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# MnO<sub>2</sub>-GO-Scroll-TiO<sub>2</sub>-ITQ2 as low-temperature NH<sub>3</sub>-SCR Catalyst with wide SO<sub>2</sub>-tolerance temperature range

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Three steps are needed to improve the steam-resistance and SO<sub>2</sub>-resistance of the catalyst for selective catalytic reduction of NO<sub>x</sub> through NH<sub>3</sub> at low temperature: The first is to introduce a protective layer to reduce the direct contact between SO<sub>3</sub> and the catalyst. Then there is delayed oxidation, which fundamentally reduces the oxidation of SO<sub>2</sub> to SO<sub>3</sub>. If the catalyst is used at a relatively high temperature, it is inevitable to produce SO<sub>3</sub>. The third step is to add a strong acid site in addition to reducing the acidity of the catalyst, which first absorbs NH<sub>3</sub> and then absorbs SO<sub>3</sub>, to seize NH<sub>4</sub>HSO<sub>4</sub>, so that it does not cover the active site. GO was used to curl and wrap around the outside of MnO<sub>2</sub> nanowires as a protective layer. TiO<sub>2</sub> was selectively deposited on oxygen-containing functional groups on GO, which delayed the oxidation ability of the catalyst. ITQ2 molecular sieves acted as strong acid sites to absorb NH<sub>4</sub>HSO<sub>4</sub>. The curling behavior of GO outside MnO<sub>2</sub> nanowires, the deposition location of TiO<sub>2</sub> and the distribution of ITQ2 were explained by morphology and elemental analysis. In the range of 150 °C to 280 °C, the conversion of MnO<sub>2</sub>-GO-scroll-TiO<sub>2</sub>-ITQ2 catalyst to N<sub>2</sub> was more than 85 %. Combined with H<sub>2</sub>-TPR and activity test, the source of the wide SO<sub>2</sub>-tolerance temperature range of the catalyst was described in detail.

### Introduction

In 2018, NO<sub>x</sub> emissions from the non-power sector accounted for 69 percent of the total emissions of 16.32 million tons, making it the largest source of emissions in China. Considering that the flue gas temperature produced by non-electric power industry is generally lower than 250 °C.<sup>1</sup> When NH<sub>3</sub>-SCR catalyst runs at low temperature, a small amount of SO<sub>2</sub> in flue gas is oxidized to SO<sub>3</sub>, on the one hand, it destroys the catalyst directly, on the other hand, in the presence of NH<sub>3</sub> and H<sub>2</sub>O, NH<sub>4</sub>HSO<sub>4</sub> forms and covers the surface of the catalyst to deactivate it.<sup>2</sup> Therefore, the denitrification of SO<sub>2</sub>-containing flue gas at low temperature is an urgent problem to be broken through.

It is found that the root cause of the poor anti-SO<sub>2</sub> poisoning ability of low-temperature NH<sub>3</sub>-SCR catalyst lies in the strong oxidation of the catalyst. Strong oxidation enables the catalyst to oxidize NO to NO<sub>2</sub>, in order to have low-temperature activity, but the catalyst with strong oxidation can also oxidize SO<sub>2</sub> to SO<sub>3</sub>, which leads to the poisoning of the catalyst.<sup>3</sup> From the standard electrode potential, it can be seen that SO<sub>2</sub> is more difficult to be oxidized than NO in Equation 1 and 2:

$$NO_{2} + H_{2}O + e^{-} \rightarrow NO + 2OH^{-} \quad E^{\theta} = -0.46V \quad (1)$$
  
$$SO_{4}^{2-} + H_{2}O + 2e^{-} \rightarrow SO_{3}^{2-} + 2OH^{-} \quad E^{\theta} = -0.93V \quad (2)$$

By adjusting the oxidation of the catalyst, the catalyst can only oxidize or preferential oxidize NO, but not or less oxidize SO<sub>2</sub>.<sup>4</sup> In this

way, the anti-SO<sub>2</sub> poisoning ability of the catalyst was improved.<sup>5</sup> One of the disadvantages of the method of adjusting the oxidation of the catalyst by coating or doping other transition metal oxides is that a certain amount must be used, which will inevitably affect the low-temperature activity of the catalyst.

