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Study on the NH_3-SCR performance and reaction mechanism of cost-effective and environment-friendly black TiO_2 catalyst

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3. Experimental

3.1 The preparation of V1.5Ti catalyst

The $V_{1.5}$Ti catalyst was prepared by impregnation method. Briefly, a certain of ammonium

paratungstate was dissolved into 60 mL deionized water, and 2 g commercial TiO_2 was added to solution under vigorous stirring. The $V_{1.5}Ti$ catalyst was obtained by drying mixture at 120 °C and calcining at 500 °C for 3 h.

3.2 Characterization

Temperature-programmed desorption of ammonia (NH_3-TPD) and temperature-programmed reduction of hydrogen (H_2-TPR) experiments was conducted in a quartz U-tube reactor equipped with an automated chemisorption analyzer (Quantachrome Instruments). Each catalyst was preheated at 120 °C for 24 h before TDP and H_2-TPR experiments, and 100 mg of each sample was used. The TDP experiments started with NH_3 adsorption under a flow rate of 70 mL·min^{-1} at room temperature for 1 h. Then, the gas was switched to He for 0.5 h. Subsequently, TPD was performed by ramping the temperature to 800 °C at a heating rated 10 °C·min^{-1} in He (70 mL·min^{-1}). In H_2-TPR experiments, the sample was purged with He at a flow rate of 70 mL·min^{-1} for 0.5 h, and the sample was then heated to 800 °C at a heating rate of 10 °C min^{-1} after switching the gas flow to a H_2/N_2 (10vol% H_2) at a flow rate of 70 mL·min^{-1}. The consumption of H_2 or NH_3 was detected using a thermal conductivity detector (TCD).

In situ FTIR experiments were carried out by a Nicolet IZ10 FTIR spectrometer, equipped with a liquid nitrogen-cooled MCT detector. During the experiment, an average of 32 scans was collected for each IR spectrum, which was recorded at a resolution of 4 cm^{-1}. The reaction conditions were as follows: 500 ppm NO, 500 ppm NH_3, 5% O_2, N_2 as the balance gas, and a flow rate of 40 mL·min^{-1}. Each catalyst was preheated at 300 °C for 60 min under N_2, and then spectra were recorded as the initial spectra. For NH_3/NO+O_2 adsorption experiments, NH_3/NO+O_2 were adsorbed for 30 min and the spectra were recorded at 1, 5, 10, 20 and 30 min. For the NO+O_2

(NH_3) reaction with pre-adsorbed NH_3 ($NO+O_2$) experiments, the catalyst was pre-adsorbed with NH_3 ($NO+O_2$) for 60 min, then purged with N_2 for 10 min, and then $NO+O_2$ (NH_3) was allowed to flow into the gas chamber, followed by recording the spectra at 1, 5, 10, 20, and 30 min.

Table S1 The XRF results for samples

Sample	TiO_2 (wt%)	C (wt%)	Others (wt%)
Commercial TiO_2	99.64	0.0017	0.3586
TiO_2-A	99.53	0.078	0.392
Black TiO_2	99.46	0.153	0.387

