Supporting Information

The mechanism of ammonium bisulfate formation and decomposition over V/WTi catalysts for NH_3-selective catalytic reduction at various temperature

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Catalyst preparation

The V_2O_5/WO_3-TiO_2 catalyst with 1wt % V_2O_5 was prepared by incipient wetness impregnation method. Commercial support (DT-52) was obtained from Millennium Inorganic Chemicals Inc. The complex of $VO(CO_2)_2$ was prepared by mixing V_2O_5 powder with oxalic acid liquid (1 M) with continuous stirring at 70 ˚C for 30 min. Subsequently, the WTi powder was added into the mixed solution and stirred for 1 h. This mixture was statically dried overnight at 100 ˚C and calcined at 500 ˚C for 5 h and named as V/WTi-F.

Design and preparation of reference samples

In order to illustrate the mechanisms of ammonium (bi)sulfate species formation and decomposition over V/WTi catalyst, a series of reference samples were prepared as follows, which were pretreated for temperature programmed decomposition (TPDC).

Samples mechanically mixed with 10 % NH_4HSO_4 or 10 % $(NH_4)_2SO_4$

The V/WTi-F catalysts were mechanically mixed with 10 % NH_4HSO_4 or 10 % $(NH_4)_2SO_4$ sufficiently and the obtained samples were donated as V/WTi-F- NH_4HSO_4 and V/WTi-F- $(NH_4)_2SO_4$, respectively.

Samples impregnated with 1 % or 10 % ABS

1 % or 10 %ABS species were deposited on V/WTi-F through the wet impregnation method. In order to simulate the samples sulfated under *in situ* condition at different temperature, these samples were calcined at 200, 250 and 300 ˚C for 24 h, respectively.

Characterization

Temperature-programmed decomposition (TPDC) experiment was carried out on MKS-2030. For TPDC, 0.2 g sample was loaded and preheated to 80 ˚C in N_2 for 0.5 h to remove any weakly adsorbed impurities. The concentration of SO_2 originated from the decomposition of ammonium (bi)sulfate species was recorded when the temperature was elevated from 80 ˚C to 600 ˚C with a 10 ˚C min^{-1} ramping rate.

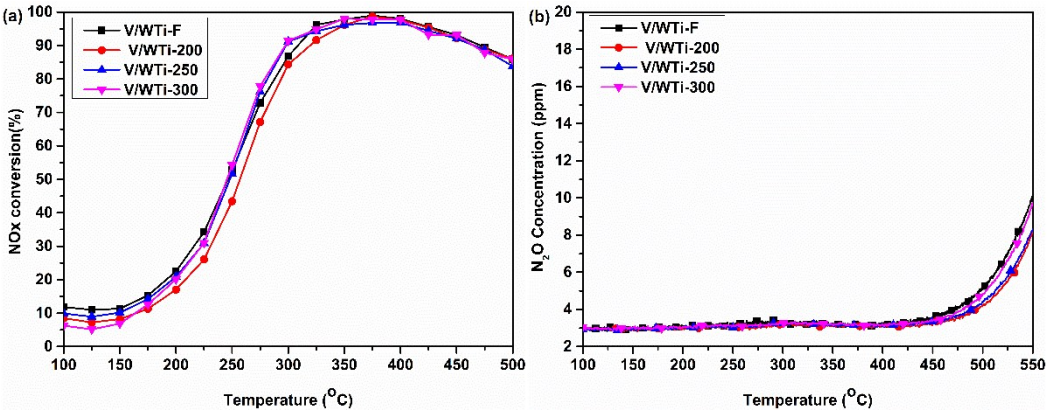

Fig. S1 the NH_3-SCR performance of these samples for the second round test: (a) NO_x conversion and (b) N_2O concentration.

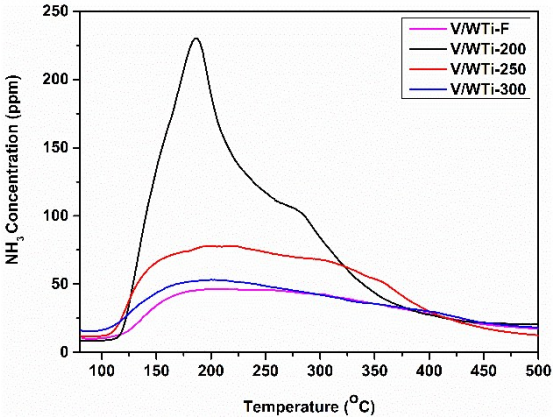

Fig.S2 NH_3-TPD profile of the obtained catalysts.

