Supporting Information for New Journal of Chemistry

MnO₂-GO-Scroll-TiO₂-ITQ2 as low-temperature NH₃-SCR Catalyst with wide SO₂-tolerance temperature range

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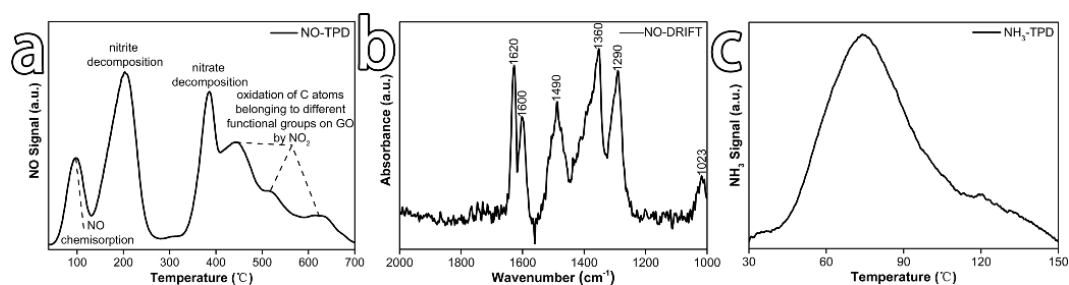
Additional Figures

Fig. S1 NO-TPD, DRIFT and NH₃-TPD results of MnO₂-GOS.

Figure S1a is the NO-TPD result of the MnO₂-GOS obtained by monitoring the ion peak (m/z) 30 with mass spectrometry. There are four kinds of NO: chemisorbed NO, NO produced by nitrite decomposition, NO produced by direct decomposition of nitrate and NO formed after nitrate oxidation of GO. The DRIFT result in Figure S1b validates the above results. Some strong bands were observed at 1350-1650, 1290 and 1023 cm^{-1}. the bands at 1360 cm^{-1} caused by and nitrite.[1] The bands at 1490 and 1290 cm^{-1} were attributed to nitrate species.[2] The results showed that NO was easily oxidized to nitrite and nitrate species on the surface of the MnO₂-GOS. Figure S1c is the NH₃-TPD result of MnO₂-GOS. Due to the existence of oxygen-containing functional groups on the surface of GO, MnO₂-GOS has a certain degree of acidity. The above results show that MnO₂-GOS is still redox and acidic which could be used as a catalyst for NH₃-SCR.
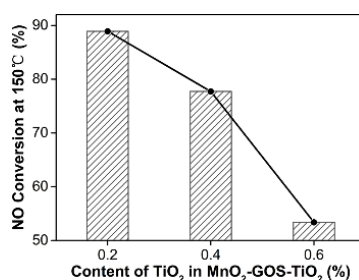

Fig. S2 The effect of the amount of TiO₂ deposition on the activity.

Changing the ratio of Mn to Ti does change oxidation capacity. However, one of the disadvantages of adjusting the oxidation activity by changing the ratio is that it will have a great impact on the low-temperature activity, as shown in the Figure S2. This is why we choose super-large specific surface area GO and ALD-Ti to reduce the amount of doping. From the point of view of the least impact on the activity, we use MnO₂(97.8 %)-GOS(2 %)-TiO₂(0.2 %) as NH₃-SCR catalyst.
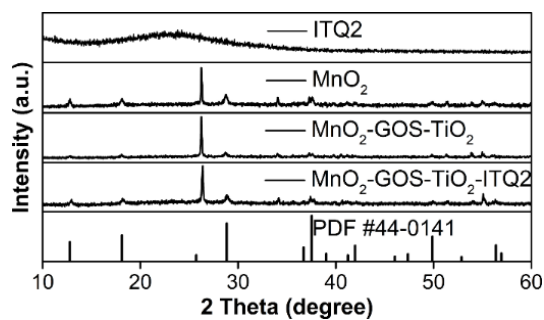
Fig. S3 Structural characterization: XRD pattern of ITQ2, MnO_2, MnO_2-GOS-TiO_2 and MnO_2-GOS-TiO_2-ITQ2.
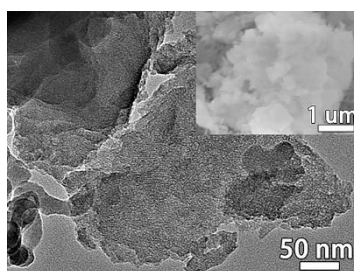

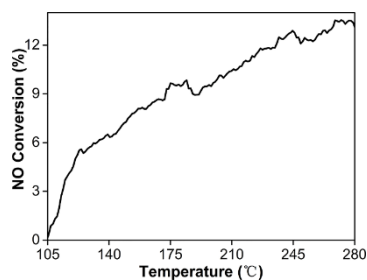**Fig. S4** Morphology characterization: TEM image of ITQ2. Inset is the SEM image.

Fig. S5 Catalyst performance: activity of ITQ2.