In addition, when the catalyst is in actual operation, the flue gas temperature is constantly changing, for example, the temperature is high when the equipment is just started, and the temperature will decrease when the equipment runs smoothly, which puts forward the requirement for the SO<sub>2</sub>-tolerance of SCR catalyst in a wide temperature range. It is true that the production of SO<sub>3</sub> can be reduced by delaying oxidation, but once the flue gas temperature rises, a small amount of SO<sub>3</sub> may be formed and the catalyst becomes intolerant to SO<sub>3</sub>. At this point, the acidity must be adjusted by adding an additional strong acid site at the same time, which adsorbs saturated NH<sub>3</sub> and then further SO<sub>3</sub>. Even if a small amount of SO<sub>2</sub> is oxidized to SO<sub>3</sub>, it will be absorbed by strong acid sites, so that the formed NH<sub>4</sub>HSO<sub>4</sub> does not cover the active site and the catalyst can maintain the activity.

In this paper, we synthesized MnO<sub>2</sub>-GO-scroll-TiO<sub>2</sub>-ITQ2 catalyst. A small amount of two-dimensional GO and ITQ2 molecular sieves were combined with TiO<sub>2</sub> deposited by ALD to form SCR catalysts with wide SO<sub>2</sub>-tolerant temperature range. Firstly, MnO<sub>2</sub> nanowires were synthesized and GO were curled and wound outside MnO<sub>2</sub> nanowires to form MnO<sub>2</sub>-GO-scroll (MnO<sub>2</sub>-GOS) nanowire-nanoscroll composite structures. GO can transfer electrons, so the composite catalyst still has redox performance and can catalyse SCR reaction. On the one hand, ALD-TiO<sub>2</sub> makes up for the surface defects of GO and protects GO from being destroyed by SCR atmosphere. On the other hand, it delays the oxidation of MnO<sub>2</sub>-GOS-TiO<sub>2</sub> catalyst and makes MnO<sub>2</sub>-GOS-TiO<sub>2</sub> catalyst have high SO<sub>2</sub> resistance before 150 °C. The acidity of the catalyst wrapped with GO and coated with TiO<sub>2</sub> decreased obviously. MnO<sub>2</sub>-GOS-TiO<sub>2</sub> catalyst was combined with ITQ2 molecular sieve to form a composite catalyst with gradient

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acid sites. When the reaction temperature is higher than 200 °C, even a little amount of resulting SO<sub>3</sub> could be fixed in ITQ2 instead of covering the surface of the catalyst. The temperature range of SO<sub>2</sub>tolerance of MnO<sub>2</sub>-GOS-TiO<sub>2</sub>-ITQ2 catalyst is broadened meeting the complex environmental treatment requirements of boilers in nonelectric power industry.

### **Experimental procedures**

### Preparation of the GO

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GO was produced by an improved Hummers' method.<sup>6</sup> In a typical reaction, 1 g expandable graphite was ground with 40 g NaCl, washed, filtered and dried, and then placed in a 250 ml round-bottom flask containing 23 ml concentrated H<sub>2</sub>SO<sub>4</sub>. The mixture was stirred at room temperature for 24 h. Then the flask was transferred in an oil bath at 40 °C. 0.1 g NaNO<sub>3</sub> was added until it was dissolved. 0.5 g KMnO<sub>4</sub> was slowly added within half an hour to oxidize and peel off the graphite sheets. After an hour of oxidation, the reaction was terminated by adding 140 mL water and 10 ml 30 % H<sub>2</sub>O<sub>2</sub> solution. After being centrifugated, the precipitate was wash twice each with 5 % HCl solution and water. The precipitate was dispersed into 150 mL water and treated with 100 W ultrasonic wave for 20 min. The suspension was centrifuged at 5000 rpm for 5 minutes. The brown uniform supernatant in which the concentration of GO was about 1 mg ml<sup>-1</sup> was used for the following experiments.

