Novel iron titanate catalyst for the selective catalytic reduction of NO with NH_3 in the medium temperature range

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Electronic Supplementary Information

Catalyst preparation

During the catalyst preparation procedure, $Fe(NO_3)_3 \cdot 9H_2O$ and $Ti(SO_4)_2$ (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% $NH_3 \cdot H_2O$ 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 ^{o}C for 12 h. Then these raw materials were calcined in muffle furnace in air condition at 400, 500, 600, 700 ^{o}C for 6 h respectively and the heating rate was kept at 5 ^{o}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, NH_3, N_2O and 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 H_2O and H_2O/SO_2 durability experiment, in order to prevent the strong absorbance of H_2O, we used $CaSO_4$ which does not adsorb any reactant as desiccant before the flue gas flowed into the gas cell. The whole 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

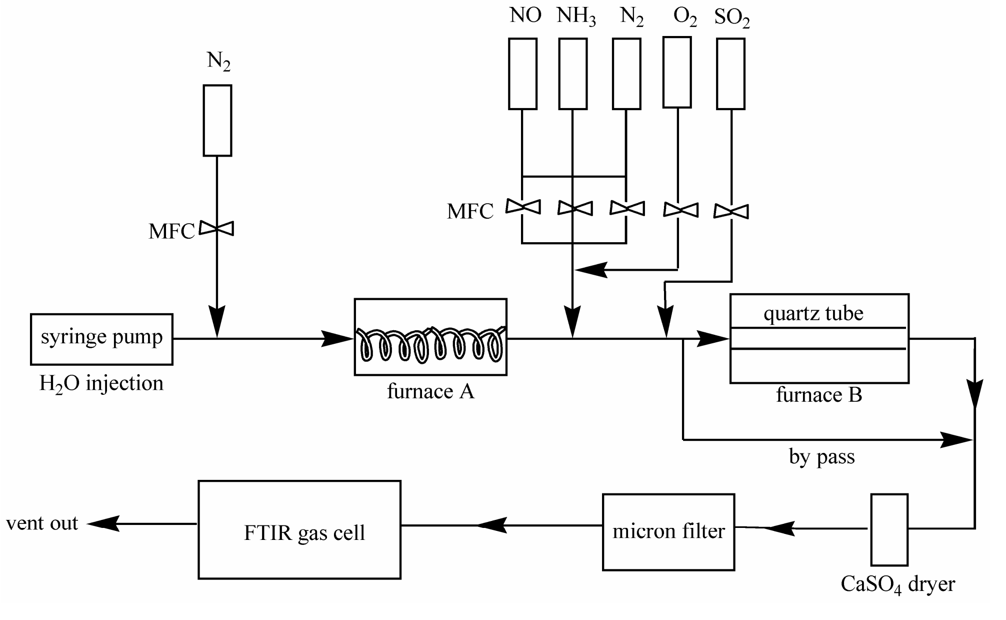


Fig.1 NH_3-SCR activity test system: Furnace A for water gasification; Furnace B for SCR reaction

SCR reaction, such as MnO_x/TiO_2, CuO_x/TiO_2 using impregnation method along with Mn_xTiO_y, Cu_xTiO_y which were prepared using the same coprecipitation method as Fe_xTiO_y. Fig.2 shows the comparative results of NO conversion and N_2 selectivity over Fe_xTiO_y, Mn_xTiO_y and Cu_xTiO_y respectively. For Mn_xTiO_y, the low temperature activity was better than that of Fe_xTiO_y, but the maximum conversion of NO could not reach 100% and the N_2 selectivity was much lower than that of Fe_xTiO_y. Cu_xTiO_y showed nearly no SCR activity due to the strong ability to oxidize NH_3 to NO_x 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_xTiO_y. We prepared MnO_x/TiO_2 (Mn:Ti=1:1 in molar ratio) and CuO_x/TiO_2 (Cu:Ti=1:1 in