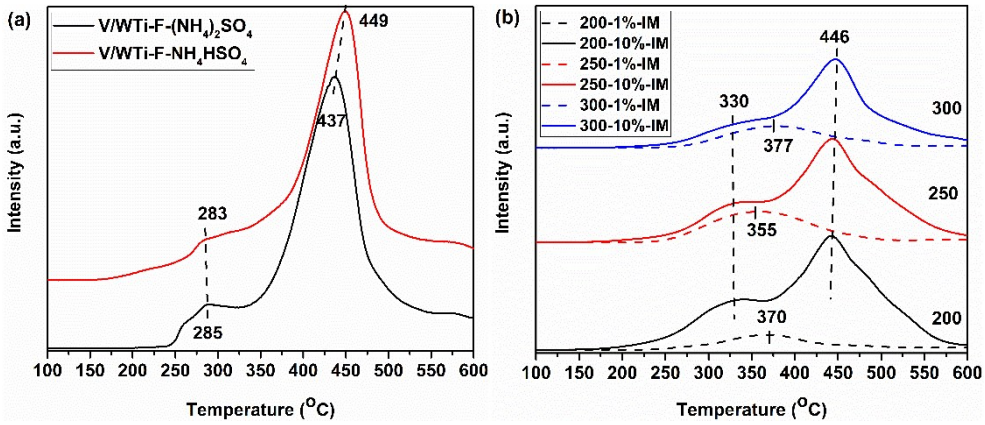

Fig.S3 The TPDC profiles of SO_2 on V/WTi-F mechanically mixed with 10 % NH_4HSO_4 or 10 % $(NH_4)_2SO_4$ (a) and V/WTi-F deposited with 1 % and 10 % ABS by wet impregnation calcined at 200 ˚C, 250 ˚C and 300 ˚C for 24 h, respectively (b).

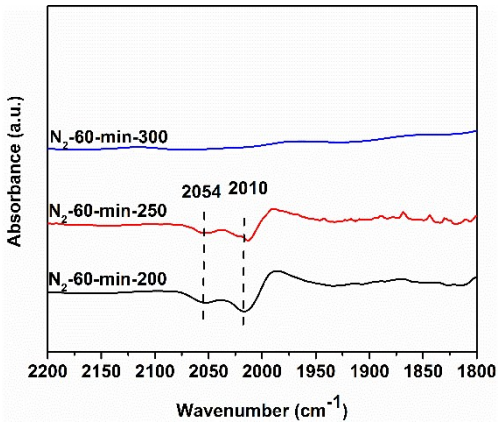

Fig.S4 the bands between 2200-1800 cm^{-1} of V/WTi exposed SO_2+O_2 for 2 h and purged with N_2 for 1 h at 200 ˚C (a), 250 ˚C (b) and 300 ˚C (c), respectively.

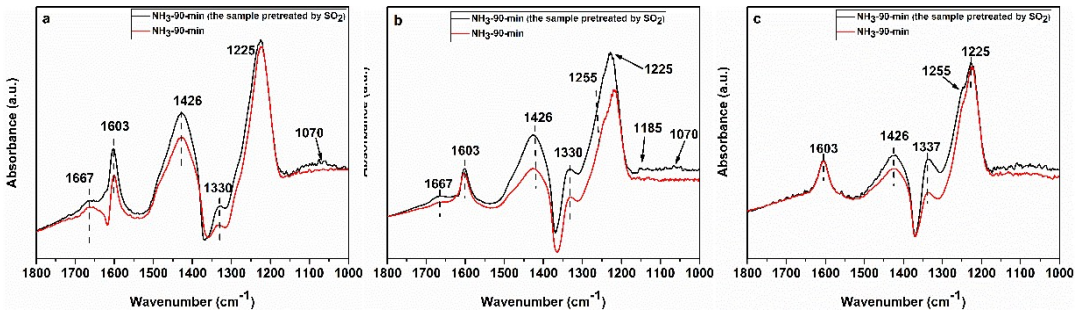

Fig.S5 *in situ* FTIR spectra of V/WTi under different conditions at 200 ˚C (a), 250 ˚C (b) and 300 ˚C (c).

