The reactivity of ‘stored NH_3’ with NO on V_2O_5/TiO_2 catalyst in NH_3-SCR (Selective catalytic reduction) at low temperature

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Abstract: In this study, transient experiments were carried out to investigate the reactivity of stored NH_3 in ‘NH_3 reservoir’, or chemisorbed NH_3 on V_2O_5/TiO_2 catalyst, with gas phase NO in lean conditions at low temperatures. DFT calculation was used to compare the reaction pathways between NH_3 adsorbed on Brønsted acid site and that on Lewis acid site.

Keywords: Selective catalytic reduction, vanadia, V_2O_5/TiO_2, transient experiment, chemisorbed NH_3.

1. Introduction

Selective catalytic reduction (SCR) using V_2O_5/TiO_2 catalysts is the state-of-the-art technology to remove NO_x from emission for stationary and mobile sources. Although many researches have been performed to investigate the structure-activity relationships of vanadium-based catalyst in SCR reaction, few works were reported regarding the correlation between the acidic properties of dispersed vanadium oxide species and its SCR performance. It has been suggested before that acid sites on catalysts can act as an ‘NH_3 reservoir’ during SCR reaction, which means that the catalyst can remove NO_x for a few minutes even after stopping the NH_3 supply.[1,2] The surface of catalyst was monitored by in situ DRIFT to track the state of adsorbed NH_3 species while checking outlet gas with NOx analyzer to measure catalytic activity simultaneously.

2. Experimental

In this experiment, V_2O_5/TiO_2 catalyst was prepared by conventional wet impregnation method using microporous TiO_2 with high surface area (251 m^2/g) as a support material.[3] *In situ* DRIFT spectra were obtained with FT-IR spectroscopy (Nicolet 6700, Thermo Scientific) equipped with high-temperature DRIFT cell fitted with ZnSe windows. Catalysts were saturated with 0.38 Torr of NH_3 at 100 °C and 200 °C, and subsequently reacted with NO and O_2 flow. During reaction, NO and NO_2 concentration were also monitored using NO_x chemiluminescence analyzer (42i High level, Thermo Scientific). The periodic density functional theory (DFT) calculations were performed with a Vienna ab initio simulation package (VASP). A slab model of anatase $TiO_2(101)$ surface was used in this work (10.38×7.65 Å^2), which has a (1×2) surface unit cell with four stoichiometric TiO_2 layers and a vacuum spacing of 15 Å.

3. Results and discussion

The experiment at 200 °C showed that SCR activity gradually slowed down with the depletion of NH_3 adsorbed on Lewis acid site (L-NH_3) and that on Brønsted acid site (B-NH_3) as shown in Figure 1(a). In contrast, the experiment at 100 °C (Figure 1(b)) showed that the reaction stopped after the depletion of L-NH_3, even in the presence of the stored B-NH_3. This implies that B-NH_3 cannot act as an NH_3 reservoir at low temperature like 100 °C, which limits the number of participating NH_3 on the catalyst surface. With increasing temperature from 100 to 200 °C, we observe the migration of residual NH_3 between different acid sites. Thus, NO reduction with stored NH_3 on V_2O_5/TiO_2 catalyst occurred more dominantly on Lewis acid site, while the participation of B-NH_3 in SCR reaction was found to be more temperature-dependent than L-NH_3, as illustrated in Figure 1(c).

