

Supporting Information

Mechanism of the H₂ Effect on NH₃-Selective Catalytic Reduction over Ag/Al₂O₃: Kinetic and Diffuse Reflectance Infrared Fourier Transform Spectroscopy Studies

Guangyan Xu[†], Jinzhu Ma^{†,‡,§}, Lian Wang[†], Zhihui Lv^{†,§}, Shaoxin Wang[†], Yunbo Yu^{,†,‡,§}, Hong He^{*,†,‡,§}*

[†] State Key Joint Laboratory of Environment Simulation and Pollution Control, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

[‡] Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China

[§] University of Chinese Academy of Sciences, Beijing 100049, China

Corresponding Author

Yunbo Yu *E-mail: ybyu@rcees.ac.cn

Hong He *E-mail: honghe@rcees.ac.cn

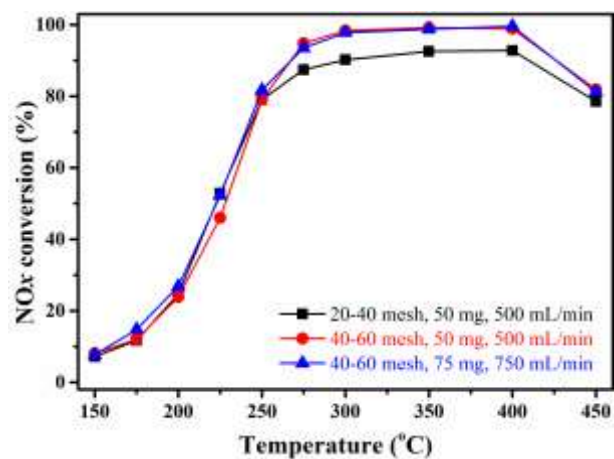


Figure S1. NO_x conversion over Ag/Al₂O₃ during H₂-NH₃-SCR at different gas flow rates and with different particle size. Feed composition: 500 ppm NO, 520 ppm NH₃, 5% O₂, 1500 ppm H₂, and N₂ balance. GHSV: 450 000 h⁻¹.

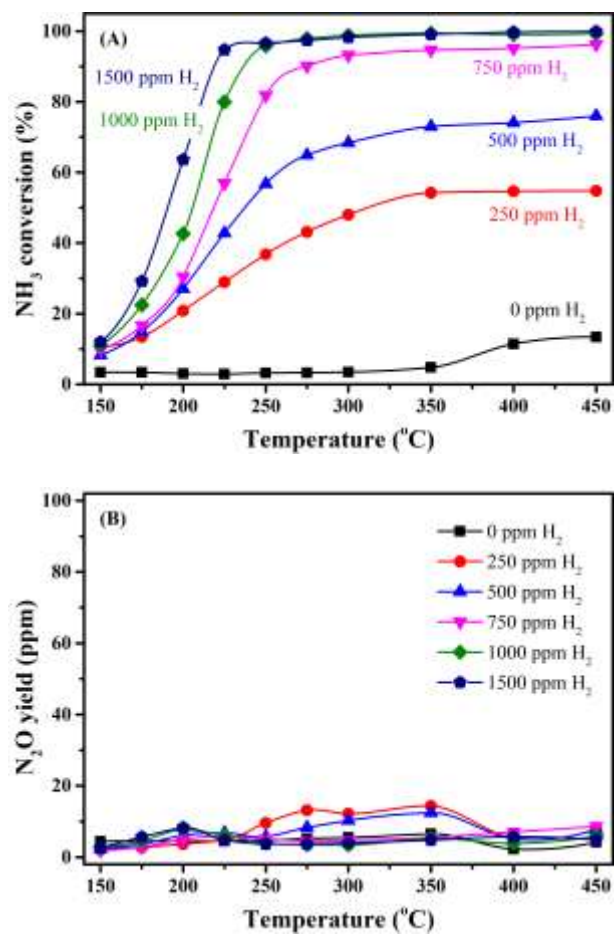


Figure S2. NH₃ conversion (A) and N₂O yield (B) over Ag/Al₂O₃ during H₂ assisted NH₃-SCR with various amount of H₂. Feed composition: 500 ppm NO, 520 ppm NH₃, 5% O₂, 0-1500 ppm H₂, and N₂ balance. GHSV: 150,000 h⁻¹.

