

Supporting information

Investigation of the promotion effect of WO_3 on the decomposition and reactivity of NH_4HSO_4 with NO on $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ SCR catalysts

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Fig. S1 XRD patterns of series Ti-based samples

Fig. S2 FTIR spectra: NH_4HSO_4 -free catalysts

Fig. S3 (a) TPSR profiles of NH_4HSO_4 with NO; Condition: 1000 ppm NO + 3% O_2 in N_2 at 1.2 L min^{-1} ; Heating rate: $5 \text{ }^\circ\text{C min}^{-1}$; 0.4 g samples; (b) TPSR profiles of NH_3 : 1000 ppm NO + 3% O_2 in N_2 at 1.2 L min^{-1} ; Heating rate: $5 \text{ }^\circ\text{C min}^{-1}$; 0.4 g samples;; (c) TPSR profiles of N_2O : 1000 ppm NO + 3% O_2 in N_2 at 1.2 L min^{-1} ; Heating rate: $5 \text{ }^\circ\text{C min}^{-1}$; 0.4 g samples; (d) FTIR spectra of the NH_4HSO_4 -deposited samples after the TPSR process

Fig. S4 (a) *In situ* DRIFTS study of the NH_4HSO_4 behavior in N_2 at $250 \text{ }^\circ\text{C}$; (b) *In situ* DRIFTS study of the reactivity behavior of NH_4HSO_4 with NO on the VW/Ti catalyst surface at $250 \text{ }^\circ\text{C}$