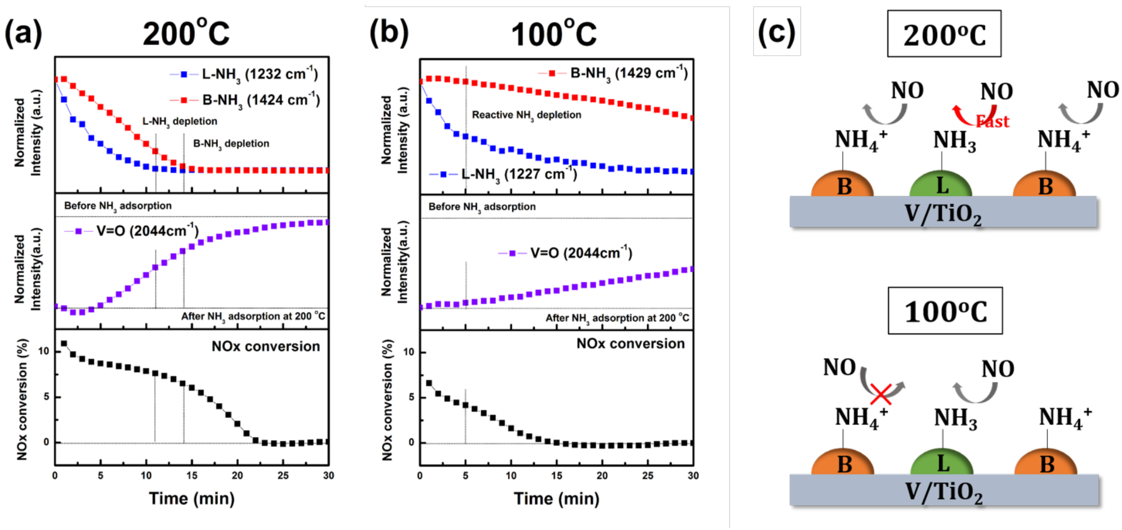

Figure 1. The reaction of adsorbed NH_3 with NO + O_2 feed was monitored with in situ DRIFT and NO_x analyzer at (a) 200 °C and (b) 100 °C. (c) Schematic illustration of the different reactivity of stored NH_3 on V_2O_5/TiO_2 catalyst.

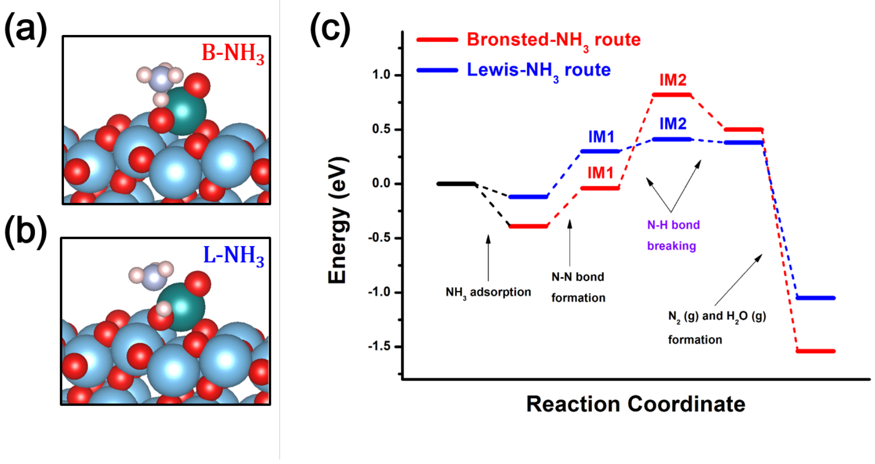

Figure 2. The optimized geometry of (a) NH_4^+ adsorbed on Brønsted acid site and (b) NH_3 on Lewis acid site. (c) Energy profile for NO reacting with Brønsted-NH_3 (red) and Lewis-NH_3 (blue), respectively.

Also, the reaction pathways of NO (g) with the adsorbed NH_3 on catalyst surface, which is known as Eley-Rideal mechanism, were simulated by DFT calculation. Monomeric vanadium oxide on anatase TiO_2(101) surface was selected as a model system. In Figure 2(a) and Figure 2(b), the most stable positions of NH_3 on Brønsted acid site and Lewis acid site were suggested, respectively. In the reaction with NO as shown in Figure 2(c), it was found that the Brønsted-NH_3 route is energetically less favorable than the Lewis-NH_3 route, which was consistent with the experimental results.

4. Conclusions

The reactivity of 'stored NH_3' on V_2O_5/TiO_2 was found to be strongly dependent on the type of acid sites. It was observed that NH_3 adsorbed on Brønsted acid site was difficult to participate in SCR reaction especially at low temperature. DFT calculation results also confirmed that Lewis-NH_3 route is energetically more favorable than Brønsted-NH_3 route.

References

1. I. Nova, L. Lietti, E. Tronconi, P. Forzatti, Catal. Today 60 (2000) 73.
2. D. Wang, L. Zhang, K. Kamasamudram, and W. S. Epling, ACS Catal. 3 (2013) 871.
3. I. Song, S. Youn, H. Lee, S. G. Lee, S. J. Cho, D. H. Kim, Appl. Catal. B 210 (2017) 421.