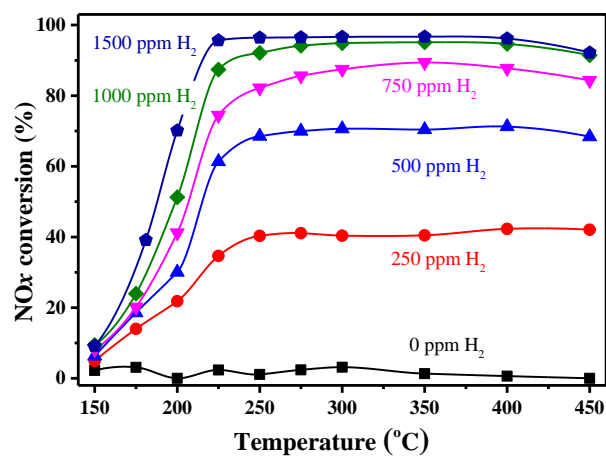


Figure S3. NO_x conversion over Ag/Al₂O₃ during H₂-NH₃-SCR in the presence of H₂O.

Feed composition: 500 ppm NO, 520 ppm NH₃, 5% O₂, 0-1500 ppm H₂, 2% H₂O, and

N₂ balance. GHSV: 150,000 h⁻¹.

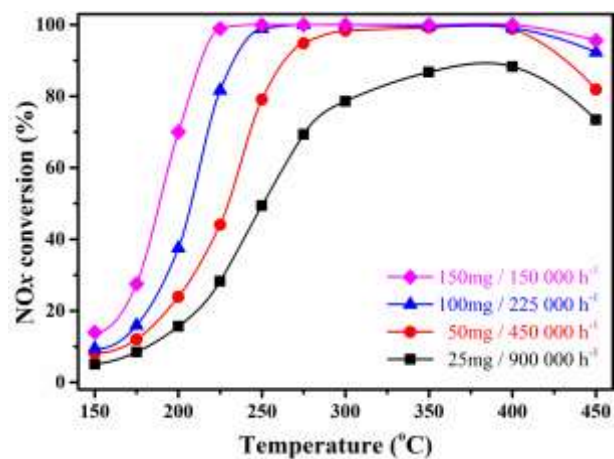


Figure S4. NO_x conversion over Ag/Al₂O₃ during H₂-NH₃-SCR under different GHSV.

Feed composition: 500 ppm NO, 520 ppm NH₃, 5% O₂, 1500 ppm H₂, and N₂ balance.

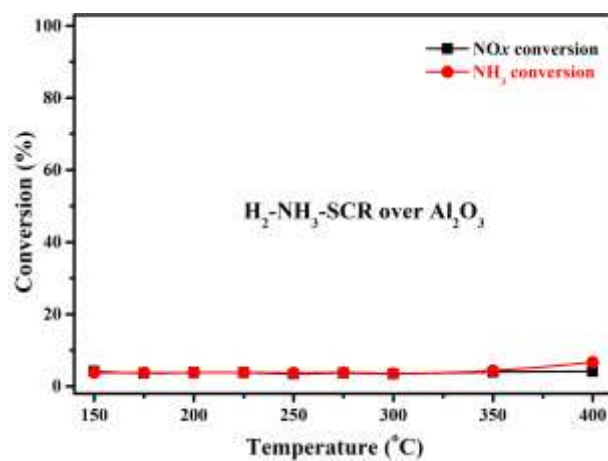


Figure S5. NO_x and NH₃ conversions over Al₂O₃ during H₂-NH₃-SCR. Feed composition: 500 ppm NO, 520 ppm NH₃, 5% O₂, 1500 ppm H₂, and N₂ balance. GHSV: 150,000 h⁻¹.

