

Supporting Information

Deeply revealing the deactivation and decomposition mechanism of ammonium bisulfate on the nanotube structured SCR catalyst for low-temperature NH₃-SCR reaction

Qiang Zhao^{a,b}, Xiaosheng Huang^{a*}, Guodong Zhang^a, Rongji Cui^a, Jiyi Zhang^b,

Zhicheng Tang^{a*}

*(^a National Engineering Research Center for Fine Petrochemical Intermediates,
State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of
Chemical Physics, Chinese Academy of Sciences, Lanzhou, 730000, China.*

^b School of Petroleum and Chemical, Lanzhou University of Technology,

Lanzhou 730050, China.)

*Corresponding author.

E-mail address: tangzhicheng@licp.cas.cn (Z. Tang).

1. Catalyst characterizations

The microstructure of the catalysts was observed by JEOL JEM-2010 transmission electron microscope. Rigaku D/MAX-RB X-ray diffractometer (XRD) was used to scan the catalysts in the range of 10-80°. The catalysts were scanned in the range of 100-2000 cm^{-1} by Lab Ram HR Evolution confocal microscope. The surface area and pore structure of the catalyst were detected and analyzed by N_2 adsorption-desorption experiment using Micromeritics ASAP 2010 instrument. The surface acidity, oxidation reduction and sulfates desorption behavior of the catalysts was measured by Tian-jinXQ TP-5080D auto-adsorption apparatus equipped with a thermal conductivity detector (TCD). The test procedure of H_2 -TPR was as follows: Firstly, 50 mg catalyst was pretreated in 30 mL/min nitrogen atmosphere at 300 °C for 1 h, then N_2 as equilibrium gas and 5 vol% H_2 as reduction gas was heated from 30 °C to 900 °C for desorption experiment. The test procedure of NH_3 -TPD was as follows: the pretreatment process was consistent with H_2 -TPR, then the catalyst was exposed to the atmosphere with N_2 as equilibrium gas and NH_3 content of 5 vol% at 100 °C for adsorption for 30 min. The temperature was raised to 800 °C in N_2 atmosphere for desorption experiment after the NH_3 valve was closed. The test procedure of He-TPD was as follows: 50 mg catalyst was pretreated in 30 mL/min helium atmosphere at 100 °C for 1 h, then the catalyst was exposed to the He atmosphere and elevated the temperature to 800 °C to observe the desorption behavior of sulfates. The NETZSCH STA 449F5 tester was used to increase the temperature from room temperature to 800 °C for TG/DSC testing of the catalyst.

The elemental compositions and valence states on the catalyst surface were qualitatively and quantitatively analyzed by XPS photoelectron spectrometer of VG ESCALAB 210 (Mg K α radiation was 1253.6 eV). The catalyst was tested at 500-4000 cm⁻¹ using Nexus 870 scanning Fourier transform infrared spectroscopy. To explore the reaction mechanism of the catalyst, in-situ DRIFTS experiment was performed on a Fourier Transform infrared (FTIR) spectrometer (VERTEX 70) equipped with a Harrick DRIFTS cell and a liquid nitrogen cooled mercury cadmium telluride (MCT) detector. Firstly, the catalyst was pretreated in the N₂ atmosphere (30 mL/min) for 30 min at 300 °C. The background spectrum was collected in the flow of N₂ after pretreatment and was automatically subtracted from the sample spectrum for each test. Then the catalyst was exposed into the NH₃ (1 vol%) or NO + O₂ (1 vol%) atmosphere for 30min at 50 °C. The desorption experiment was carried out in the N₂ atmosphere with the temperature gradually increased from 50 °C to 300 °C. For the transient reaction of NO + O₂ and pre-adsorption of NH₃, the catalyst was first exposed to 1 vol% NH₃ gas at 200 °C for 30 min, then 1 vol% NO + O₂ was introduced for reaction. For the transient reaction of NH₃ and NO + O₂ pre-adsorption, the rest of the operation was the same as the previous steps except that the gas addition sequence was reversed.

Figure S1. N₂ selectivity of catalysts at different temperatures.

Figure S2. SEM images of Ce-Mn-TNTs (a) and Ce-Mn-TNTs-R (b).

Figure S3. XRD patterns of Ce-Mn-TNTs-R and Ce-Mn-TNTs-F.

