

Remarkable enhancement of SO₂ resistance for NO reduction with NH₃ over a novel TiO₂/CeO₂ catalyst

L. Zhang^{1,2}, C.J. Tang^{1,2}, Y. Deng², F. Gao^{1,2}, L. Dong^{1,2*}

¹ Key Laboratory of Mesoscopic Chemistry of MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, PR China

² Jiangsu Key Laboratory of Vehicle Emissions Control, Center of Modern Analysis, Nanjing University, Nanjing 210093, PR China

*corresponding author: donglin@nju.edu.cn

Introduction

The selective catalytic reduction of NO_x with NH₃ (NH₃-SCR) technique has been used for effective removal of NO_x from stationary sources, CeO₂-TiO₂ based catalyst is environmentally-benign and one of potential alternatives for V₂O₅-WO₃/TiO₂ catalyst. However, it is reported that CeO₂/TiO₂ catalyst prepared by impregnation method has poor SO₂ resistance performance, which limits its practical application. Herein, we found TiO₂/CeO₂ displayed much better SO₂ resistance performance than CeO₂/TiO₂. *In situ* DRIFT technique was employed to approach the interaction of SO₂ with catalysts and disclose the possible mechanism.

Materials and Methods

TiO₂/CeO₂ and CeO₂/TiO₂ samples were prepared by incipient wetness impregnation. Catalytic reaction was performed in a fixed-bed quartz reactor tube. The effluent gases were continuously analyzed by an online Nicolet IS10 infrared spectrometer equipped. The *in situ* DRIFT experiments were performed on a Nicolet Nexus 5700 FTIR spectrometer by using a diffuse reflectance attachment (HARRICK) equipped with a reaction cell (ZnSe windows).

Results and Discussion

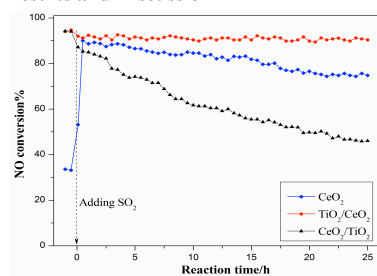


Figure 1. NH₃-SCR activities of samples with 200 ppm SO₂ at 300 °C.

conversion was keeping at ca.90%. Thus, TiO₂/CeO₂ had the evident SO₂ resistance.

Figure 1 showed the results of catalytic activity with SO₂ over samples. CeO₂ had only about 33% NO removal rate at 300 °C before adding SO₂. After injecting SO₂ for 30 min, the NO conversion of CeO₂ was up to ca.90%, which displayed the similar effect with the pre-sulfation of pure CeO₂ [1]. With the increase of test time, NO conversion gradually dropped to ca.74% at 25 h. For CeO₂/TiO₂, the NO conversion was continuously declining from ca.94% to ca.46% during the whole testing time, indicating the serious poisoning effect of SO₂ on CeO₂/TiO₂. In contrast, the NO conversion of TiO₂/CeO₂ just slightly decreased within 30 min after the injection of SO₂ and the NO

The co-adsorption DRIFT of SO₂ + O₂ at 300 °C was conducted to investigate the interaction between sulfates and samples. As shown in **Figure 2**, both the bands at 997-1105 cm⁻¹ due to the symmetric stretching frequencies of O-S-O species and the bands at 1310-1363 cm⁻¹ due to the asymmetric stretching frequencies of O=S=O species were assigned to surface adsorbed sulfates, and a broad band at 1180 cm⁻¹ was ascribed to sulfates located in bulk or subsurface of CeO₂ [2]. All the three samples had surface adsorbed sulfates. Both CeO₂ and CeO₂/TiO₂ exhibited bulk sulfates at 1180 cm⁻¹. However, negligible bulk sulfates were detected in TiO₂/CeO₂ as evidenced by the absence of the band at 1180 cm⁻¹.

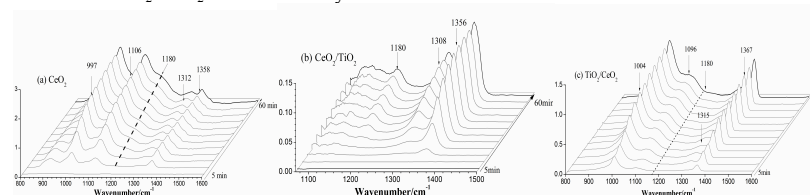


Figure 2. *In situ* DRIFT SO₂+O₂ co-adsorption spectra over samples at 300 °C.

In situ DRIFT results indicated that the configurations of catalysts had a distinct effect on the formation of sulfates. It is well documented that NH₃-SCR performances of catalysts are dependent on synergistic catalysis between acid sites and redox sites. Two reaction routes proceed over the sulfated samples. Route I is based on the active site of surface sulfates-bulk CeO₂ for sulfated CeO₂ catalyst [1]. Route II is represented by the active site of Ce-O-Ti for CeO₂/TiO₂ and TiO₂/CeO₂ catalysts [3]. Based on the results of DRIFT, when bulk sulfates is formed in CeO₂, the synergistic catalysis between surface sulfates and bulk CeO₂ is inhibited by bulk sulfates. For CeO₂/TiO₂, the main reason for the deactivation by SO₂ is the formation of surface metal sulfates which covers the active sites of Ce-O-Ti. Interestingly, the NH₃-SCR reaction can also proceed by route I over TiO₂/CeO₂ due to the support of bulk CeO₂. Although the active sites of Ce-O-Ti are covered, the synergistic catalysis between surface sulfates and bulk CeO₂ still pushes forward the NH₃-SCR process.

Significance

TiO₂/CeO₂ has better SO₂ resistance than CeO₂/TiO₂ because the configurations of catalysts can influence on the interaction between sulfates and catalysts. We have provided some theoretical guidances to prepare high performance CeO₂-TiO₂ based catalyst with good SO₂ resistance for NH₃-SCR by the investigation of TiO₂/CeO₂ catalyst.

References

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