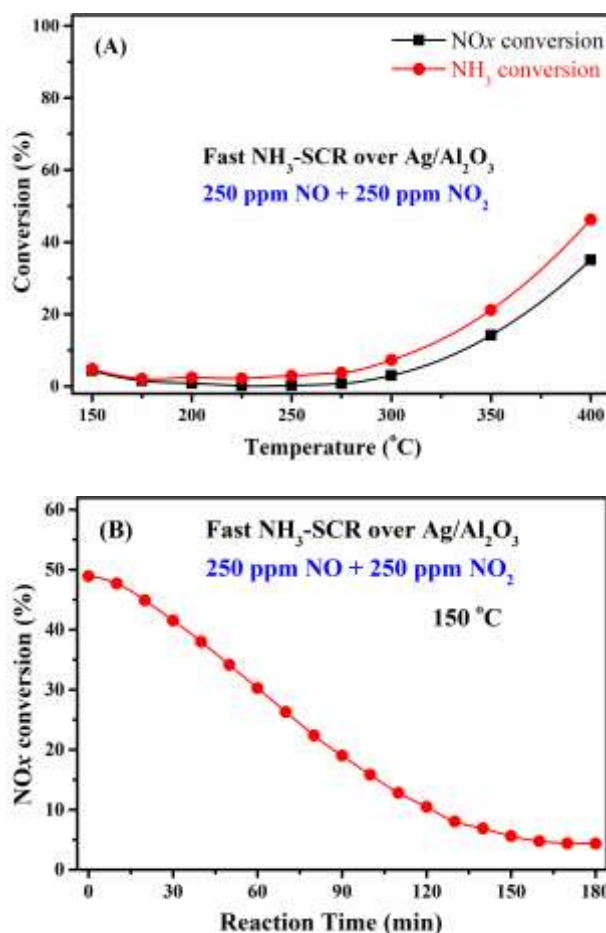


Figure S6. NO_x and NH₃ conversions over Ag/Al₂O₃ during fast NH₃-SCR (A) and NO_x conversion at 150 °C (B). Feed composition: 250 ppm NO, 250 ppm NO₂, 520 ppm NH₃, 5% O₂, and N₂ balance. GHSV: 150,000 h⁻¹.

As shown in the Figure S6B, the Ag/Al₂O₃ catalyst was gradually deactivated at 150 °C during the fast NH₃-SCR. Therefore, the NO_x conversion was measured at 150 °C for 180 min until the reaction reached a steady state. Afterward, the experiment was further performed at each temperature point for 40 min because the reaction reached a steady state more quickly at a higher temperature. Besides, other activity tests were performed at each temperature point for 40 min because those reactions reached a steady state more quickly.

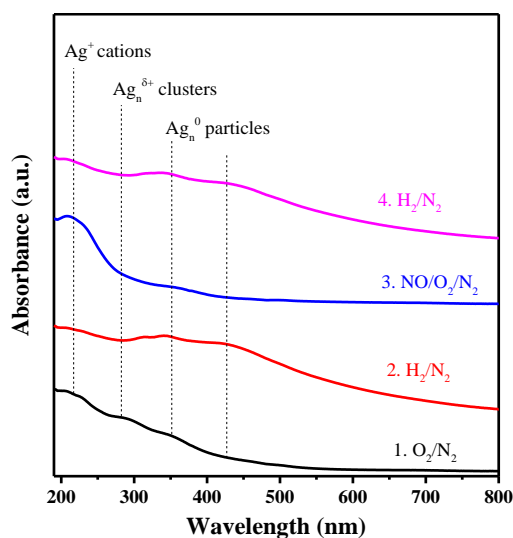


Figure S7. UV-vis spectra of Ag/Al₂O₃ catalyst pretreated in O₂/N₂ (a), H₂/N₂ (b), NO/O₂/N₂ (c), and H₂/N₂ (d) at 200 °C for 1 hour, respectively. Feed composition: 500 ppm NO, 1500 ppm H₂, 5% O₂, and N₂ balance.

