Novel iron titanate catalyst for the selective catalytic reduction of NO with \( \text{NH}_3 \) in the medium temperature range

Fudong Liu, Hong He* and Changbin Zhang

State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China.
Fax: +86 10 62849123; Tel: +86 10 62849123;
E-mail: honghe@rcees.ac.cn (H. He).

Electronic Supplementary Information

Catalyst preparation

During the catalyst preparation procedure, \( \text{Fe(NO}_3\)\text{)\text{3}·9\text{H}_2\text{O} \) and \( \text{Ti(SO}_4\)\text{)2} \) (molar ratio=1:1) were firstly dissolved using distilled water with subsequent mixing for 1 h. Then the iron and titanium ions were coprecipitated using 25wt% \( \text{NH}_3\cdot\text{H}_2\text{O} \) as precipitator with the titrating rate of nearly 1 drop per second until pH rose to 10. Without aging at all, the precipitates were filtrated with the help of air pump. Then the precipitate cakes were washed using distilled water and filtrated again for at least 4 times. The final precipitate cakes were put into oven keeping at 100 °C for 12 h. Then these raw materials were calcined in muffle furnace in air condition at 400, 500, 600, 700 °C for 6 h respectively and the heating rate was kept at 5 °C/min. The calcined samples were crushed and sieved to 20-40 mesh for activity test.

Reactants quantification

As all components in the flue gas (NO, \( \text{NH}_3 \), \( \text{N}_2\text{O} \) and \( \text{NO}_2 \)) have infrared response, we use an FTIR spectrometer (Thermo Nicolet Corporation Nexus 670, OMNIC Quantpad software) equipped with a heated, low volume multiple-path gas cell (2 m) to quantify the concentration of reactants. During the \( \text{H}_2\text{O} \) and \( \text{H}_2\text{O}/\text{SO}_2 \) durability experiment, in order to prevent the strong absorbance of \( \text{H}_2\text{O} \), we used \( \text{CaSO}_4 \) which does not adsorb any reactant as desiccant before the flue gas flowed into the gas cell. The whole \( \text{NH}_3\)-SCR activity test system is shown in Fig.1.

Comparison with Mn and Cu-based catalysts

Prior to our investigation of iron titanate catalyst, we also tried Mn and Cu-based catalysts for this

![Fig.1 NH3-SCR activity test system: Furnace A for water gasification; Furnace B for SCR reaction](image-url)
SCR reaction, such as MnO$_x$/TiO$_2$, CuO$_x$/TiO$_2$ using impregnation method along with Mn$_x$TiO$_y$, Cu$_x$TiO$_y$ which were prepared using the same coprecipitation method as Fe$_x$TiO$_y$. Fig. 2 shows the comparative results of NO conversion and N$_2$ selectivity over Fe$_x$TiO$_y$, Mn$_x$TiO$_y$ and Cu$_x$TiO$_y$ respectively. For Mn$_x$TiO$_y$, the low temperature activity was better than that of Fe$_x$TiO$_y$, but the maximum conversion of NO could not reach 100% and the N$_2$ selectivity was much lower than that of Fe$_x$TiO$_y$. Cu$_x$TiO$_y$ showed nearly no SCR activity due to the strong ability to oxidize NH$_3$ to NO, and NO to NO$_2$ which might be used as NO pre-oxidation catalyst to enhance the “fast SCR”.

Fig. 3 shows the results of NO conversion and N$_2$ selectivity over MnO$_x$/TiO$_2$, CuO$_x$/TiO$_2$. 10wt% MnO$_x$/TiO$_2$ also had better low temperature activity and lower N$_2$ selectivity comparing with Fe$_x$TiO$_y$. We prepared MnO$_x$/TiO$_2$ (Mn:Ti=1:1 in molar ratio) and CuO$_x$/TiO$_2$ (Cu:Ti=1:1 in molar ratio).
molar ratio) in order to see whether the impregnation and coprecipitation methods had influence on the samples’ SCR activity. From the results we can see that: Mn$_x$TiO$_y$ had better activity than MnO$_x$/TiO$_2$ while Cu$_x$TiO$_y$ had lower activity than CuO$_x$/TiO$_2$. Therefore, we can say that different preparation methods result in different properties of catalysts and this Fe$_x$TiO$_y$ catalyst must have different structures comparing with other Fe$_2$O$_3$ loaded type catalysts.

