Supporting Information

The mechanism of ammonium bisulfate formation and decomposition over V/WTi catalysts for NH₃-selective catalytic reduction at various temperature

Chenxu Li, Meiqing Shen, Tie Yu, Jianqiang Wang, Jun Wang and Yanping Zhai

a Key Laboratory for Green Chemical Technology of State Education Ministry, School of Chemical Engineering & Technology, Tianjin University, Tianjin 300072, PR China
b Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, PR China
c State Key Laboratory of Engines, Tianjin University, Tianjin 300072, PR China
d Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, PR China
e China Huadian Science and Technology Institute, Beijing 100070, PR China

* Corresponding author: Meiqing Shen, Yanping Zhai

Postal address:
School of Chemical Engineering and Technology, Tianjin University, 92 Weijin Road, Nankai District, Tianjin 300072, China
China Huadian Science and Technology Institute, Beijing 100070, China

Email: mqshen@tju.edu.cn; yanpingzhai@chai.ac.cn
Tel./Fax: (+86) 22-27892301; (+86)-10-59216261
Catalyst preparation

The V$_2$O$_5$/WO$_3$-TiO$_2$ catalyst with 1 wt % V$_2$O$_5$ 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$_2$O$_5$ 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$_4$HSO$_4$ or 10 % (NH$_4$)$_2$SO$_4$

The V/WTi-F catalysts were mechanically mixed with 10 % NH$_4$HSO$_4$ or 10 % (NH$_4$)$_2$SO$_4$ sufficiently and the obtained samples were donated as V/WTi-F- NH$_4$HSO$_4$ and V/WTi-F- (NH$_4$)$_2$SO$_4$, 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 N₂ for 0.5 h to remove any weakly adsorbed impurities. The concentration of SO₂ 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 NH₃-SCR performance of these samples for the second round test: (a) NOₓ conversion and (b) N₂O concentration.

**Fig. S2** NH₃-TPD profile of the obtained catalysts.
Fig.S3 The TPDC profiles of SO$_2$ on V/WTi-F mechanically mixed with 10 % NH$_4$HSO$_4$ or 10 % (NH$_4$)$_2$SO$_4$ (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$_2$O+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$_2$O 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$_2$O 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$^{-1}$ attributed to H$_2$O is observed at first 2 min. 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$_2$O, which indicates that more ABS species form. The bands at 1603 and 1225 cm$^{-1}$ obviously decrease, which reveals that the presence of H$_2$O 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$_2$O adding, as shown in Fig. S9 (c). These results indicate that the competitive adsorption of H$_2$O 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**