Figure S7 shows the UV-vis spectra of Ag/Al₂O₃ catalyst pretreated in different atmosphere. Four adsorption peaks (220, 290, 350, and 425 nm) were observed on the Ag/Al₂O₃, and they were attributed to dispersed Ag cations (Ag⁺, 220 nm), oxidized Ag clusters (Ag_n^{δ+}, 290 nm), and metallic Ag particles (Ag_n⁰, 350 and 425 nm). On the fresh sample, dispersed Ag cations were predominant, and Ag_n^{δ+} and Ag_n⁰ were also observed. After exposure to H₂, the oxidized silver species were reduced and thus increased the amount of metallic silver species. Afterward, the metallic silver species were converted to oxidized species in a flow of NO+O₂, possibly due to the formation of AgNO₃. Moreover, the oxidized silver species were further converted to metallic silver species in a flow of H₂/N₂. Therefore, metallic silver species catalytically oxidized NO to produce nitrates, and H₂ reduced the oxidized silver species, thus completing the redox cycle for the oxidized and reduced states of Ag species.

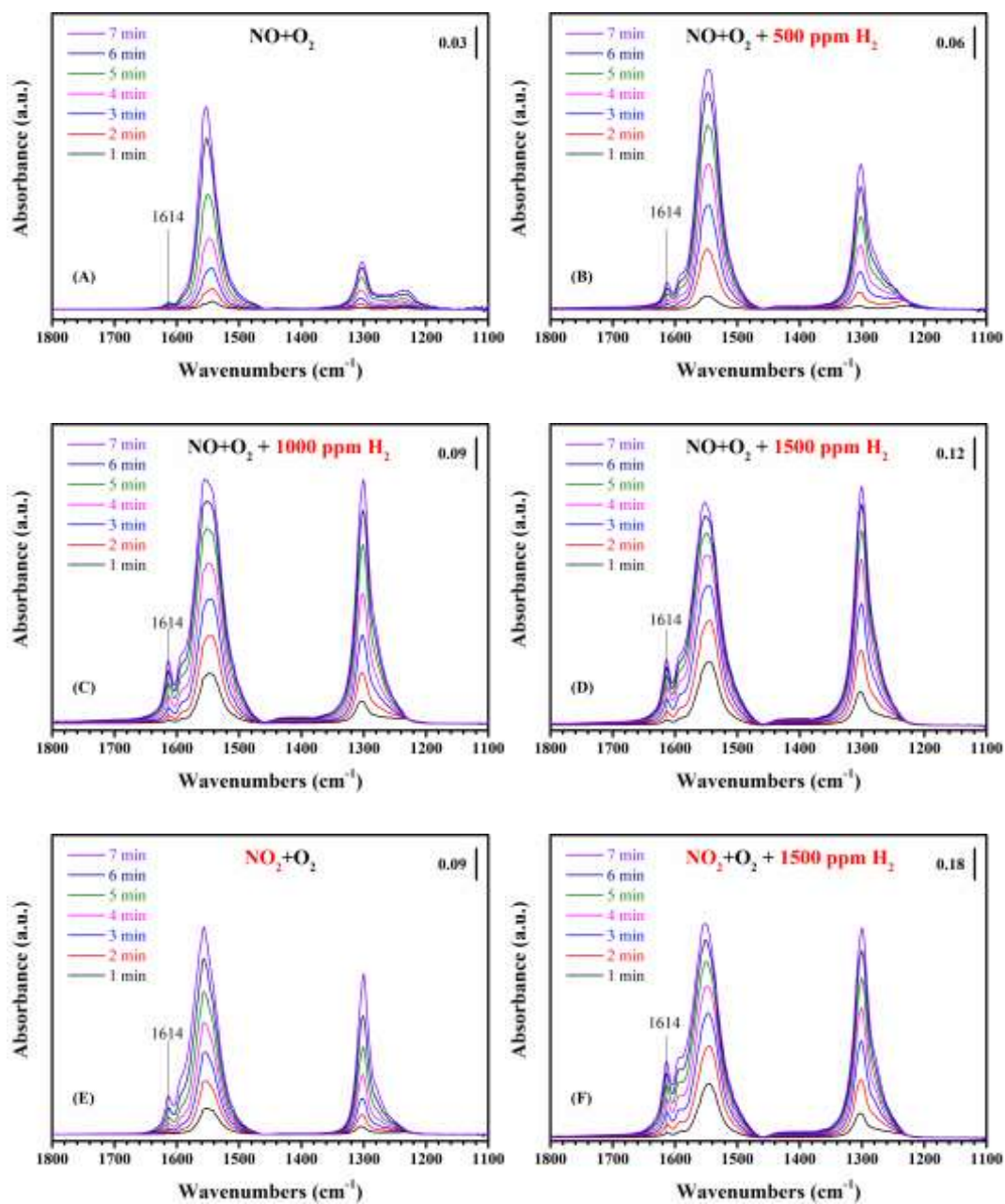


Figure S8. The DRIFTS spectra of adsorbed nitrate species over $\text{Ag}/\text{Al}_2\text{O}_3$ after exposure to a flow of $\text{H}_2 + \text{NO} + \text{O}_2$ or $\text{H}_2 + \text{NO}_2 + \text{O}_2$ with different amount of H_2 . Feed composition: 500 ppm NO (or NO_2), 5% O_2 , 0-1500 ppm H_2 , N_2 balance, 200 $^\circ\text{C}$.

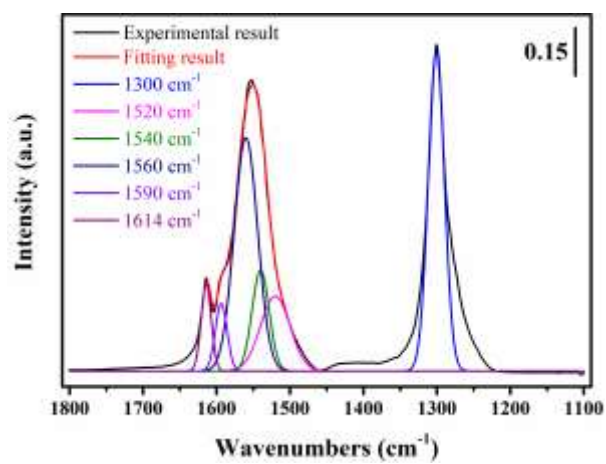


Figure S9. The deconvolution and curve fitting results for DRIFTS spectra in Figure 6 and S8.