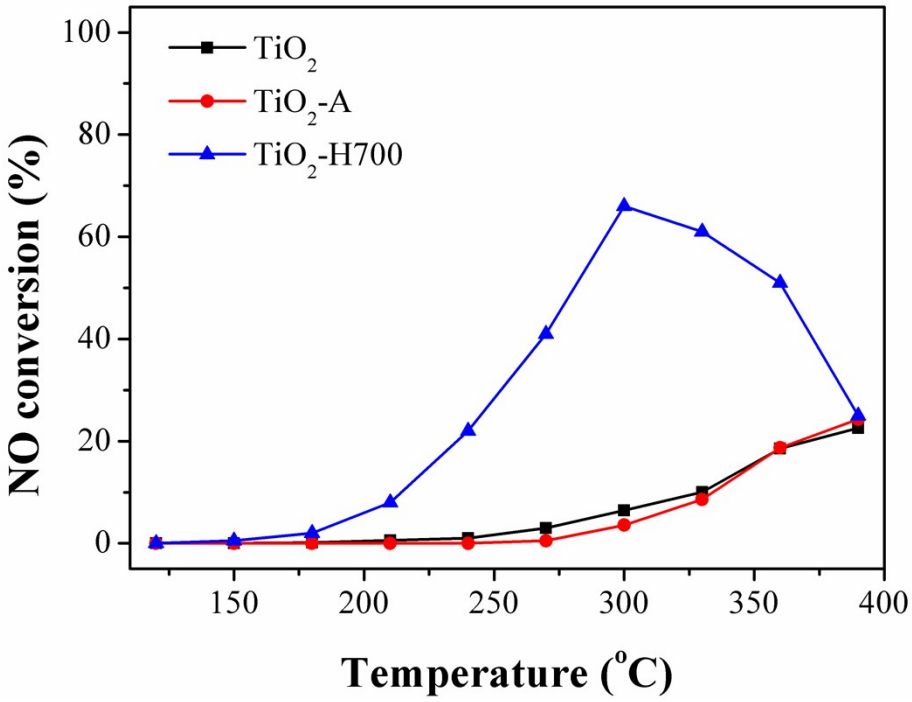

Fig S1 The NO conversion for TiO_2, TiO_2-A and TiO_2-H700

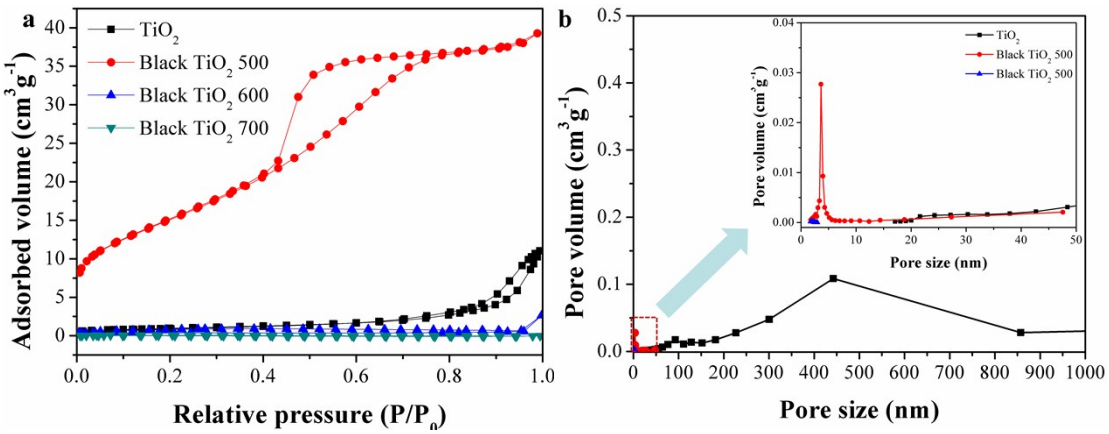

Fig S2 N_2 adsorption-desorption isotherms (a) and pore size distributions (b) of catalysts