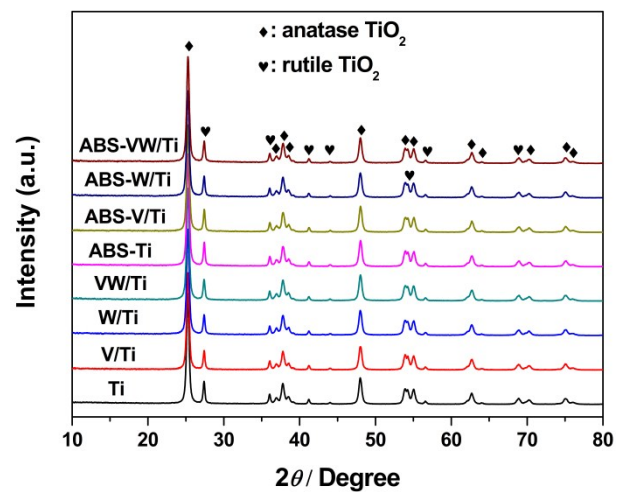


Fig. S1 XRD patterns of series Ti-based samples

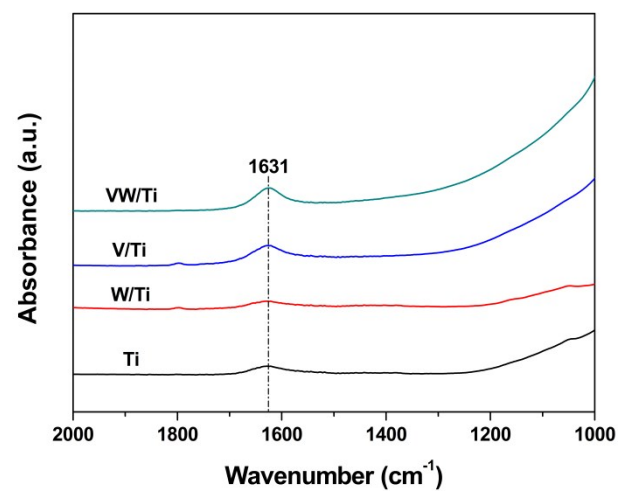


Fig. S2 FTIR spectra: NH₄HSO₄-free catalysts

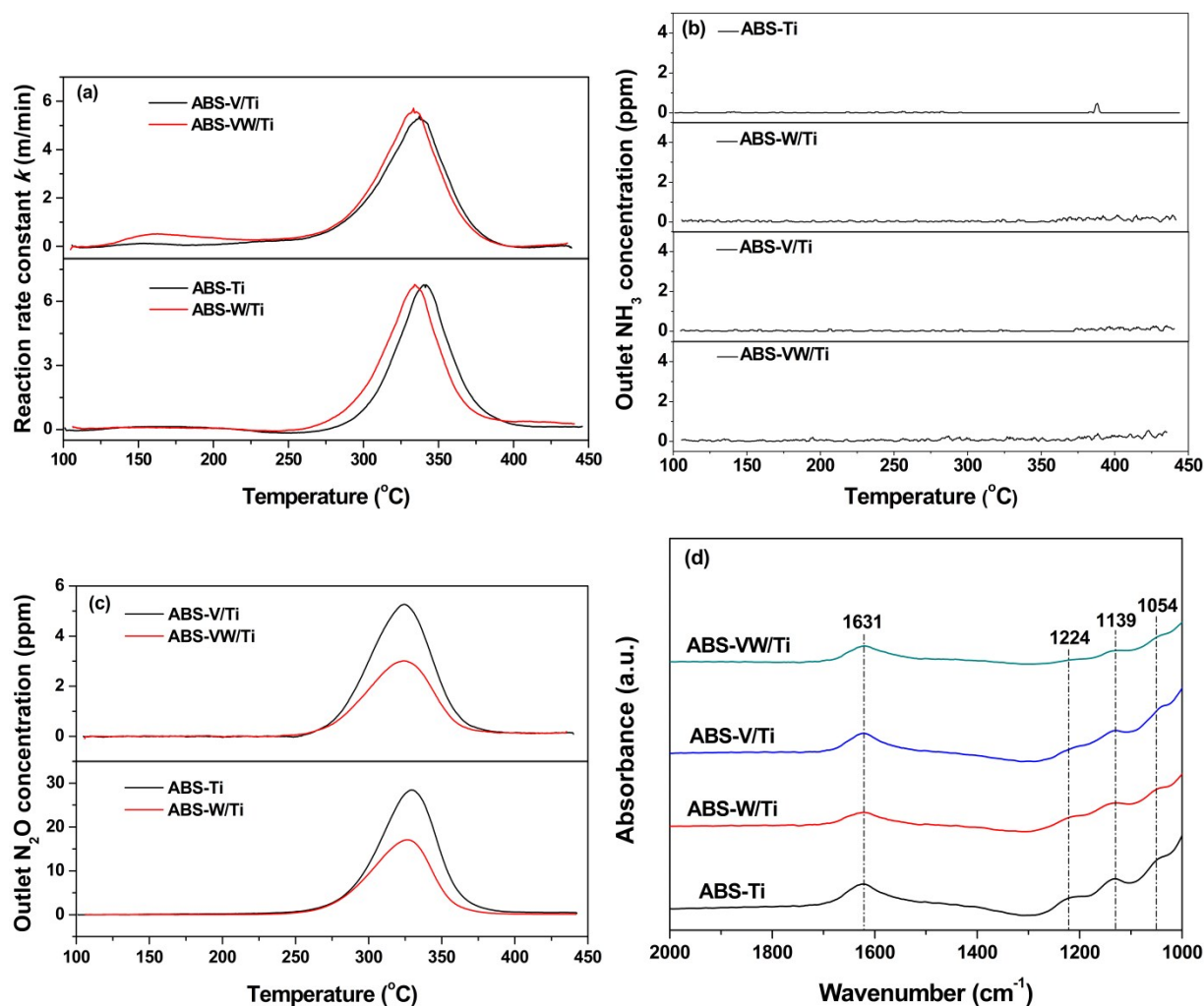


Fig. S3 (a) TPSR profiles of NH_4HSO_4 with NO ; Condition: 1000 ppm NO + 3% O_2 in N_2 at 1.2 L min^{-1} ; Heating rate: $5 \text{ }^\circ\text{C min}^{-1}$; 0.4 g samples; (b) TPSR profiles of NH_3 : 1000 ppm NO + 3% O_2 in N_2 at 1.2 L min^{-1} ; Heating rate: $5 \text{ }^\circ\text{C min}^{-1}$; 0.4 g samples;; (c) TPSR profiles of N_2O : 1000 ppm NO + 3% O_2 in N_2 at 1.2 L min^{-1} ; Heating rate: $5 \text{ }^\circ\text{C min}^{-1}$; 0.4 g samples; (d) FTIR spectra of the NH_4HSO_4 -deposited samples after the TPSR process

Fig. S3(a) illustrates the NO TPSR profiles with NH_4HSO_4 on the W-free or W-added catalysts. Variations in the reaction rate constant reflect the reactivity behavior of NH_4HSO_4 with NO . In the case of NH_4HSO_4 deposited on the Ti catalyst, this reaction starts at *ca.* $275 \text{ }^\circ\text{C}$, as is illustrated by the increased reaction rate constant. With increasing temperature, the reaction rate constant continuously increases, whose highest point is at *ca.* $340 \text{ }^\circ\text{C}$. The reaction rate constant then begins to decline and gradually restores to 0, which illustrates the depletion of NH_4^+ on the catalyst surface. As for the NH_4HSO_4 reactivity behavior on the W/Ti catalyst, a little higher reaction rate constant of NH_4HSO_4 with NO occurs in the temperature region of $250\text{--}330 \text{ }^\circ\text{C}$. Similar phenomenon can be seen in

