



Investigations of surface VO_x species and their contributions to activities of $\text{VO}_x/\text{Ti}_{0.5}\text{Sn}_{0.5}\text{O}_2$ catalysts toward selective catalytic reduction of NO by NH_3

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ABSTRACT

High surface area $\text{Ti}_{0.5}\text{Sn}_{0.5}\text{O}_2$ mixed oxide with rutile phase was prepared by a coprecipitation method. The surface area of $\text{Ti}_{0.5}\text{Sn}_{0.5}\text{O}_2$ sample is $76.7 \text{ m}^2 \text{ g}^{-1}$, and $\text{VO}_x/\text{Ti}_{0.5}\text{Sn}_{0.5}\text{O}_2$ catalysts were prepared using the mixed oxide as support. Characterizations using XRD, FT-IR, LRS, EPR, UV-vis, and TEM demonstrated that vanadium oxide species are highly dispersed on the surface of $\text{Ti}_{0.5}\text{Sn}_{0.5}\text{O}_2$ support when the loading amount of vanadium oxide is $\leq 1.5 \text{ mmol V}/100 \text{ m}^2 \text{ Ti}_{0.5}\text{Sn}_{0.5}\text{O}_2$. The dispersed vanadium oxide species form epitaxial-growth layer on the support. In situ FT-IR (NH_3 adsorption), combined with NH_3 -TPD, indicate that the catalyst with vanadium loading amount of $1.5 \text{ mmol V}/100 \text{ m}^2 \text{ Ti}_{0.5}\text{Sn}_{0.5}\text{O}_2$, which equals to the dispersion capability, possesses a maximum amount of Brønsted acid sites. The $1.5\text{V}/\text{Ti}_{0.5}\text{Sn}_{0.5}\text{O}_2$ catalyst exhibits the best catalytic performance and good resistance to water vapor poison for the " $\text{NO} + \text{NH}_3 + \text{O}_2$ " reaction, indicating that surface dispersed polymeric vanadium oxide species are the primary active species. A possible reaction mechanism is proposed on the basis of in situ FT-IR results.

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1. Introduction

The selective catalytic reduction (SCR) of NO_x with ammonia is an established technique for removal of NO_x from stationary power stations and diesel engines [1,2]. Vanadium oxide and TiO_2 -anatase based catalysts, such as $\text{V}_2\text{O}_5/\text{TiO}_2$ and $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ [3–8], have received extensive interest from SCR researchers. Such catalysts have indicated significant activities in some oxidation reactions, and more importantly, they are only partially and reversibly sulfated in SCR reaction in the presence of SO_2 (this sulfating is also believed to enhance the SCR activity) [9–11]. However, Saleh et al. [12] found that the presence of vanadium oxide species facilitates the transformation of anatase to rutile, leading to the detachment of vanadium oxide active phase and loss of surface area, and consequently a quick decrease in the activity of $\text{V}_2\text{O}_5/\text{TiO}_2$ (anatase) catalysts. Furthermore, some researches have indicated that TiO_2 (rutile) based catalysts appear to be highly active on a unit surface area basis [13]. Nevertheless, the conventional synthesis method for rutile via anatase annealing does not give rise to a sufficiently high specific surface area [14,15]. Najbar et al. [16,17] addressed

this problem and reported that the addition of tin oxide into TiO_2 formed $\text{Ti}_x\text{Sn}_{1-x}\text{O}_2$ mixed oxides with high specific surface area. Obviously, such mixed oxide can be a potential support for NO_x -SCR catalyst.

Investigating the structure of vanadium oxide species has been one of the key subjects for supported vanadium oxide catalysts. It is acknowledged that the structures of vanadium oxides vary with their loading amount and the adopted metal oxide support. Vanadium oxides can exist as isolated vanadium oxide species (in tetrahedral, octahedral or square pyramidal coordination), polymeric vanadium oxide species (in tetrahedral or octahedral coordination), and crystalline vanadium oxide species (in octahedral or square pyramidal coordination) [18–21]. Even though a large number of researches have been carried out, the relationship between the state of the surface vanadium oxide species and loading of vanadium oxide or metal oxide support is not clear.

On the other hand, it is acknowledged that the surface acidity plays an important role in the activity of vanadium oxide based catalysts [4,7,22–30]. In the past decades, some in situ IR studies of the " $\text{NO} + \text{NH}_3 + \text{O}_2$ " reaction over vanadium oxide based catalysts have been conducted to explore the relationship between the surface acidity and the activity of the catalysts [22–29]. Topsøe et al. [23] proposed the adsorption of NH_3 on Brønsted acid sites as protonated ammonium (NH_4^+) ion dominated the " $\text{NO} + \text{NH}_3 + \text{O}_2$ " reaction. However, these results were not supported by Lietti et al.

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