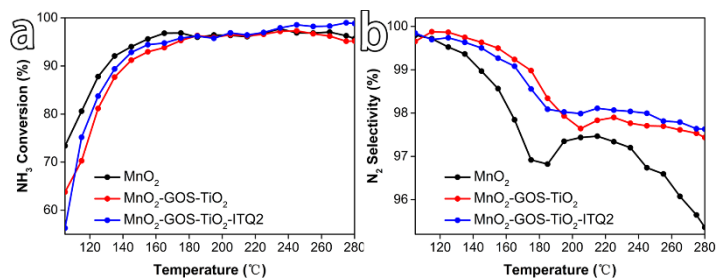ITQ2 almost have no de-NO catalytic activity in the range of reaction temperature.

Fig. S6 Catalyst performance: (a) NH_3 conversion and (b) N_2 selectivity of MnO_2, MnO_2-GOS-TiO_2 and MnO_2-GOS-TiO_2-ITQ2 in the presence of steam.
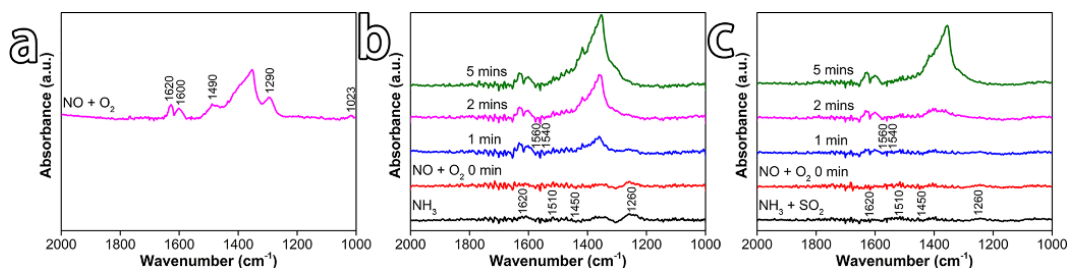
Fig. S7 DRIFT spectra of MnO$_2$-GOS-TiO$_2$ treated by flowing (a) 1000 ppm NO + 2 vol % O$_2$ (b) 50 °C upon passing NO + O$_2$ over the 1000 ppm NH$_3$ (c) 50 °C upon passing NO + O$_2$ over the NH$_3$ + SO$_2$.

Figure S7a showed the NO + O$_2$ DRIFT spectra of MnO$_2$-GOS-TiO$_2$, while Figures S7b and S7c showed that the catalyst adsorbed NH$_3$ and NH$_3$ + SO$_2$ first and then passed through NO + O$_2$. From the 2 min results of Figures S7b and S7c, we could see that the introduction of SO$_2$ does increase the adsorption of NH$_3$ on the surface and it takes a longer time for NO + O$_2$ to consume NH$_3$. Therefore, the addition of SO$_2$ (H$_2$SO$_3$, Brönsted acid) was conducive to the adsorption of NH$_3$ on the catalyst. The activity of catalyst was naturally increased.

Table S1 The S concentration of each catalyst measured by ICP after SO$_2$-tolerance test

Catalysts and conditions	S concentration (mg/g$_{MnO2}$)
MnO$_2$ at 150℃ for 3 h	5.11
MnO$_2$-GOS-TiO$_2$ at 150℃ for 30 h	0.36
MnO$_2$-GOS-TiO$_2$ at 200℃ for 6 h	4.10
MnO$_2$-GOS-TiO$_2$-ITQ2 at 200℃ for 6 h	3.97

Table S2 Comparison of SO$_2$-tolerant performance

Catalyst	Space Velocity (mL g^{-1} h^{-1})	SO$_2$ Concentration (ppm)	Temperature (°C)	SO$_2$-Tolerant Time[a] (h)	NO Conversion (%)	Reference
MnO$_2$-CeO$_2$-OMS2	64,000	150	150	1.8	55	[3]
Fe$_2$O$_3$-SBA150	15,000	800	250	16	50	[4]
La$_x$Sr$_{1-x}$MnO$_3$	120,000	100	250	0.5	55	[5]
MnO$_2$-TiO$_2$-CeO$_2$-V$_2$O$_5$	70,000	100	200	13	80	[6]
MnO$_2$-TiO$_2$	150,000	100	200	5	83	[7]
MnO$_2$-TiO$_2$	150,000	100	150	5	64	[7]
MnO$_2$-CuO-TiO$_2$	20,000	200	150	6	75	[8]
CuO-Fe$_2$O$_3$-WO$_3$-TiO$_2$	40,000	100	220	13	93	[9]
MnO$_2$-MoO$_3$-Al$_2$O$_3$	35,000	100	150	2	81	[10]
MnO$_2$-CuO-TiO$_2$	8,0000	100	200	6	65	[11]
CeO$_2$-SnO$_2$-TiO$_2$	30,000	300	240	8	55	[12]
CeO$_2$-Sm$_2$O$_3$-TiO$_2$	90,000	200	250	29	80	[13]
CuO-Sb$_2$O$_3$-TiO$_2$	60,000	500	250	9	86	[14]
MnO$_2$-Co$_3$O$_4$	80,000	50	180	10	60	[15]
MnO$_2$-GOS-TiO$_2$	40,000	100	150	>100	90	This work
MnO$_2$-GOS-TiO$_2$-ITQ2	20,000	100	200	>100	90	This work

[a] SO$_2$-tolerance time is only the test time, not the longest time to resist SO$_2$ poisoning.

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