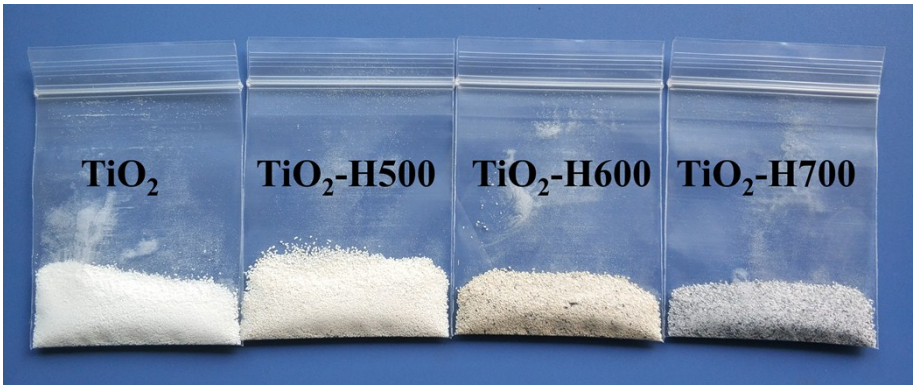

Fig S3 The images of samples prepared by hydrogen reducing TiO_2

Fig S4 The used TiO_2-H700 and black TiO_2-500 samples

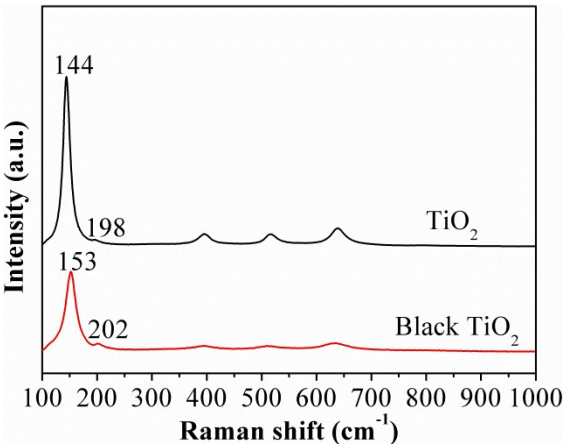

Fig S4 Raman spectra for TiO_2 and black TiO_2

Fig S5 shows the Raman spectra of black TiO_2-500 and TiO_2. The Raman peaks were observed at around 143, 399, 518, and 639 cm^{-1}, confirming that black TiO_2-500 and TiO_2 were composed of anatase phase.[1, 2]