Figure S4. He-TPD of catalysts.

Figure S5. N₂ adsorption-desorption isotherms (a-b) and BJH desorption pore size distribution (c) of catalysts.

Figure S6. N 1s spectra of the catalysts loaded with ABS.

Table S1. ICP results of catalysts.

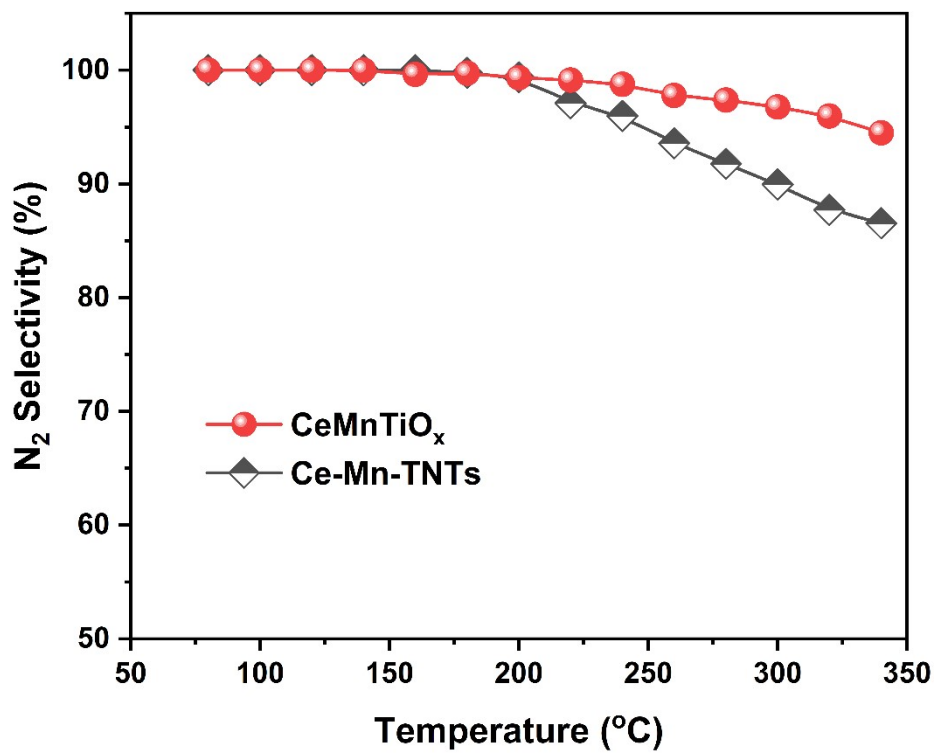


Figure S1. N₂ selectivity of catalysts at different temperatures.

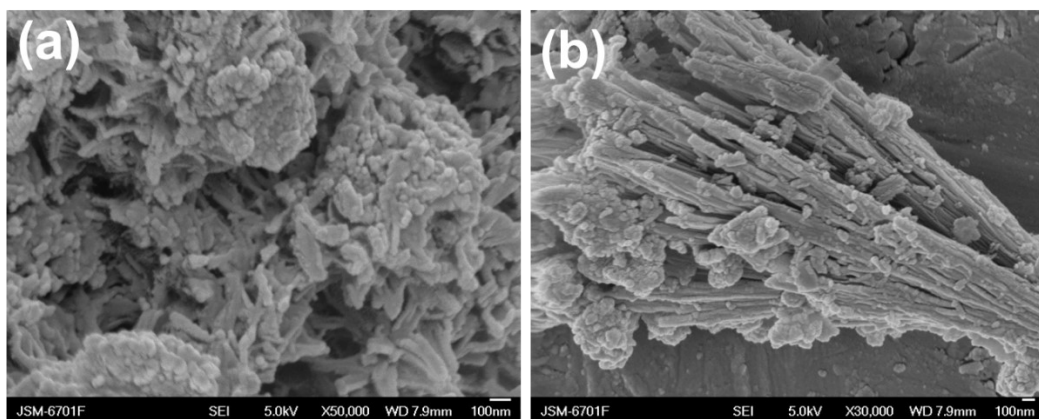


Figure S2. SEM images of Ce-Mn-TNTs (a) and Ce-Mn-TNTs-R (b).