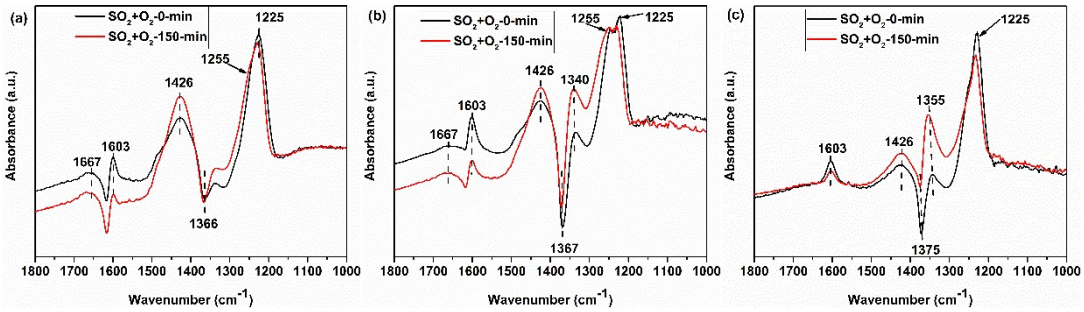

Fig.S6 *in situ* FTIR spectra of V/WTi pretreated by NH_3 exposed to SO_2+O_2 for 0 min and 150 min time at 200 ˚C (a), 250 ˚C (b) and 300 ˚C (c), respectively.

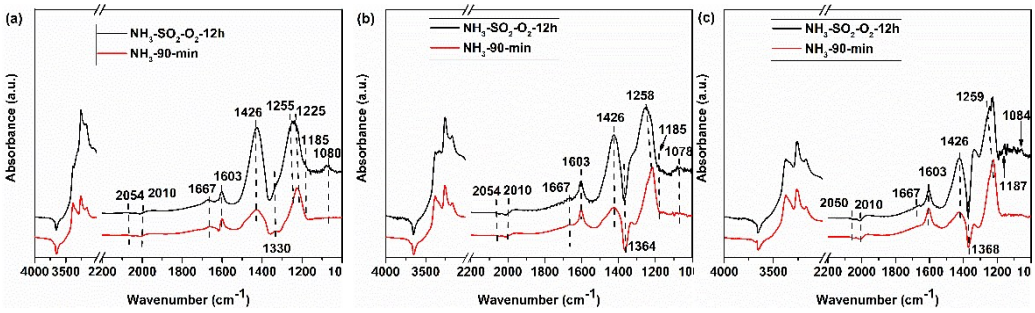

Fig.S7 *in situ* FTIR spectra of V/WTi under different conditions at 200 ˚C (a), 250 ˚C (b) and 300 ˚C (c), respectively.

H_2O+NH_3+SO_2+O_2 co-adsorption

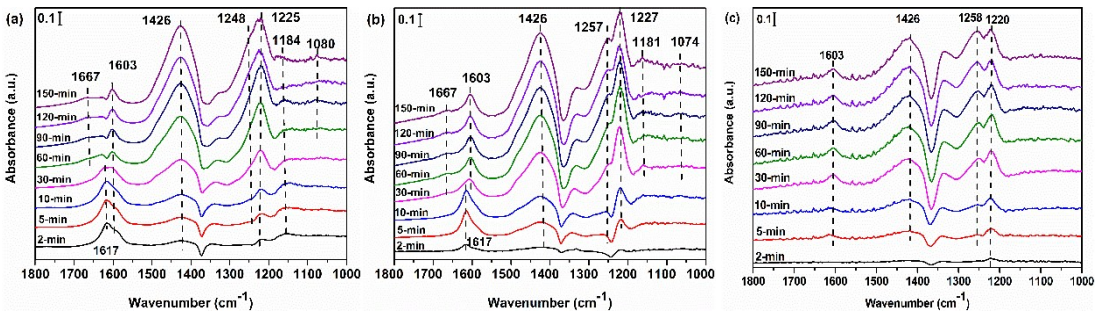

Fig.S8 *in situ* FTIR spectra of V/WTi exposed to NH_3+ SO_2+O_2+H_2O for various time at 200 ˚C (a), 250 ˚C (b) and 300 ˚C (c), respectively.