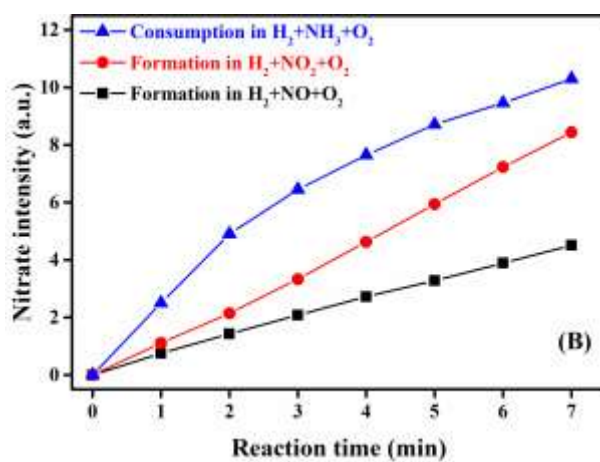
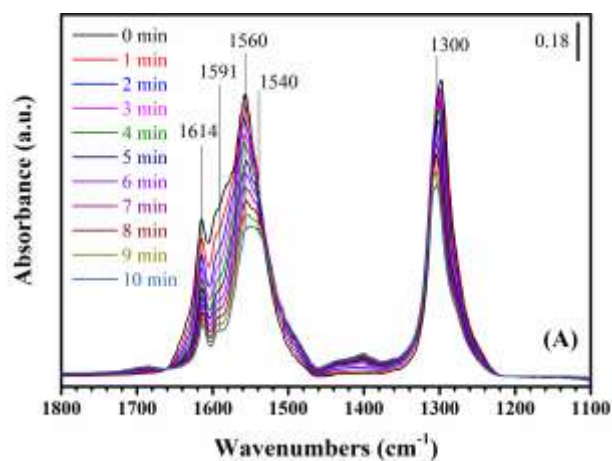


Figure S10. Reactivity of nitrate species toward $\text{H}_2+\text{NH}_3+\text{O}_2$ over $\text{Ag}/\text{Al}_2\text{O}_3$ at 200 °C (A). Comparison of the formation rate of bridge nitrate (1614 cm^{-1}) in a flow of $\text{H}_2+\text{NO}+\text{O}_2$ or $\text{H}_2+\text{NO}_2+\text{O}_2$ and the consumption rate of bridge nitrate in a flow of $\text{H}_2+\text{NH}_3+\text{O}_2$ over $\text{Ag}/\text{Al}_2\text{O}_3$ (B).