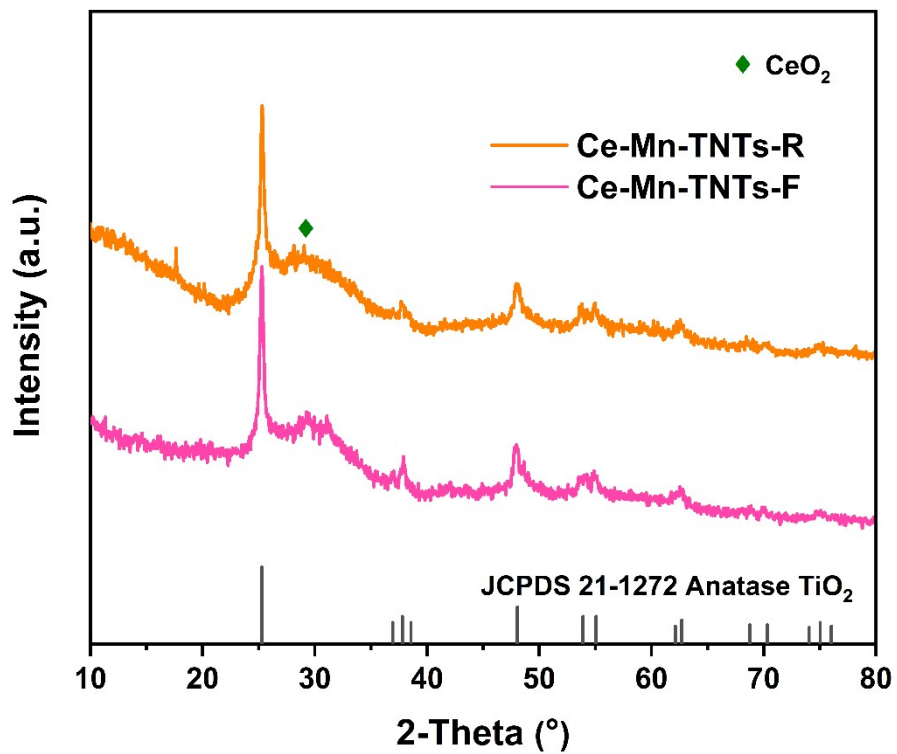


Figure S3. XRD patterns of Ce-Mn-TNTs-R and Ce-Mn-TNTs-F.

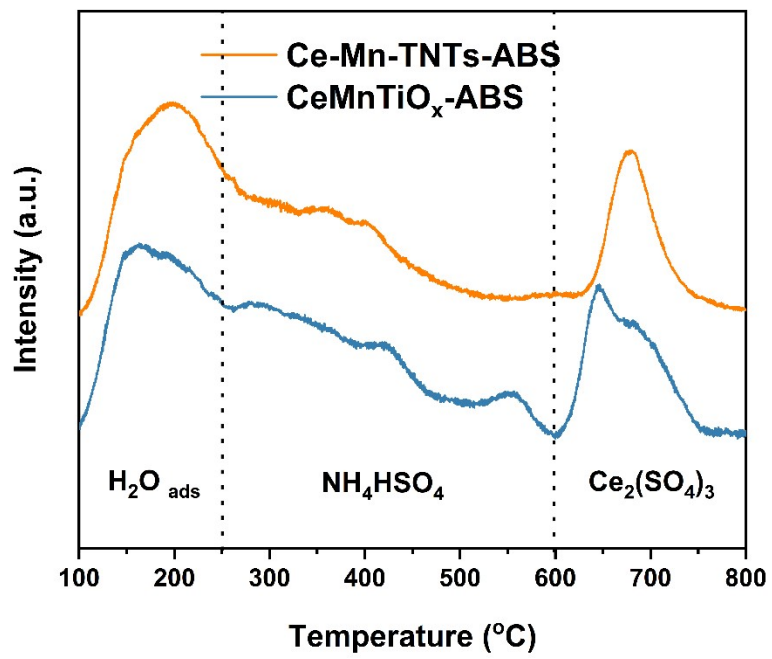


Figure S4. He-TPD of catalysts.