**Preliminary experiments on active component determination**

In order to know whether the iron titanate crystallite is the active component, we firstly used

![Graph](image.png)

**Fig.3** NO conversion (A) and N$_2$ selectivity (B) over (a) 10wt%MnO$_x$/TiO$_2$; (b) MnO$_x$/TiO$_2$ (Mn:Ti=1 in molar ratio); (c) CuO$_x$/TiO$_2$ (Cu:Ti=1 in molar ratio).

...
and there is no obvious difference between these two samples. Because the BET surface areas of these catalysts under different calcination temperature differ a lot, we calculated the specific activity per surface area under different reaction temperature and the results are shown in Fig.6. During the whole temperature range, the calculated NO conversion result is totally reverse with the following order: Fe$_x$TiO$_y$-700 °C > Fe$_x$TiO$_y$-600 °C > Fe$_x$TiO$_y$-500 °C > Fe$_x$TiO$_y$-400 °C. Fe$_x$TiO$_y$-700 °C shows the best activity implying that Fe$_2$TiO$_5$ is indeed one of the active phases with very high turnover frequency in SCR process. However, the situation is not so simple in these catalysts. Surface area is indeed an important factor influencing the SCR activity, but not the only one. The crystal phase of iron titanate is also very important. According to the Raman and XRD results, we deduce that the good SCR activity at relative low temperature range is mainly contributed by crystallite FeTiO$_3$ and Fe$_2$TiO$_5$, but at high temperature range all species including well crystallized Fe$_2$TiO$_5$ and even Fe$_2$O$_3$ formed on the surface have SCR
activity. Therefore, although the calculation of specific activity per surface area can help us to judge whether iron titanate is the active phase, it still can not give us the intrinsic activity of each active site because we do not know how many active sites have participated into the reaction. Other methods including ESR and EXAFS may be helpful to figure this out and the further experiments are under way.

XPS results of the catalysts under different calcination temperature are shown in Fig.7. The valence of iron in FeTiO$_x$-400 °C and 500 °C is mainly +3 along with a small amount of Fe$^{2+}$ implying the existence of FeTiO$_3$. With the increase of calcination temperature, the Fe$^{2+}$ peaks disappeared indicating that only Fe$^{3+}$ in Fe$_2$TiO$_5$ or Fe$_2$O$_3$ exists on the surface. It is more obvious to compare the binding energy of Ti 2p$_{3/2}$ in different samples. From 400, 500 °C to 600, 700 °C, the binding energy of Ti 2p$_{3/2}$ shifted from 458.6 eV to 458.8 eV which meant that the valence of Ti increased resulting in a decrease of redox ability in SCR reaction.

**Fig.6** Specific activity per surface area of catalysts under different calcination temperature for 6 h: (a) 400 °C, (b) 500 °C, (c) 600 °C, (d) 700 °C.
In order to investigate the influence of SO₂ on the NH₃-SCR activity, we further carried out in situ DRIFTS experiments to observe the change of surface species after SO₂ addition. The in situ DRIFTS spectra were recorded on an FTIR spectrometer (Thermo Nicolet Corporation Nexus 670, OMNIC Quantpad software) equipped with a smart collector and an MCT/A detector cooled by liquid nitrogen. The reaction temperature was controlled precisely by an Omega programmable temperature controller. Finely ground catalyst sample (ca. 30 mg) was placed into a ceramic crucible and the surface was made as flat as possible. Prior to each experiment, the sample (FeₓTiOᵧ-400 °C) was pretreated at 400 °C in a flow of 20% O₂ + 80% N₂ for 30 min to remove the possible contaminants adsorbed on the surface and then cooled to the desired temperature. At the desired temperature, the background spectrum was collected in flowing N₂ and was subtracted.