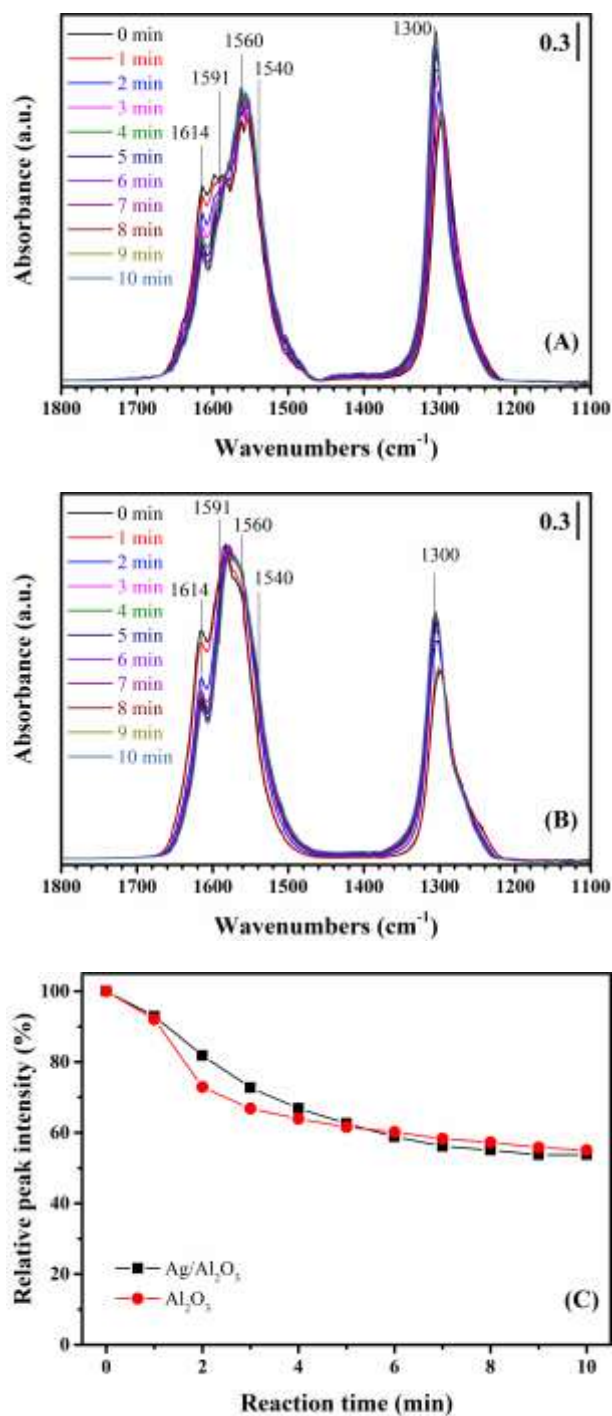


Figure S11. Reactivity of nitrate species toward $\text{NH}_3 + \text{O}_2$ over $\text{Ag}/\text{Al}_2\text{O}_3$ (A) and Al_2O_3 (B) at 200°C . Comparison of the consumption rate of bridge nitrate (1614 cm^{-1}) over $\text{Ag}/\text{Al}_2\text{O}_3$ and Al_2O_3 (C).

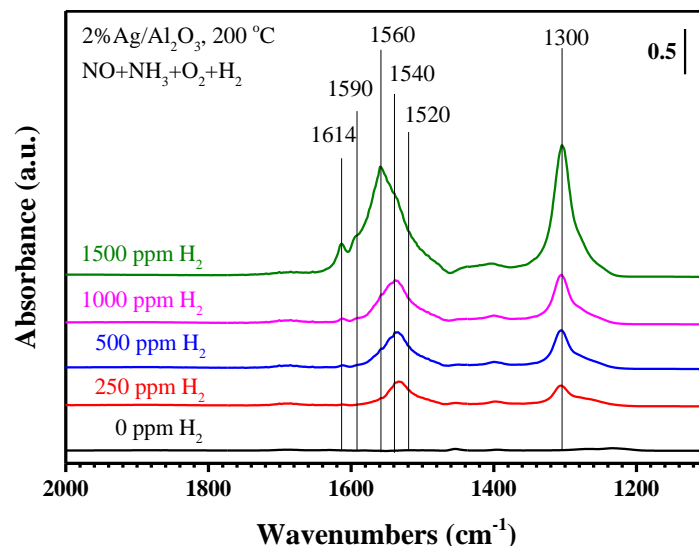


Figure S12. In situ DRIFTS of H₂-NH₃-SCR over Ag/Al₂O₃ with different concentration of H₂. Feed composition: 500 ppm NO, 500 ppm NH₃, 5% O₂, 0-1500 ppm H₂, N₂ balance, 200 °C.

Figure S12 shows in situ DRIFTS of the H₂-NH₃-SCR over Ag/Al₂O₃ with different amount of H₂ at 200 °C. In this experiment, bridging nitrates (1614 cm⁻¹), bidentate nitrates (1590 cm⁻¹), and monodentate nitrates (1560, 1540, 1520, and 1300 cm⁻¹) were observed on the surface of catalyst. Adsorbed NH₃ species was not observed possibly due to its low intensity (as shown in Figure 7). As the H₂ concentration increased, the amount of adsorbed nitrates gradually increased. Notably, the reactive nitrate species (bridging nitrate and bidentate nitrate) were only observed when a high concentration of H₂ (1500 ppm) was employed. As demonstrated in Figure 6, the formation rate of nitrate species on the Ag/Al₂O₃ was determined by the H₂ concentration. During the H₂-NH₃-SCR reaction with low concentration of H₂ (≤ 1000 ppm), the formation of reactive nitrates was slower than its further reaction with NH₃ species, thus resulting in the absence of these reactive nitrate species. When the H₂ concentration was rather high

(1500 ppm), the formation of reactive nitrates was fast enough and thus resulted in the accumulation of these species. This experiment further confirmed that the formation of reactive nitrates was the rate-determining step for the $\text{H}_2\text{-NH}_3\text{-SCR}$ reaction.