### Preparation of the MnO<sub>2</sub> nanowires

2 mmol KMnO<sub>4</sub> and 2 mmol NH<sub>4</sub>F were dispersed into 80 ml water and stirred at room temperature for 30 min. The sample was then transferred into a 100 ml autoclave and heated at 180 °C for 48 h. After being washed and dried, the dark-brown powder was obtained.<sup>7</sup> The BET specific surface area of MnO<sub>2</sub> nanowires is 60.3 m<sup>2</sup> g<sup>-1</sup>.

# Preparation of the $MnO_2$ nanowires and GO nanoscrolls composite ( $MnO_2$ -GOS)

The order of operation for preparation of  $MnO_2$ -GOS composite was similar to that of  $MnO_2$  nanowires. 80 ml GO aqueous solution was used instead of water. CHN elemental analysis showed that the content of GO in  $MnO_2$ -GOS was 2 %. The NO-TPD, DRIFT and NH<sub>3</sub>-TPD results of  $MnO_2$ -GOS were in Figure S1.

# Preparation of the $MnO_2$ -GOS and ALD-TiO<sub>2</sub> composite ( $MnO_2$ -GOS-TiO<sub>2</sub>)

ALD-TiO<sub>2</sub> was selectively deposited on the oxygen-containing functional group of GO scroll by ALD technology in the Picosun R200A device. The carrier gas was 99.99 % high-purity N<sub>2</sub> and the flow rate was 400 mL min<sup>-1</sup>. The MnO<sub>2</sub>-GOS sample was putted in the ALD reaction chamber. TiCl<sub>4</sub> and H<sub>2</sub>O alternately past through the surface of the sample with a total of 4 cycles. The time of TiCl<sub>4</sub>, N<sub>2</sub>, H<sub>2</sub>O and N<sub>2</sub> were 0.3 s, 13 s, 0.3 s and 13 s, respectively. ICP analysis showed that the content of TiO<sub>2</sub> was 0.2 %. The BET Specific surface area of MnO<sub>2</sub>-GOS-TiO<sub>2</sub> was 61.3 m<sup>2</sup> g<sup>-1</sup>. The effect of the amount of TiO<sub>2</sub> deposition on the activity is shown in the Figure S2.

### Preparation of ITQ2 molecular sieves

The typical 0.23 g NaAlO<sub>2</sub> and 0.81 g NaOH were dissolved in 103 g water, and then 6.35 g hexamethyleneimine and 7.86 g silica were

added in turn. The mixture was stirred at room temperature for 30 min and then transferred into a 100 ml autoclave03hd meated at 135 °C for 11 d. The crystal product was washed with water to pH < 9, and then the precipitate was mixed with water to make a slurry with a solid content of 20 %. 27 g slurry was stirred with 105 g 29 wt % hexadecyltrimethylammonium bromide solution and 33 g 40 wt % tetrapropylammonium hydroxide solution at 80 °C for 16 h and then treated with 100 W ultrasonic wave for 1 h. A few drops of concentrated HCl were added to the slurry until the pH was adjusted below 2. After being centrifugated, ITQ2 was obtained by calcinating the precipitate at 540 °C for 5 h.<sup>8</sup> The BET Specific surface area of ITQ2 was 806.1 m<sup>2</sup> g<sup>-1</sup>.

### Preparation of the MnO<sub>2</sub>-GOS-TiO<sub>2</sub> and ITQ2 composite (MnO<sub>2</sub>-GOS-TiO<sub>2</sub>-ITQ2)

The composited MnO<sub>2</sub>-GOS-TiO<sub>2</sub> were dispersed in ethanol, and mixed with ITQ2 (MnO<sub>2</sub>: ITQ2 = 1: 1 in weight ratio). The mixture was stirred under 80 °C until it was dry. Then, the blend was collected. The BET Specific surface area of MnO<sub>2</sub>-GOS-TiO<sub>2</sub>-ITQ2 was 440.0 m<sup>2</sup> g<sup>-1</sup>.