the V-doped samples that WO_3 addition has a slight promotion effect on the NH_4HSO_4 reactivity behavior at low-temperature regions, because of the higher reaction rate constant below *ca.* 330 °C and a decline in the temperature for the maximum reaction rate constant. Fig. S3(c) illustrates the outlet N_2O (the unwanted byproduct) concentration during the TPSR process for the NH_4HSO_4 -deposited samples. Considering the fairly low outlet NH_3 concentration (lower than 1 ppm), it can be concluded that the addition of WO_3 leads to an enhancement in the catalytic selectivity to N_2 during the TPSR process. In order to identify the variations in the surface functional groups during reaction, FTIR was applied. As shown in Fig. S3(d), four characteristic peaks assigned to H_2O and bidentate SO_4^{2-} are observed after reaction. The disappearance of NH_4^+ characteristic peak illustrates the depletion of NH_4^+ on the catalyst surface after the exposure in an NO-containing flue gas.

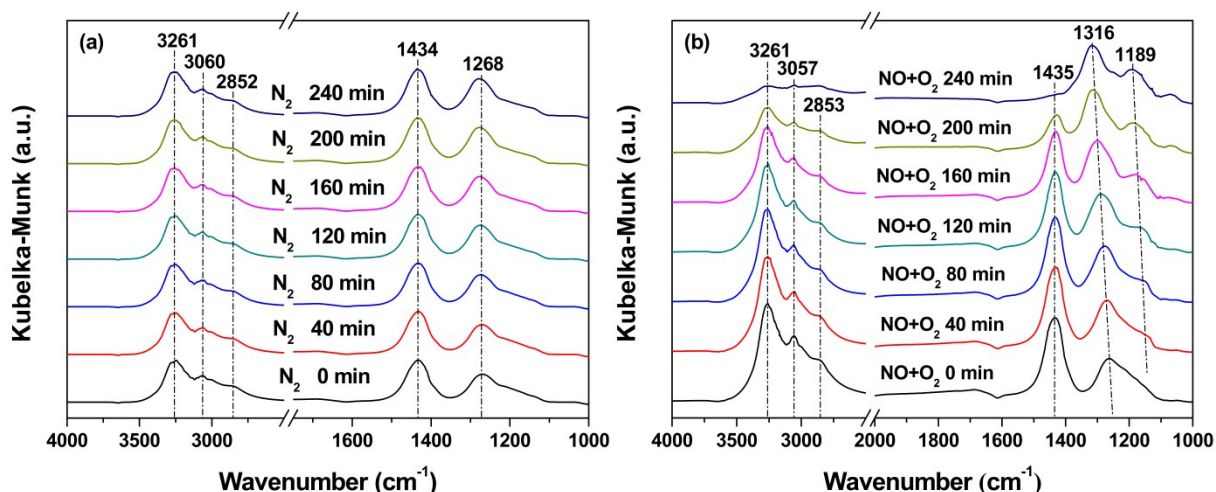


Fig. S4 (a) *In situ* DRIFTS study of the NH_4HSO_4 behavior in N_2 at 250 °C; (b) *In situ* DRIFTS study of the reactivity behavior of NH_4HSO_4 with NO on the VW/Ti catalyst surface at 250 °C

Based on the TG-DTG results, the decomposition behavior of NH_4HSO_4 on the catalyst surface is greatly enhanced at a temperature higher than 300 °C. Therefore, the increasing reaction rate constant during the heat process might be related to the accelerated reaction between NO and NH_3 coming from the decomposition of NH_4HSO_4 . In order to investigate the detailed reactivity behavior of NH_4HSO_4 with NO on the VW/Ti catalyst surface, a special experiment should be conducted at a constant temperature. According to the IR spectra in Fig. 8 and S4(a), it seems that NH_4HSO_4 remains almost unchanged below 250 °C. Therefore, a temperature at or below 250 °C should be chosen to avoid the NH_4HSO_4 decomposition behavior. As is shown in Fig. S4(b), characteristic bands at 1262 and 1435 cm^{-1} , which can be attributed to the asymmetrical stretching vibrations of S=O in bidentate SO_4^{2-} and NH_4^+ bonded to Bronsted acid sites, come out ¹. With the introduction of NO + O₂, a decrease in the intensity of the band attributed to NH_4^+ occurs, illustrating the gradual consumption of NH_4^+ on the catalyst. Given an ongoing reaction process, a characteristic band at 1138 cm^{-1} which is assigned to the symmetrical stretching vibrations of S=O in bidentate SO_4^{2-} , appears ². The bidentate sulfate species undergo a blue shift during the reaction process together with the occurrence of a slight increase in the intensity of the SO_4^{2-} bands, which might be attributed to the gradual consumption of NH_4^+ bonded to sulfate sites ³.

Reference

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