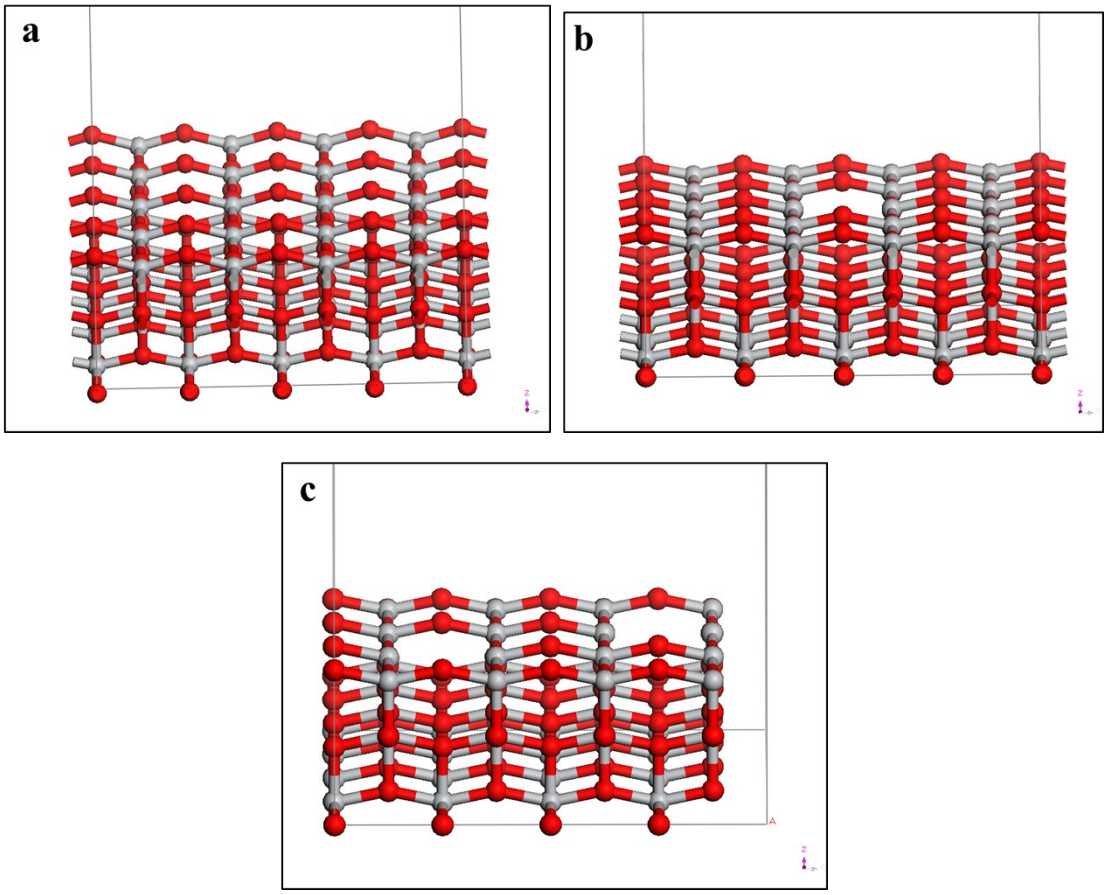

Fig S6 Optimized structure of the (a) TiO2, (b) TiO_2-1O_V and (c) TiO_2-2O_V

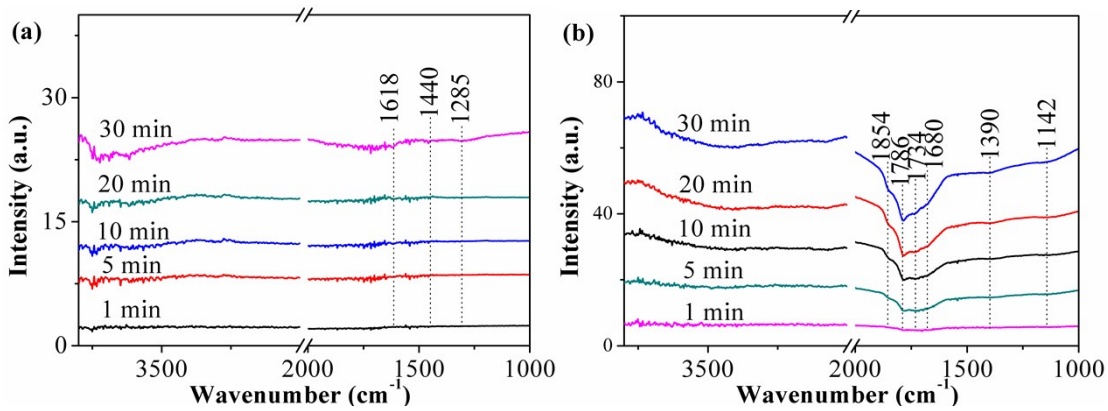

Fig S7 In situ DRIFT spectra of NO+O_2 adsorption over TiO_2 (a) and black TiO_2 (b) at 300 °C

NO+O_2 adsorption spectra were recorded at 300 °C for investigating their adsorption over catalysts. As presented in Fig S7a, three weak peaks, respectively attributed to monodentate nitrates (1285 cm^{-1}) and bridging nitrates (1618 cm^{-1} and 1440 cm^{-1}), were observed in TiO_2 spectra. [3] This result indicated that nitrogen oxides cannot be easily generated on the TiO_2 surface, which could be assigned to its poor redox properties. Combined with the results of in situ DRIFT of NH_3 adsorption, it could be proposed that the poor catalytic activity of TiO_2 might result from its poor redox properties and low capacity for NH_3. For black TiO_2, six peaks were found in spectra (Fig S7b). The peak observed at 1152 cm^{-1} was attributed to bridging nitrates, while the pair of peaks observed at 1390 and 1680 cm^{-1} was ascribed to the N_2O_4 formed by NO_2 dimerization.[3] Furthermore, triplet peaks were observed in the region of 1900-1700 cm^{-1}, attributed to the NO^+ species on Brønsted acid sites.[4] These results suggested that black TiO_2 had a high catalytic activity in NO oxidation, which could attribute to its excellent redox properties. Additionally, it was obvious that there was a competitive adsorption between NH_3 and nitrogen oxides, attributed to adsorption on Brønsted acid sites.