### Activity test

The NH<sub>3</sub>-SCR of NO<sub>x</sub> activity of the catalyst was measured in a fixedbed reactor. The catalyst was located between two stages of quartz cotton. Quartz sand was placed on the top of quartz cotton as the preheating zone. Every tested temperature from 105 °C to 280 °C was held for 0.5 h. The flow was 500 ppm NO, 500 ppm NH<sub>3</sub>, 5 vol % O<sub>2</sub>, 10 vol % steam, 100 ppm SO<sub>2</sub> (when used) and Ar as the equilibrium gas with the space velocity of 40 000 mL g<sup>-1</sup> h<sup>-1</sup>. The online mass spectrometer (QIC-20, Hiden) was used to continuously monitor the types and concentrations of gases in the inlet and outlet streams. The gas was cooled in the ice bath before entering the mass spectrometry. The ion peaks (m/z) of these substances were determined as follows: 30 NO, 15 NH<sub>3</sub> and 44 N<sub>2</sub>O. The NO conversion and N<sub>2</sub> selectivity were calculated as follows:

$$\begin{split} C_{NO} &= ([NO]_{in} - [NO]_{out}) / [NO]_{in} \times 100\% \eqno(3) \\ S_{N2} &= \{1 - [N_2O]_{out} / ([NH_3]_{in} - [NH_3]_{out} + [NO]_{in} - [NO]_{out})\} \times 100\% \end{split}$$

### Catalyst characterization

The X-ray diffraction (XRD) measurements with Cu K $\alpha$  radiation in the range from 10° to 60° were recorded on the D/Max 2400 X-ray diffractometer. X-ray photoelectron spectroscopy (XPS) was measured by using Escalab 250 spectrometer with monochromatic X-ray source (Al K $\alpha$ , hv = 1486.6 eV). The spectrometer has been calibrated with the Au 4f<sup>7/2</sup>, Cu 2p<sup>3/2</sup> and Ag 3d<sup>5/2</sup> peaks. The standard deviation of binding energy (BE) is 0.1 eV. The morphological images were captured by the field emission scanning electron microscope (FESEM, Hitachi SU8010). The transmission electron microscope (TEM) images and scanning transmission electron microscope (STEM) maps under the voltage of 200 kV were obtained on the FEI Tecnai G<sup>20</sup>.

The temperature-programmed desorption of NH<sub>3</sub> (NH<sub>3</sub>-TPD) was carried out by the quadrupole mass spectrometer. NH<sub>3</sub> signal (m/z = 17) was recorded. Before the TPD experiment, the sample (50 mg) was pre-treated at 200 °C for 2 h and cooled to room temperature in Ar flows. The sample was then exposed to the 1000 ppm NH<sub>3</sub>/Ar flow

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at room temperature for 1 h, then purged with Ar flow for another 1 h. Finally, the temperature was raised to 200 °C in Ar flow with a heating rate of 5 °C min<sup>-1</sup>.

In the experiment of temperature-programmed reduction of H<sub>2</sub> (H<sub>2</sub>-TPR), the sample (50 mg) was pre-treated at 200 °C for 2 h and cooled to room temperature in Ar flows. The temperature was raised to 500 °C in 5 vol % H<sub>2</sub>/Ar flow with a heating rate of 5 °C min<sup>-1</sup>. The consumption of H<sub>2</sub> was detected by the thermal conductivity cell detector.

### **Results and discussion**

The preparation of MnO<sub>2</sub>-GOS-TiO<sub>2</sub>-ITQ2 was divided into three steps. Firstly, a layer of GO was coated around the MnO<sub>2</sub> nanowire by oriented assembly and self-scroll. Full coating can be achieved with the least amount by using the large specific surface area of GO. Secondly, a small amount of TiO<sub>2</sub> was selectively deposited on the oxygen-containing functional groups of GO by ALD technique. At the same time of delaying the oxidation of the catalyst, the effect of inactive TiO<sub>2</sub> on the overall activity of the catalyst was reduced. Finally, MnO<sub>2</sub>-GOS-TiO<sub>2</sub> was compounded with ITQ2 molecular sieve to form MnO<sub>2</sub>-GOS-TiO<sub>2</sub>-ITQ2 catalyst. The main reason for choosing ITQ2 molecular sieve is that it is a kind of material which can meet the requirements of specific surface area and acidity.

