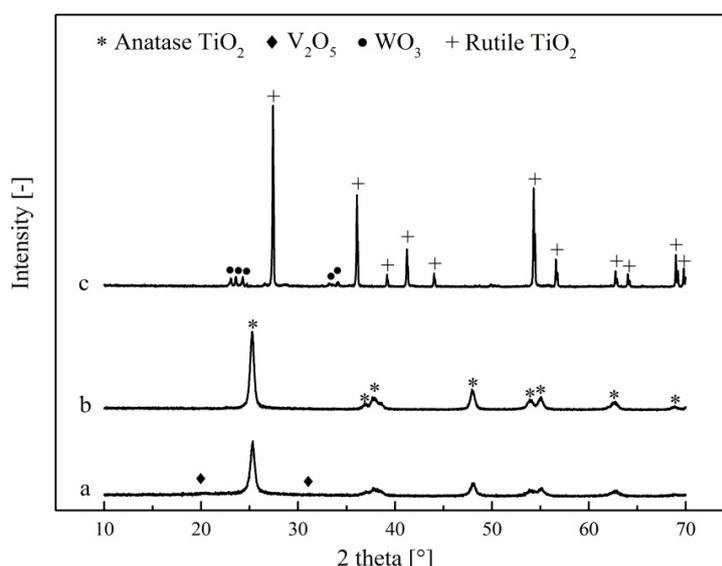


Figure 2. XRD over prepared catalyst (a) prepared catalyst in this study (b) commercial TiO_2-WO_3 (c) calcine b at $1100^\circ C$.

XPS results in **Figure 3** further explained the existence of anatase TiO_2 and WO_3 over prepared catalyst. The existence of

45% V^{5+} , 45% V^{4+} and 10% V^{3+} were detected also. According to Youn *et al.* [5], the existence of V^{3+} and V^{5+} in XPS most likely form the polymerized species, while the V^{4+} may result in both isolated and polymerized surface vanadium species. Due to the higher liability of lattice oxygen atoms, the polymeric vanadium species were reported to be 10 times more active than the monomeric species at low temperature 200–250 °C. The influence of the V state over the De-NO_x activity at lower temperature will be discussed in detail in our other study.

Effect of Coating Thickness

The influence of coated catalyst layer thickness on the De-NO_x activity was investigated in **Figure 4**. At both 200 and 250 °C, the De-NO_x activity increased significantly with increasing the catalyst layer thickness until 0.2 mm. Continuing increase the catalyst layer thickness from 0.2 to 0.4 mm, negligible improvement of De-NO_x activity was evidenced. This suggested that the De-NO_x reaction was confined into a narrow surface layer. Yang *et al.* reported that over a honeycomb monolith support wash coated SCR catalyst, the activity increased with increasing the coating thickness and reached at 0.11 mm thickness as comparable as that of the 100% active components-molded catalyst [6].

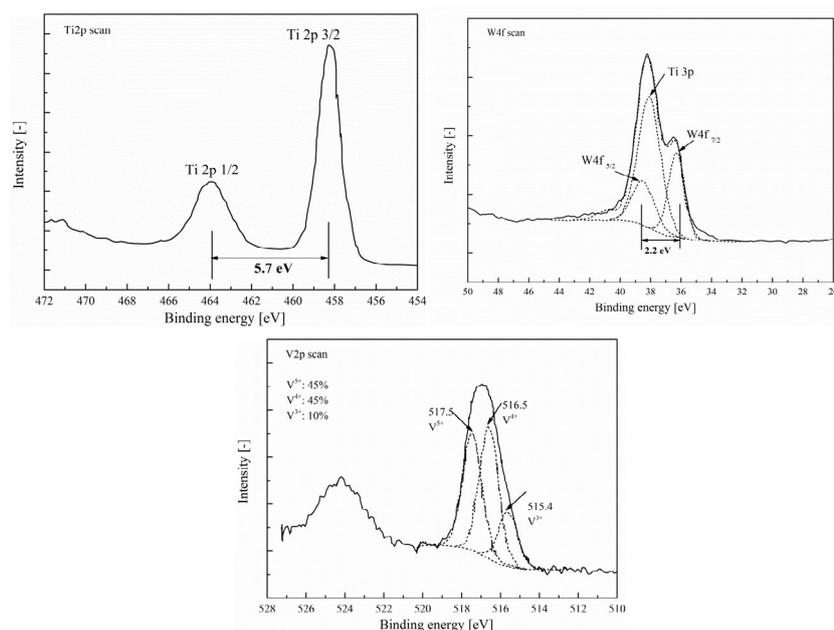


Figure 3. XPS over prepared catalyst in this study.

