Electronic Supplementary Material (ESI) for Catalysis Science & Technology.
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Suppression of N_2O formation by H_2O and SO_2 in selective catalytic reduction of NO with NH_3 over Mn/Ti–Si catalyst

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Powder X–ray diffraction (XRD) patterns were measured on a Rigaku Ultima IV diffractometer (Japan) with Cu Kα radiation (λ = 1.5406 Å) by a sampling interval of 0.02 degrees. As depicted in Figure S1, the Ti–Si support existed as a single form of anatase phase. There are no peaks corresponding to SiO_2, implying that the 4.4% SiO_2 may be dispersed uniformly as amorphous or micro-crystalline phase on TiO_2. A new phase of pyrolusite MnO_2 was detected for Mn/Ti–Si catalyst.

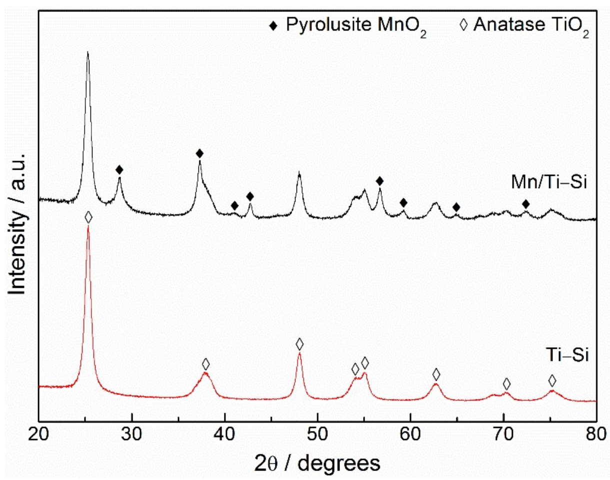

Figure S1. Powder XRD patterns of Ti–Si support and Mn/Ti–Si catalyst.

Nitrogen adsorption–desorption isotherms at 77 K were carried on an ASAP 2010 instrument (Micromeritics, USA) to calculate the BET specific surface area, pore volume and average pore diameter. As shown in Figure S2, the results should be indicative of type IV isotherms with H3 loops in terms of IUPAC classification, which suggests non-rigid mesoporous structures. The BJH desorption pore distribution profiles show that the pore diameter of both Ti–Si support and Mn/Ti–Si catalyst range mainly from 6 to 21 nm.

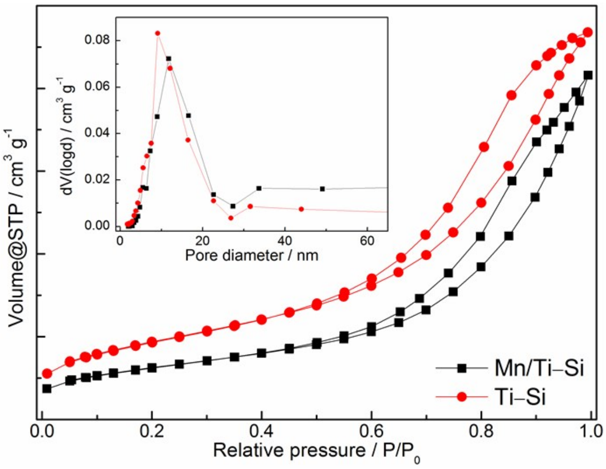

Figure S2. Nitrogen adsorption-desorption isotherms and the corresponding BJH desorption pore distribution (insert) for Mn/Ti–Si catalyst and Ti–Si support.

As shown in Table S1, the average pore diameter of Ti–Si support increased from 8.6 to 11.5 nm and the pore volume decreased from 0.36 to 0.32 $cm^3\ g^{-1}$ after the impregnation of Mn component. Additionally, the BET surface area decreased from 168 to 112 $m^2\ g^{-1}$. These results indicate that a part of the small pores of Ti–Si support were blocked after impregnation.

Table S1 BET surface area, average pore diameter and pore volume for Ti–Si and Mn/Ti–Si.

Samples	BET surface area / $m^2\ g^{-1}$	Average pore diameter / nm	Pore volume / $cm^3\ g^{-1}$
Mn/Ti–Si	112	11.5	0.32
Ti–Si	168	8.6	0.36

Table S2 H_2 consumption of MnO_x and $MnSO_4$ reduction for different samples.

Samples	H_2 consumption / mmol g^{-1}	
	MnO_2–Mn_2O_3–Mn_3O_4–MnO	Reduction of $MnSO_4$
Fresh Mn/Ti–Si	3.92	–
Mn/Ti–Si regenerated by NH_3 at 350 °C for 5h	3.75	0.25
Mn/Ti–Si after SCR with SO_2 at 200 °C for 1.5h	2.87	1.56
$MnSO_4$/Ti–Si calcined at 400 °C	1.10	3.66