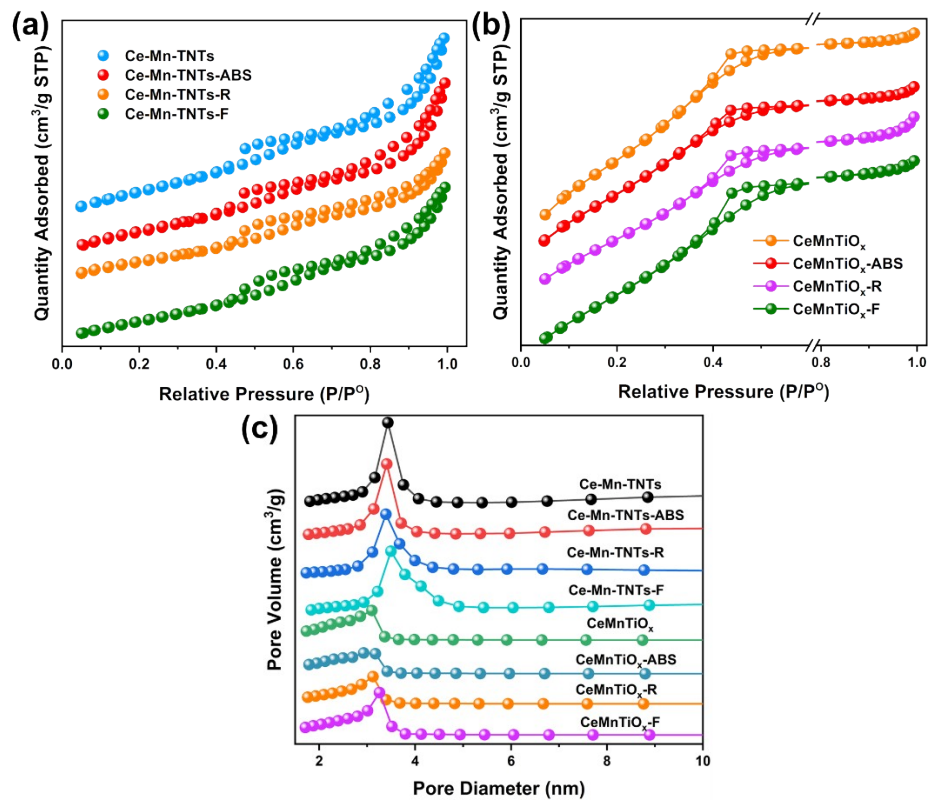


Figure S5. N₂ adsorption-desorption isotherms (a-b) and BJH desorption pore size distribution (c) of catalysts.

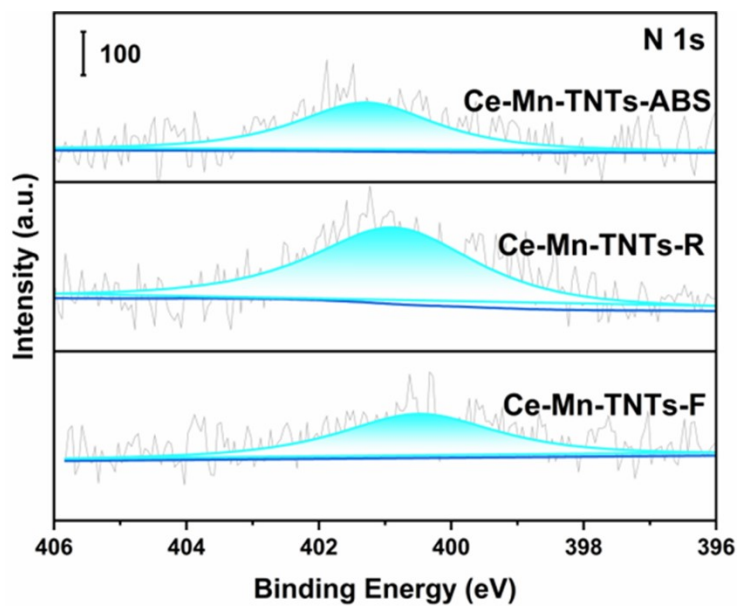


Figure S6. N 1s spectra of the catalysts loaded with ABS.

Table S1. ICP results of catalysts.

Samples	S content (wt%)
CeMnTiO _x -ABS	0.80
CeMnTiO _x -R	0.76
CeMnTiO _x -F	0.73
Ce-Mn-TNTs-ABS	1.0
Ce-Mn-TNTs-R	0.91
Ce-Mn-TNTs-F	0.52