Study on the NH$_3$-SCR performance and reaction
mechanism of cost-effective and environment-friendly black
TiO$_2$ catalyst

Yiqing Zeng, Yanan Wang, Shule Zhang*, Qin Zhong*

School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, PR China

* Corresponding author, Tel.: +86 25 84315517, fax: +86 25 84315517, E-mail: shulezhang@163.com

Supplementary Material

1. Table

Table S1 The XRF results for samples

2. Figures

Fig S1 The NO conversion for TiO2 and TiO2-A

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 TiO2

Fig S4 The used TiO$_2$-H700 and black TiO$_2$-500 samples

Fig S5 Raman spectra for TiO$_2$ and black TiO$_2$

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

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

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 TiO₂ was added to solution under vigorous stirring. The V₁₅Ti 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 (NH₃-TPD) and temperature-programmed reduction of hydrogen (H₂-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 H₂-TPR experiments, and 100 mg of each sample was used. The TDP experiments started with NH₃ 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 rate of 10 °C·min⁻¹ in He (70 mL·min⁻¹). In H₂-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 H₂/N₂ (10vol% H₂) at a flow rate of 70 mL·min⁻¹. The consumption of H₂ or NH₃ 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 NH₃, 5% O₂, N₂ as the balance gas, and a flow rate of 40 mL·min⁻¹. Each catalyst was preheated at 300 °C for 60 min under N₂, and then spectra were recorded as the initial spectra. For NH₃/NO+O₂ adsorption experiments, NH₃/NO+O₂ were adsorbed for 30 min and the spectra were recorded at 1, 5, 10, 20 and 30 min. For the NO+O₂
(NH₃) reaction with pre-adsorbed NH₃ (NO+O₂) experiments, the catalyst was pre-adsorbed with NH₃ (NO+O₂) for 60 min, then purged with N₂ for 10 min, and then NO+O₂ (NH₃) 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

<table>
<thead>
<tr>
<th>Sample</th>
<th>TiO₂ (wt%)</th>
<th>C (wt%)</th>
<th>Others (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial TiO₂</td>
<td>99.64</td>
<td>0.0017</td>
<td>0.3586</td>
</tr>
<tr>
<td>TiO₂-A</td>
<td>99.53</td>
<td>0.078</td>
<td>0.392</td>
</tr>
<tr>
<td>Black TiO₂</td>
<td>99.46</td>
<td>0.153</td>
<td>0.387</td>
</tr>
</tbody>
</table>
Fig S1 The NO conversion for TiO$_2$, TiO$_2$-A and TiO$_2$-H700
Fig S2 N₂ adsorption-desorption isotherms (a) and pore size distributions (b) of catalysts
Fig S3 The images of samples prepared by hydrogen reducing TiO₂
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+O2 adsorption over TiO2 (a) and black TiO2 (b) at 300 °C

NO+O2 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 TiO2 spectra. This result indicated that nitrogen oxides cannot be easily generated on the TiO2 surface, which could be assigned to its poor redox properties. Combined with the results of in situ DRIFT of NH3 adsorption, it could be proposed that the poor catalytic activity of TiO2 might result from its poor redox properties and low capacity for NH3. For black TiO2, 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 N2O4 formed by NO2 dimerization. Furthermore, triplet peaks were observed in the region of 1900-1700 cm⁻¹, attributed to the NO⁺ species on Brønsted acid sites. These results suggested that black TiO2 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 NH3 and nitrogen oxides, attributed to adsorption on Brønsted acid sites.
Fig S8 In situ DRIFT spectra of NO+O\textsubscript{2} reaction with pre-adsorbed NH\textsubscript{3} (a) and NH\textsubscript{3} reaction with pre-adsorbed NO+O\textsubscript{2} (b) over black TiO\textsubscript{2} at 300 °C

For investigating the reaction between NO+O\textsubscript{2} (NH\textsubscript{3}) and pre-adsorbed NH\textsubscript{3} (NO+O\textsubscript{2}) over black TiO\textsubscript{2}, the samples were purged with N\textsubscript{2} for 10 min after treating with 500 ppm NH\textsubscript{3} (500 ppm NO+5% O\textsubscript{2}) for 1 h, followed by introducing 500 ppm NO+5% O\textsubscript{2} (NH\textsubscript{3}), then the spectra were recorded with time. Fig S8a shows the results obtained from the reaction between NO+O\textsubscript{2} (NH\textsubscript{3}) and pre-adsorbed black TiO\textsubscript{2}. Clearly, series of peaks due to adsorbed NH\textsubscript{3} were observed in spectra after pre-treated by NH\textsubscript{3} for 1 h. Notably, all of the pre-adsorbed NH\textsubscript{3} decreased with the introduction of NO+O\textsubscript{2}. More interestingly, the peaks of pre-adsorbed NH\textsubscript{3} first disappeared after 20 min, followed by the appearance of peaks of nitrate species. Notably, the NH\textsubscript{3} adsorbed on the Lewis and Brønsted acid sites simultaneously disappeared. These results indicated that the reaction between NO+O\textsubscript{2} and pre-adsorbed NH\textsubscript{3} on the Lewis and Brønsted acid sites simultaneously occurs. Fig S8b shows the results obtained for black TiO\textsubscript{2}. After the pre-adsorption of NO+O\textsubscript{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\textsubscript{3} for 30 min. On the other hand, the triplet peaks in the region of 3400-3100 cm\textsuperscript{-1}, attributed to coordinate NH\textsubscript{3}, emerged. These results demonstrated that the adsorbed nitrogen oxides species could not react with the NH\textsubscript{3} adsorbed on the TiO\textsubscript{2} and black TiO\textsubscript{2} surface.

Reference

