

Resolving the Contributions of Surface Lewis and Brønsted Acid Sites during NO_x/NH₃ SCR: An *Operando* TP-IR Spectroscopic Investigation

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Introduction

The selective catalytic reduction of NO_x with NH₃ over supported V₂O₅-WO₃/TiO₂ catalysts has been investigated for almost 30 years, yet a fundamental understanding of the relative contributions of the surface Lewis and Brønsted acid sites for the SCR reaction is still being debated. To resolve this long standing debate, the objective of this investigation was to perform an *operando* Temperature Programmed-IR spectroscopy investigation (FT-IR analysis of the surface NH₃ and NH₄⁺ species with simultaneous IR and MS analysis of the gas phase products) over a model supported V₂O₅-WO₃/TiO₂/SiO₂ catalyst.

Materials and Methods

The model supported catalyst was initially prepared by the incipient-wetness impregnation technique using isopropanol solutions of titanium isopropoxide inside a glovebox under a continuously flowing N₂ environment on the SiO₂ support (~15 nm particles) due to the moisture sensitivity of the titania precursor. HR-TEM analysis revealed that the resulting TiO₂ nanoparticles (NPs) are 3-5 nm. Tungsten oxide was subsequently added to the 30% TiO₂/SiO₂ catalyst by incipient-wetness impregnation of aqueous solutions of ammonium metatungstate ((NH₄)₁₀W₁₂O₄₁·5H₂O) and calcined in flowing air at 450 °C for 4 h. Raman analysis demonstrated that the supported 5% WO₃ phase was 100% dispersed as surface WO_x species (square-pyramidal mono-oxo structure) that preferentially self-assembled on the TiO₂ NPs in the supported 5% WO₃/30% TiO₂/SiO₂ catalyst. Vanadium oxide was introduced in the final preparation step by the incipient-wetness impregnation of isopropanol solutions of vanadium tri-isopropoxide (VO[CHO(CH₃)₂]₃) inside a glovebox with continuously flowing N₂. Raman analysis revealed that the supported 1% V₂O₅ phase was 100% dispersed as surface VO_x species (trigonal mono-oxo VO₄ structure). The *in situ* surface and gas phase IR spectra for NH₃ chemisorption on the supported 1% V₂O₅-5% WO₃/30% TiO₂/SiO₂ catalyst were collected during NH₃ adsorption at 150 °C while simultaneously monitoring the gas phase species by mass spectroscopy (MS). Subsequent surface and gas phase IR spectra were collected during the surface reaction between gas phase NO/O₂ and adsorbed NH₃ while simultaneously monitoring the gas phase species by MS during the temperature ramp to 400 °C (5 °C/minute).

Results and Discussion

Chemisorption of NH₃ on the supported V₂O₅-WO₃/TiO₂/SiO₂ catalyst gave rise to IR peaks characteristic of surface NH₃ species (~1610 and 3100-3500 cm⁻¹) on Lewis acid sites and surface ammonium NH₄⁺ species (~1420 and 2600-3000 cm⁻¹) on surface Brønsted acid sites. It was found that nearly all 700 ppm of gas phase NH₃ sent to the catalysts was adsorbed onto the catalysts surface, and that the rate of chemisorption on Lewis and Brønsted sites are

comparable. *Operando* TP-IR-MS spectroscopy revealed that both adsorbed surface NH₃ and NH₄⁺ react with gas phase NO on the model supported 1% V₂O₅-5% WO₃/30% TiO₂/SiO₂ catalyst to produce N₂ (T_p~295 and 392 °C), shown in Fig. 1. Between 295 and 320 °C, the surface NH₄⁺ species are predominantly consumed whereas the surface NH₃ species concentration remains relatively constant. Interestingly, the concentration of surface NH₄⁺ species initially slightly increases at ~290 °C by the transformation of some surface NH₃ species to surface NH₄⁺ species. The slight increase in the concentration surface NH₄⁺ species coincides with the conversion of surface NH₄⁺ to gaseous N₂ and H₂O products. This suggests that some surface NH₃ species become converted to surface NH₄⁺ species in the presence of moisture. Both types of surface species are continuously consumed in the temperature range of ~320-390 °C. In the 390-400 °C temperature window, only surface NH₃ species remain and are mostly responsible for N₂ formation in the SCR reaction in this temperature range.

Significance

In the lower SCR reaction temperature regime of ~295-320 °C, the surface NH₄⁺ species on Brønsted acid sites are preferentially consumed and some surface NH₃ species on Lewis acid sites are converted to surface NH₄⁺ species in the presence of moisture. In the intermediate temperature regime of ~320-390 °C, both surface NH_x species are consumed in the production of N₂. At the highest temperature regime of ~390-400, the surface NH₃ species are predominantly responsible for N₂ formation. The combined *operando* TP-IR-MS spectroscopy experiment was able to distinguish between the different reactivity of the surface NH₄⁺ species on Brønsted acid sites and the surface NH₃ species on Lewis acid sites during the SCR reaction, and revealed the higher reactivity of Brønsted acid surface sites

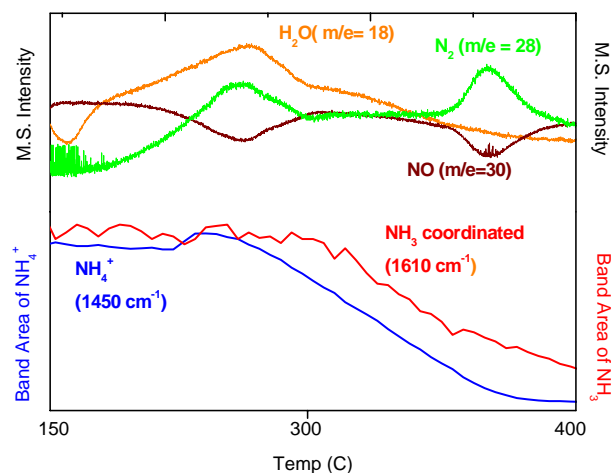


Figure. 1: *Operando* IR-MS of surface Lewis and Brønsted species and gas phase species during the SCR of NO_x with NH₃.