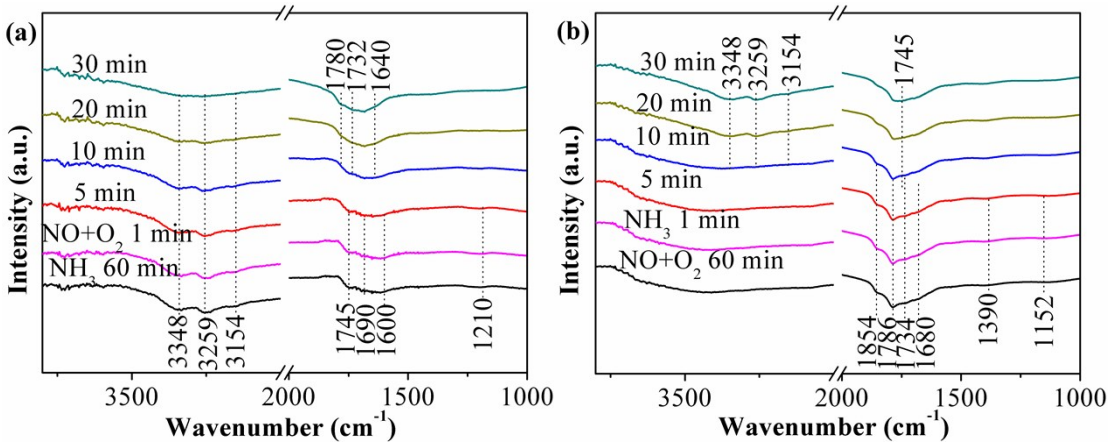

Fig S8 In situ DRIFT spectra of $NO+O_2$ reaction with pre-adsorbed NH_3 (a) and NH_3 reaction with pre-adsorbed $NO+O_2$ (b) over black TiO_2 at 300 °C

For investigating the reaction between $NO+O_2$ (NH_3) and pre-adsorbed NH_3 ($NO+O_2$) over black TiO_2, the samples were purged with N_2 for 10 min after treating with 500 ppm NH_3 (500 ppm NO+5% O_2) for 1 h, followed by introducing 500 ppm NO+5% O_2 (NH_3), then the spectra were recorded with time. Fig S8a shows the results obtained from the reaction between $NO+O_2$ (NH_3) and pre-adsorbed black TiO_2. Clearly, series of peaks due to adsorbed NH_3 were observed in spectra after pre-treated by NH_3 for 1 h. Notably, all of the pre-adsorbed NH_3 decreased with the introduction of $NO+O_2$. More interestingly, the peaks of pre-adsorbed NH_3 first disappeared after 20 min, followed by the appearance of peaks of nitrate species. Notably, the NH_3 adsorbed on the Lewis and Brønsted acid sites simultaneously disappeared. These results indicated that the reaction between $NO+O_2$ and pre-adsorbed NH_3 on the Lewis and Brønsted acid sites simultaneously occurs. Fig S8b shows the results obtained for black TiO_2. After the pre-adsorption of $NO+O_2$ pre-adsorbed for 1 h, six bands attributed to nitrogen oxides were observed. Notably, the intensity of the six peaks observed for nitrogen oxides hardly changed after the flow of NH_3 for 30 min. On the other hand, the triplet peaks in the region of 3400-3100 cm^{-1}, attributed to coordinate NH_3, emerged. These results demonstrated that the adsorbed nitrogen oxides species could not react with the NH_3 adsorbed on the TiO_2 and black TiO_2 surface.

Reference

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