### Catalyst characterization

SEM and TEM observations were used to investigate the formation and micro-structure of the composite catalyst. The lowmagnification SEM image in Figure 1a inset shows that the MnO<sub>2</sub> nanowire has a length of tens of micrometres. Figure 1a showed the morphology of typical MnO<sub>2</sub> nanowires. The width of nanowires produced by hydrothermal reaction is uniform, mainly distributed around 50 nm. The construction of MnO<sub>2</sub>-nanowires-GO-nanoscrolls is derived from self-assembly and self-crimping, which has been investigated by Yan.7 We plotted a possible schematic anaphrof the formation mechanism of MnO<sub>2</sub>-GOS in Figure 1b. The GO pieces are curled around the outside of the MnO<sub>2</sub> nanowires to form the MnO<sub>2</sub>-GOS composite structure. Figure 1d was the resulting TEM image of taking the sample out of the autoclave during the formation of MnO<sub>2</sub>-GOS. It is obvious that the GO is winding outside the MnO<sub>2</sub>. Because GO is conductive, after coating GO layer, electrons can be transferred between MnO<sub>2</sub>-GOS and O<sub>2</sub> through GO, which makes it possible for MnO<sub>2</sub>-GOS to be used in NH<sub>3</sub>-SCR reaction. After the formation of MnO<sub>2</sub>-GOS composite structure, the result of selective deposition of trace TiO<sub>2</sub> on the surface of GO by ALD technology shows that the operation of ALD does not destroy the existing structure in Figure 1e. The lattice image of GO does exist in HRTEM observation in Figure 1f, and the surface of MnO<sub>2</sub> is surrounded by a layer of GO. Because TiO<sub>2</sub> would delay the oxidation of the catalyst, in order not to affect the low-temperature activity, only a minimal amount of TiO<sub>2</sub> was used from being visible in XRD pattern in Figure S3. MnO<sub>2</sub>-GOS-TiO<sub>2</sub> has the same crystal structure as the original MnO2. Even if the amount is very low, it still shows the existence of Ti in the STEM image in Figure 1g, and the distribution of Ti is particularly uneven compared with Mn and C elements. This is because the characteristics of ALD technology determine that the TiO<sub>2</sub> formed after depositing 4 cycles of TiCl<sub>4</sub> and H<sub>2</sub>O can only exist on the oxygen-containing functional groups of GO. The above observations could reveal the existence of GO-scroll and TiO<sub>2</sub> in the composite structure. The GOS-TiO<sub>2</sub> can be used as an effective shield to prevent the formation of MnSO<sub>4</sub> and NH<sub>4</sub>HSO<sub>4</sub> at low temperature. Figure S4 showed the SEM and TEM images of ITQ2. ITQ2 has an obvious layered structure. After the combination of ITQ2 and MnO2-GOS-TiO<sub>2</sub>, one-dimensional and two-dimensional composite structures were formed in Figure 1c and 1 h.



**Fig. 1** Morphology characterization: (a) TEM image of MnO<sub>2</sub> nanowires; (b) schematic diagram of the formation of MnO<sub>2</sub>-nanowires-GOnanoscrolls; (c) Schematic diagram of the formation of 1D MnO<sub>2</sub>-GOS and 2D ITQ2 composite catalyst; (d) TEM image during the formation of MnO<sub>2</sub>-GOS; (e) TEM, (f) HRTEM and (g) STEM images of MnO<sub>2</sub>-GOS-TiO<sub>2</sub>; insets are the width distribution and SEM image; (h) TEM image of MnO<sub>2</sub>-GOS-TiO<sub>2</sub>-ITQ2; inset is the SEM image. The content of GO, TiO<sub>2</sub> and ITQ2 in MnO<sub>2</sub>-GOS-TiO<sub>2</sub>-ITQ2 were 1 %, 0.1 % and 50 %, respectively.