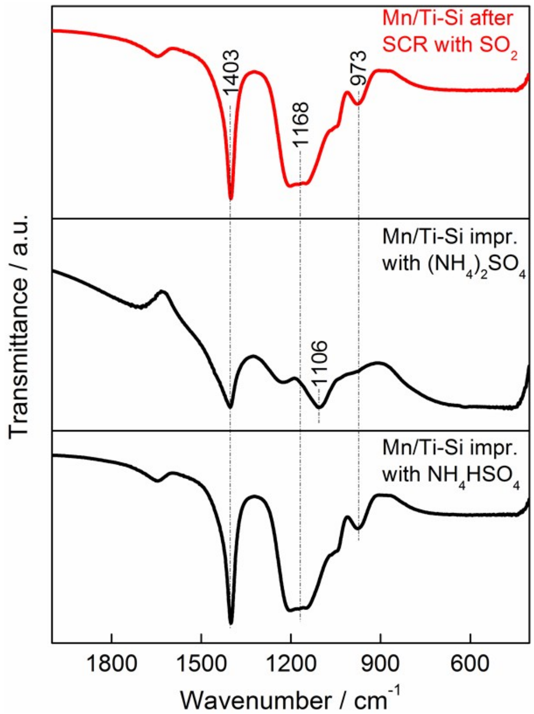

Figure S3. IR spectra for Mn/Ti–Si after SCR with 50 ppm SO_2 at 200 °C for 20h, and Mn/Ti–Si impregnated with $(NH_4)_2SO_4$ and NH_4HSO_4.

The proposed decomposition reaction of $(NH_4)_2SO_4$ and NH_4HSO_4 [1, 2]:

$$2(NH_4)_2SO_4 \rightarrow (NH_4)_2S_2O_7 + 2NH_3 + H_2O \quad \text{(S1)}$$

$$(NH_4)_2S_2O_7 \rightarrow NH_4HSO_4 + SO_3 + NH_3 \quad \text{(S2)}$$

$$6NH_4HSO_4 \rightarrow 2NH_3 + 6SO_2 + 9H_2O + 2N_2 \quad \text{(S3)}$$

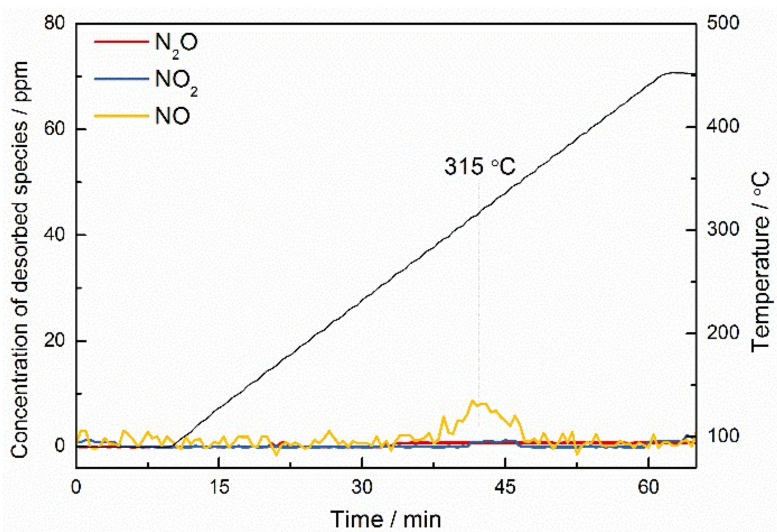

Figure S4. NO_x–TPD profile for Mn/Ti–Si after SCR with 50 ppm SO_2 at 200 °C for 20h.

The N_2 selectivity was calculated according to the following formula:

$$N_2\ selectivity = \frac{[NO]_{in} - [NO]_{out} - [NO_2]_{out} - 2[N_2O]_{out}}{[NO]_{in} - [NO]_{out}} \times 100\ \% \qquad \text{(S1)}$$

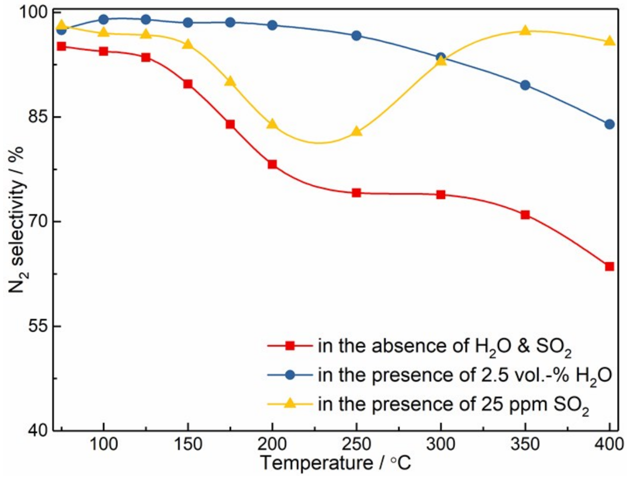

Figure S5. N_2 selectivity for SCR reaction in the absence of H_2O and SO_2, in the presence of 2.5 vol.-% H_2O and in the presence of 25 ppm SO_2 over Mn/Ti–Si catalyst ([NO] = 500 ppm, [NH_3] = 575 ppm, [O_2] = 4 %, He balance and GHSV = 50 000 h^{-1}).

1. H. I. Saleh and K. M. Hassan, *J. Chem. Technol. Biot.*, 2004, **79**, 397-402.
2. C. K. Pang, Y. Q. Zhuo and Y. D. Qin, *Proceedings of 2018 2nd International Conference on Green Energy and Applications*, 2018, 254-262.