Fig. 6 XPS results of catalysts under different calcination temperature for 6 h:
(a) 400 °C, (b) 500 °C, (c) 600 °C, (d) 700 °C. A: Fe 2p; B: Ti 2p.

in situ DRIFTS study
In order to investigate the influence of SO₂ on the NH₃-SCR activity, we further carried out in situ DRIFTS experiments to observe the change of surface species after SO₂ addition. The in situ DRIFTS spectra were recorded on an FTIR spectrometer (Thermo Nicolet Corporation Nexus 670, OMNIC Quantpad software) equipped with a smart collector and an MCT/A detector cooled by liquid nitrogen. The reaction temperature was controlled precisely by an Omega programmable temperature controller. Finely ground catalyst sample (ca. 30 mg) was placed into a ceramic crucible and the surface was made as flat as possible. Prior to each experiment, the sample (FeₓTiOᵧ-400 °C) was pretreated at 400 °C in a flow of 20% O₂ + 80% N₂ for 30 min to remove the possible contaminants adsorbed on the surface and then cooled to the desired temperature. At the desired temperature, the background spectrum was collected in flowing N₂ and was subtracted.
from the sample spectrum which was obtained at the same temperature. The total flow rate of the feed gas was kept at 300 ml/min and all spectra were recorded by accumulating 100 scans with a resolution of 4 cm\(^{-1}\). The concentration of reactants was kept the same as those used in SCR activity test experiments, i.e. 500 ppm NO, 500 ppm NH\(_3\), 5% O\(_2\) and 100 ppm SO\(_2\) (when used).

As the desorption of adsorbed species at 300 °C may become more obvious, we chose 200 °C to investigate the influence of SO\(_2\) addition. We firstly studied the influence of SO\(_2\) on NO+O\(_2\) adsorption and the result is shown in Fig.8. As we can see, in a flow of NO+O\(_2\) at 200 °C, the sample surface was mainly covered by nitrate species (1614 cm\(^{-1}\) assigned to bridging nitrate; 1578 cm\(^{-1}\) assigned to bidentate nitrate; 1556 and 1196 cm\(^{-1}\) assigned to monodentate nitrate). After SO\(_2\) addition, the peaks of nitrate species decreased sharply and sulfate species (1373, 1296 and 1070 cm\(^{-1}\)) increased. Peak at 1620 cm\(^{-1}\) was assigned to H\(_2\)O produced by the reaction between SO\(_2\) and hydroxyl. After 20 min, the nitrate species was completely substituted by sulfate species which implied that the competitive adsorption of SO\(_2\) could strongly inhibit the formation of nitrate species.

![In situ DRIFTS spectra of adsorbed species on Fe\(_x\)TiO\(_y\) after SO\(_2\) addition in a flow of NO+O\(_2\) at 200 °C.](image)

**Fig.8** in situ DRIFTS spectra of adsorbed species on Fe\(_x\)TiO\(_y\) after SO\(_2\) addition in a flow of NO+O\(_2\) at 200 °C.

The influence of SO\(_2\) on NH\(_3\) adsorption is shown in Fig.9. After SO\(_2\) addition, the peaks of NH\(_3\) adsorbed species increased slightly (1676 and 1431 cm\(^{-1}\) assigned to NH\(_4^+\) on Brönsted acid sites; 1605, 1200 and 1067 cm\(^{-1}\) assigned to NH\(_3\) on Lewis acid sites) and there was no sulfate species appearing. This result suggested that SO\(_2\) addition could enhance the adsorption of NH\(_3\) over this catalyst due to the acidity increase. The inverse peak at 1367 cm\(^{-1}\) was due to the coverage of SO\(_4^{2-}\) by NH\(_3\) species and this SO\(_4^{2-}\) was remained in the catalyst structure during the preparation procedure using Fe(NO\(_3\))\(_3\) and Ti(SO\(_4\))\(_2\) as precursors.
Fig. 10 shows the result of the influence of SO$_2$ addition on the surface adsorbed species in SCR condition. Without adding SO$_2$, the catalyst surface was mainly covered by NH$_3$ adsorbed species and only a small amount of monodentate nitrate species (1186 cm$^{-1}$). After adding SO$_2$ into the feed gas, the peaks of NH$_3$ adsorbed species (mainly NH$_4^+$ adsorbed on Brönsted acid sites at 1676 and 1433 cm$^{-1}$) also had an increase in intensity due to the acidity enhancement caused by sulfate formation (1259 cm$^{-1}$). At the same time, the monodentate nitrate species disappeared. Therefore, the addition of SO$_2$ into the SCR system could enhance the adsorption of NH$_3$ and blocked the adsorption of NO$_x$. NO oxidation to NO$_2$ might be weakened by SO$_2$ coexistence resulting in the deactivation of “fast SCR” in the low temperature range. However, the enhancement of NH$_3$ adsorption in the high temperature range could promote the SCR activity to a certain extent.