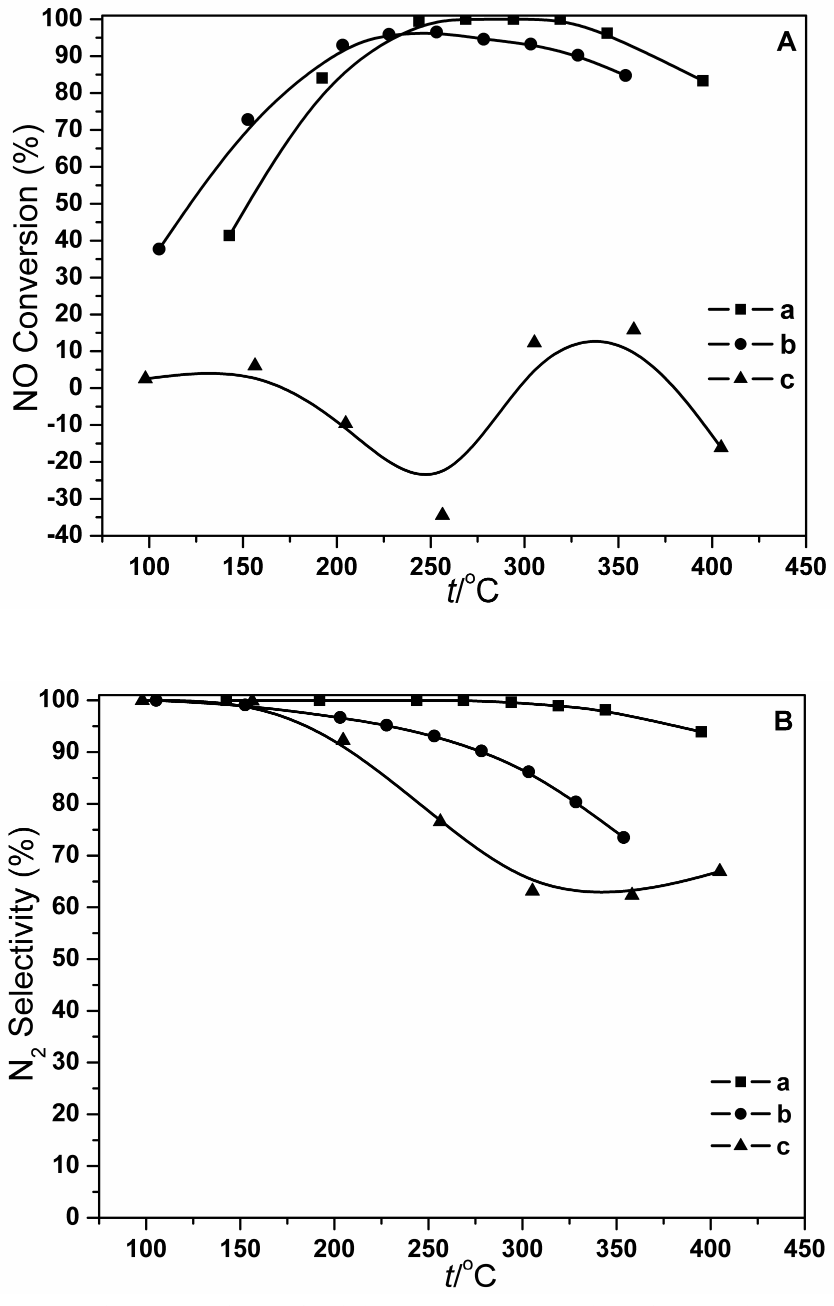


Fig.2 NO conversion (A) and N_2 selectivity (B) over (a) Fe_xTiO_y; (b) Mn_xTiO_y; (c) Cu_xTiO_y.

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_xTiO_y had better activity than MnO_x/TiO_2 while Cu_xTiO_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_xTiO_y catalyst must have different structures comparing with other Fe_2O_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 exactly the same way to prepare Fe_2O_3 and TiO_2 pure oxides. Then we prepared mechanically mixed sample (Fe_2O_3+TiO_2 mixed) and mechanically mixed plus calcined sample at 400 °C for 6 h again (Fe_2O_3+TiO_2 mixed and calcined) and test their SCR activity respectively. The result is shown in Fig.4 and we can see that after the calcination again, maybe some iron titanate crystallite phase occurred which was responsible for activity promotion. The XRD results are shown in Fig.5