### Catalyst performance

The temperature range of micro-reaction was set from 105 °C to 280 °C. Water vapor does not condense above 105 °C and GO's maximum antioxidant temperature is 280 °C. In Figure 2a the temperature range of NO to N<sub>2</sub> conversion greater than 86 % are 130-230 °C for MnO<sub>2</sub>, 150-280 °C for MnO<sub>2</sub>-GOS-TiO<sub>2</sub> and 140-280 °C for

 $MnO_2$ -GOS-TiO<sub>2</sub>-ITQ2. The NH<sub>3</sub> conversion and N<sub>2</sub> selectivity data were shown in Figure S5 and S6. At the relatively high temperature stage  $MnO_2$  and  $MnO_2$ -GOS-TiO<sub>2</sub> showed high oxidation in Figure 2b, but the acidity shown in Figure 2c was insufficient. At this time, the direct oxidation of NH<sub>3</sub> to NO leads to the decrease of NO conversion and N<sub>2</sub> selectivity. In comparison, the strong acidity of ITQ2

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the catalyst by SO<sub>2</sub>. In comparison, the MnO<sub>2</sub>-GOS<sub>7</sub>TiO<sub>2+i</sub>catalyst reached stable after about 0.8 h and could run continued stable after about 0.8 h and could run continue the stable after than 100 h at 150 °C. According to the S-XPS analysis of Figure 2e and S-ICP analysis of Table S1, running in the same SO<sub>2</sub>-containing atmosphere, MnO<sub>2</sub> surface contains S after 3 h, while MnO<sub>2</sub>-GOS-TiO2 surface has no S even after 30 h. The above results show that the protective layer of GOS-TiO2 can reduce the production of SO3 and improve the SO<sub>2</sub> resistance of the catalyst by delayed oxidation at 150 °C.



Fig. 2 Catalyst performance and characterization: (a) activity, (b) oxidation (H<sub>2</sub>-TPR) and (c) acidity (NH<sub>3</sub>-TPD) for each of the catalysts: MnO<sub>2</sub>, MnO<sub>2</sub>-GOS-TiO<sub>2</sub> and MnO<sub>2</sub>-GOS-TiO<sub>2</sub>-ITQ2; (d) anti-SO<sub>2</sub> poisoning time of MnO<sub>2</sub>, and MnO<sub>2</sub>-GOS-TiO<sub>2</sub> at 150 °C in the presence of steam (a and d) and SO<sub>2</sub> (d); (e) XPS analysis of S after reaction: MnO<sub>2</sub> after 3 h reaction (black) and MnO<sub>2</sub>–GOS–TiO<sub>2</sub> after 30 h reaction (red).

After comparing the XPS results of Mn and O in MnO<sub>2</sub> and MnO<sub>2</sub>-GOS-TiO<sub>2</sub> catalysts in Figure 3, it is found that the protective layer of GOS-TiO<sub>2</sub> has no obvious effect on the valence distribution of Mn, but slightly increases the content of O on the surface.<sup>9</sup> Therefore, the delayed oxidation of MnO<sub>2</sub>-GOS-TiO<sub>2</sub> may be mainly due to the difficulty of electron transfer.

molecular sieve increased the NO conversion of the catalyst at high

In Figure 2d, we compared the SO<sub>2</sub>-tolerance performance of

MnO2 and MnO2-GOS-TiO2 at 150 °C. There is an effect on the mass

spectrometer when the gas flow is switched, so there is a jump in the

NO conversion. The improvement of the performance of catalyst

after the addition of SO<sub>2</sub> is related to the reaction mechanism of the

catalyst in Figure S6.<sup>4</sup> After about 0.5 h, the catalytic activity of MnO<sub>2</sub>

began to stabilize, and gradually decreased due to the poisoning of



Fig. 3 XPS spectra for Mn 2P3/2 and O 2P3/2 for MnO2 and MnO2-GOS-TiO<sub>2</sub>.