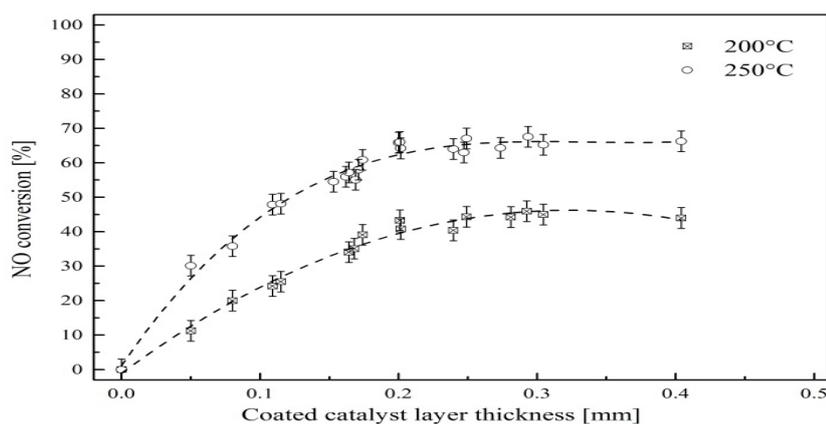


Figure 4. Influence of catalyst layer thickness on the De-NO_x activity and reactivity comparison between prepared and commercial catalysts.

Reactivity Comparison between Prepared Catalyst and Commercial Catalyst

Figure 5 showed the performance comparison results in terms of K_{NO} and SO_2/SO_3 conversion over corrugated paper coated catalyst (catalysts layer thickness 0.2×2 mm) and commercial extruded honeycomb catalyst (catalysts layer thickness 0.8 mm). The prepared corrugated paper catalyst exhibited comparable NO conversion but lower SO_2/SO_3 conversion than that of commercial catalyst. It is known that, the reduction of NO depends mainly on the external geometric surface area and therefore is little influenced by the change of the catalyst layer thickness. But, the conversion of SO_2 to SO_3 occurs in the whole catalytic volume and thus can be reduced by decreasing the thickness of the active phase layer [7]. However, we must notice that the $V_2O_5-WO_3/TiO_2$ catalyst is weak in the presence of SO_2 in the temperature range of 200 and 250 °C. And further research to improve its resistance against SO_2 is under progress by modifying the catalysts with Mo.

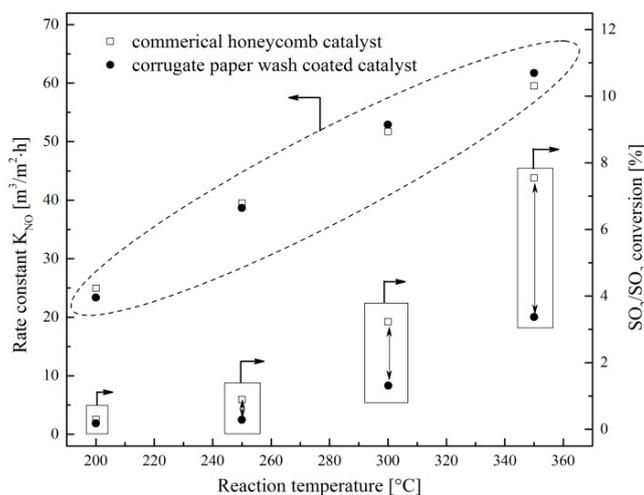


Figure 5. The De-NOx performance comparison between prepared and commercial catalysts.

CONCLUSIONS

The compact issue of the De-NOx catalyst for vessel is always neglected by many researchers, a novel catalyst $V_2O_5-WO_3/TiO_2$ based on the corrugated paper support with low bulk density but good reactivity was proposed in this study. With increasing the coated catalyst layer until 0.2 mm, the De-NOx activity increases significantly. Comparing with a commercial extruded honeycomb catalyst with 0.8 mm catalyst layer thickness, the prepared catalyst in this study with 0.2×2 mm catalyst layer thickness showed better performance in terms of K_{NO} and SO_2/SO_3 conversion.

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