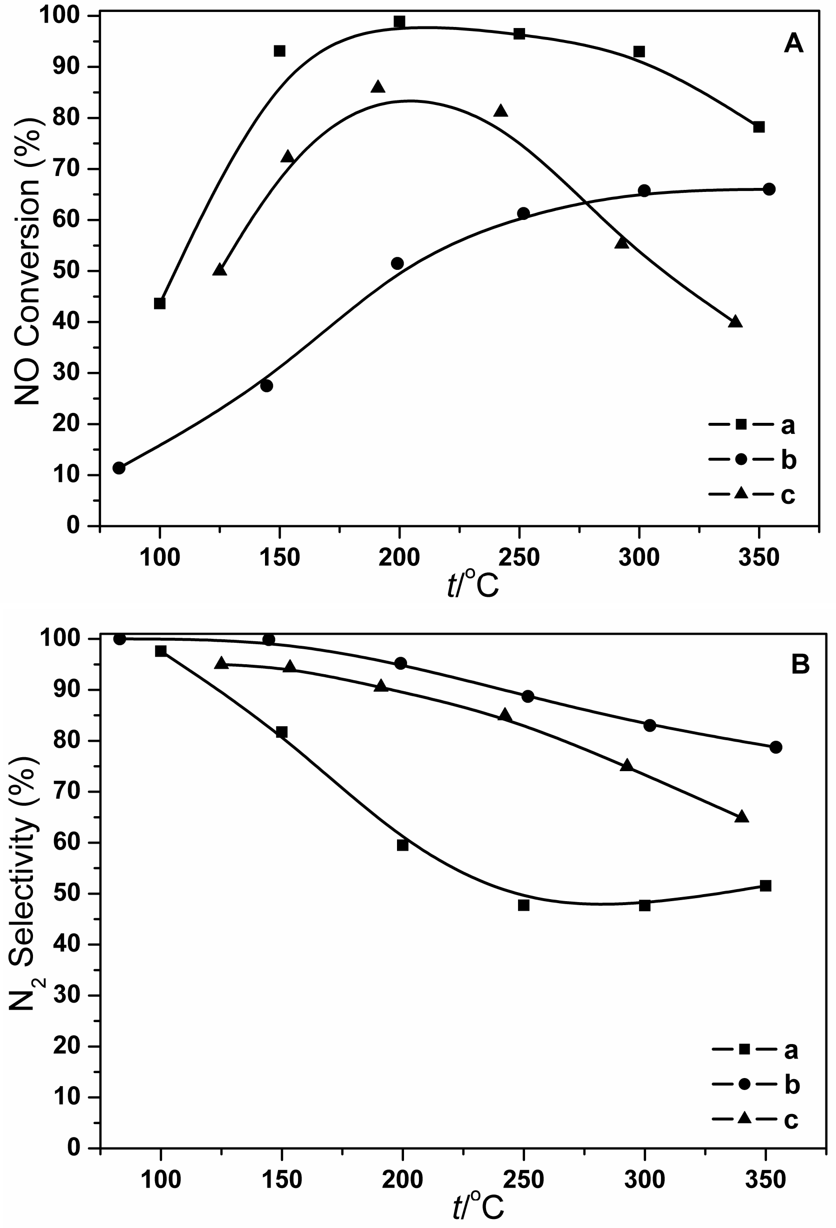


Fig.3 NO conversion (A) and N_2 selectivity (B) over (a) 10wt%MnO_x/TiO_2; (b) MnO_x/TiO_2 (Mn:Ti=1 in molar ratio); (c) CuO_x/TiO_2 (Cu:Ti=1 in molar ratio).

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_xTiO_y-700 °C > Fe_xTiO_y-600 °C > Fe_xTiO_y-500 °C > Fe_xTiO_y-400 °C. Fe_xTiO_y-700 °C shows the best activity implying that Fe_2TiO_5 is indeed one of the active phases with very high turn over 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_2TiO_5, but at high temperature range all species including well crystallized Fe_2TiO_5 and even Fe_2O_3 formed on the surface have SCR