### SO<sub>2</sub>-tolerant mechanism at 200 °C



Fig. 4 Catalyst performance and characterization: (a) anti-SO<sub>2</sub> poisoning time of MnO2-GOS-TiO2 and MnO2-GOS-TiO2-ITQ2 at 200 °C in the presence of steam and SO<sub>2</sub>; (b) XPS analysis of S after reaction: MnO<sub>2</sub>-GOS-TiO<sub>2</sub> (red) and MnO<sub>2</sub>-GOS-TiO<sub>2</sub>-ITQ2 after 6 h reaction (blue).

When the temperature of the SO<sub>2</sub>-tolerance experiment continued to rise to 200 °C, we found that the MnO<sub>2</sub>-GOS-TiO<sub>2</sub> catalyst was not tolerant of SO<sub>2</sub> at this time in figure 4a, mainly because the oxidation of the catalyst was further enhanced with the increase of temperature. The NH<sub>4</sub>HSO<sub>4</sub> formed from a small amount of SO<sub>3</sub> covered the surface of the catalyst so that it was deactivated. S was indeed detected in S-XPS in Figure 4b and S-ICP in Table S1. Although S was also detected in MnO<sub>2</sub>-GOS-TiO<sub>2</sub>-ITQ2 catalyst, catalyst could run stably for 100 h in SO2-containing atmosphere, mainly because of the different coverage position of NH<sub>4</sub>HSO<sub>4</sub>.

In order to verify this hypothesis, we used 0.1 M NH<sub>4</sub>HSO<sub>4</sub> aqueous solution to wash ITQ2 molecular sieve three times, and then compounded with MnO2-GOS-TiO2 catalyst to carry out de-NOx experiments. It was found that the activity of the catalyst decreased obviously at high temperature in Figure 5a, mainly because ITQ2 lost the role of strong acid centre, and could neither supply NH<sub>3</sub> nor absorb SO<sub>3</sub>. SO<sub>2</sub>-tolerance performance became significantly worse in Figure 5b.



Fig. 5 Catalyst performance and characterization: (a) activity and (b) anti-SO2 poisoning time of MnO2-GOS-TiO2-ITQ2(containing NH<sub>4</sub>HSO<sub>4</sub>) at 200 °C in the presence of steam and SO<sub>2</sub>.

By changing the amount of TiO<sub>2</sub> deposition, the temperature window of MnO<sub>2</sub>-GOS-TiO<sub>2</sub> catalyst for NO conversion can be adjusted, and ITQ2 can help the catalyst work at the temperature slightly higher than this window for a period of time. The advantage of this composite catalyst is that it will not be deactivated as a result of a sudden increase in temperature.

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### Conclusions

Through the introduction of GO protective layer into manganesebased catalyst, the direct contact between  $SO_3$  and catalyst was prevented, thus the formation of MnSO<sub>4</sub> was prevented. TiO<sub>2</sub> was selectively deposited on the surface of GO to delay the oxidation ability of the catalyst, only oxidizing or preferentially oxidizing NO, but not oxidizing or reducing the oxidation of SO<sub>2</sub>, to reduce the production of NH<sub>4</sub>HSO<sub>4</sub>. When the catalyst works at higher temperature for a short time, the adsorption of SO<sub>3</sub> by ITQ2 can reduce the adhesion of NH<sub>4</sub>HSO<sub>4</sub> on the surface of active centre. The above three steps improved the low-temperature  $SO_2$ -resistance of manganese-based NH<sub>3</sub>-SCR catalyst.

### **Conflicts of interest**

The authors declare no competing financial interest.

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GO-Scroll-TiO<sub>2</sub>-ITQ2 improve the steam-resistance and SO<sub>2</sub>-resistance of the low-temperature manganese-based  $NH_3$ -SCR catalyst.