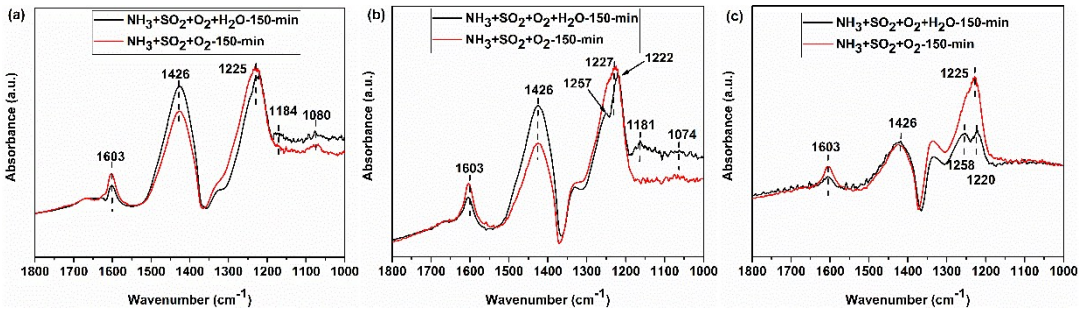

Fig.S9 *in situ* FTIR spectra of V/WTi exposed to NH_3+ SO_2+O_2 with or without H_2O for 150 min at 200 ˚C (a), 250 ˚C (b) and 300 ˚C (c), respectively.

The water vapor is introduced to simulate the real operation process. In Fig.S8(a), the band at 1617 cm^{-1} attituded to H_2O is observed at first 2 min [1]. With time increasing, the bands at 1667, 1603, 1426 and 1225 cm^{-1} assigned to adsorbed ammonium species and the bands at 1256, 1180, 1084 cm^{-1} attributed to ABS also appear. As shown in Fig.S9 (a), the intensities of bands at 1426, 1184 and 1080 cm^{-1} increase with the presence of H_2O, which indicates that more ABS species form. The bands at 1603 and 1225 cm^{-1} obviously decrease, which reveals that the presence of H_2O promotes to generate more Brønsted acid sites and is beneficial for the formation of ABS. At 250 ˚C, the similar phenomenon could be detected. At 300 ˚C, the bands ascribed to NH_4^+ species remain also unchanged, while the bands attributed to sulfate species sharply decrease with the H_2O adding, as shown in Fig.S9 (c). These results indicate that the competitive adsorption of H_2O on the catalyst results in less amounts of sites available for the adsorption of NH_3 and SO_2, which results in less ABS species.

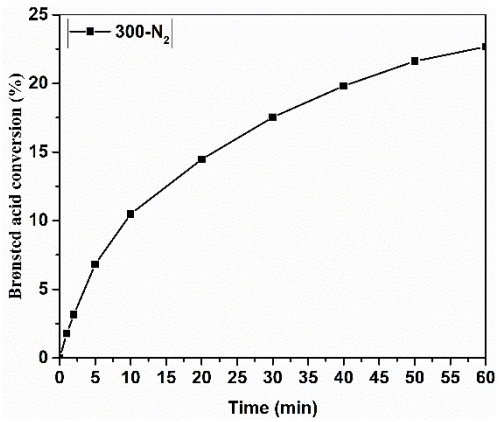

Fig.S10 the integral conversion of NH_4^+ adsorbed on Brønsted acid sites (1426 cm^{-1}) over the catalyst pretreated by exposing to NH_3+ SO_2+O_2 for 12h as a function of time in the presence of N_2 purging at 300 ˚C.

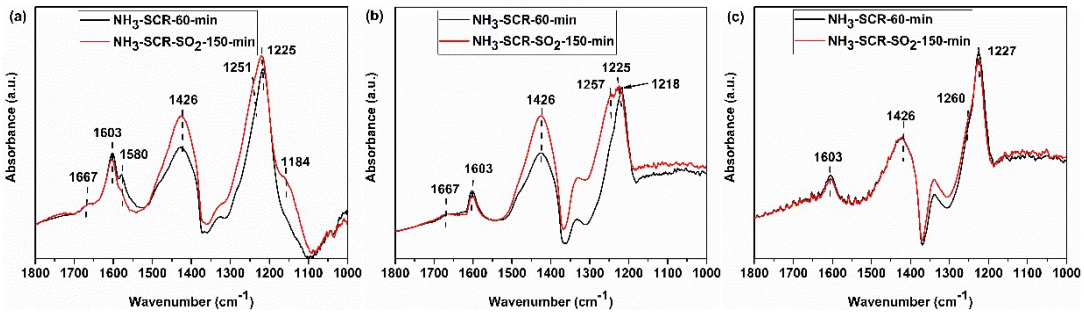

Fig. S11 *in situ* FTIR spectra of V/WTi exposed to NH_3-SCR with or without SO_2 at 200 ˚C (a), 250 ˚C (b) and 300 ˚C (c), respectively.

References

1. W. Xu, H. He and Y. Yu, *J. Phys. Chem. C*, 2009, **113**, 4426-4432.