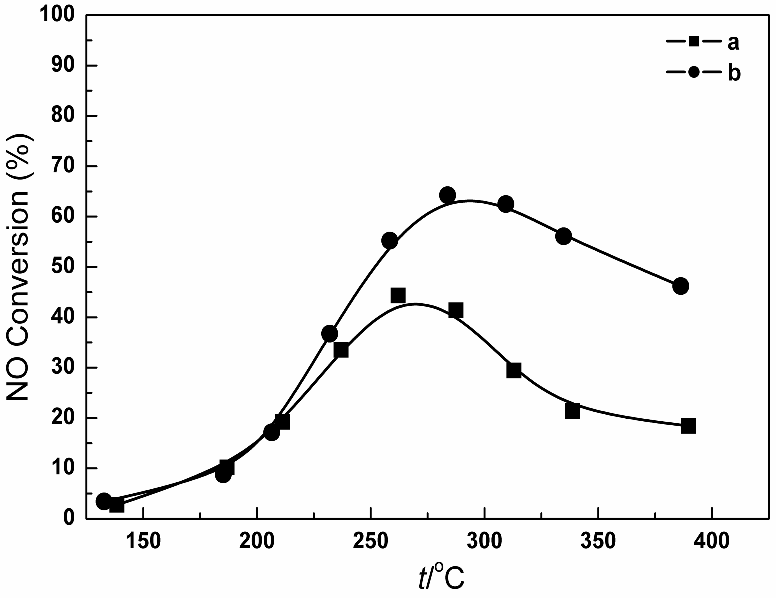


Fig.4 NO conversion over (a) Fe_2O_3+TiO_2 mixed; (b) Fe_2O_3+TiO_2 mixed and calcined.

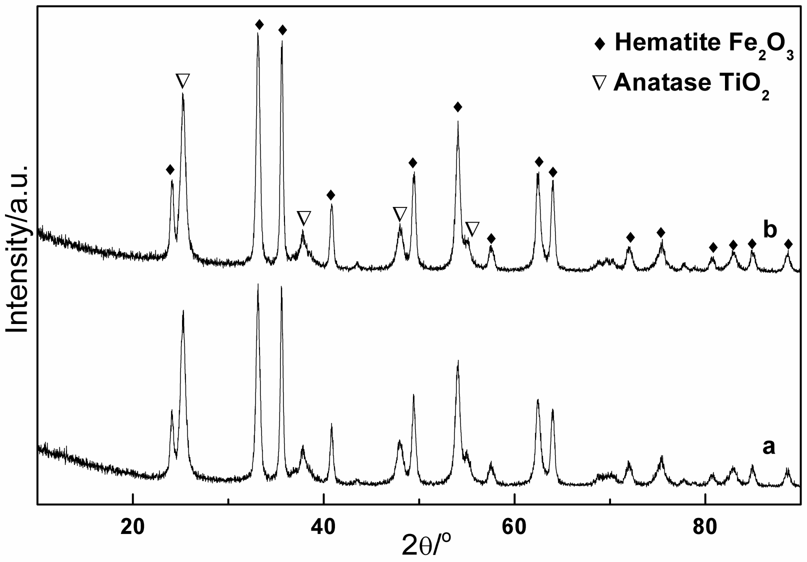


Fig.5 XRD patterns of (a) Fe_2O_3+TiO_2 mixed; (b) Fe_2O_3+TiO_2 mixed and calcined.

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 Fe_xTiO_y-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_2TiO_5 or Fe_2O_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.

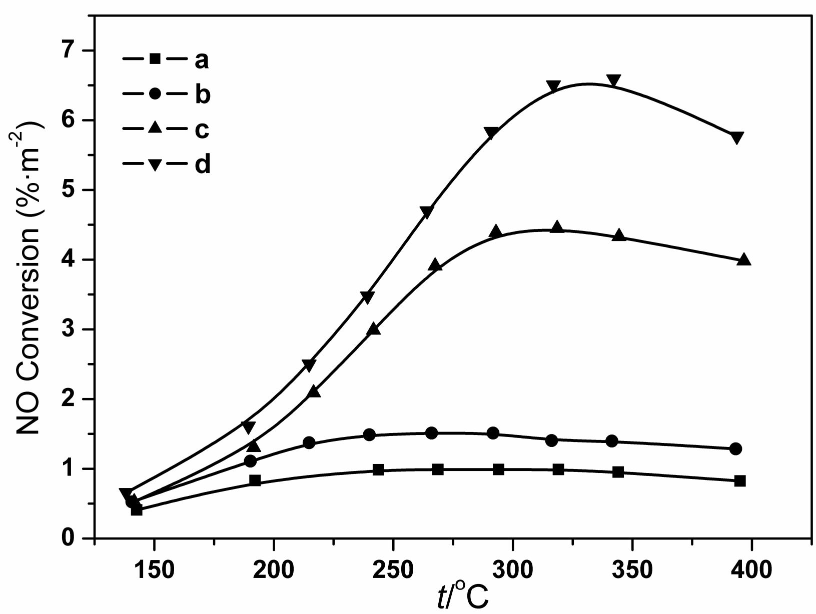
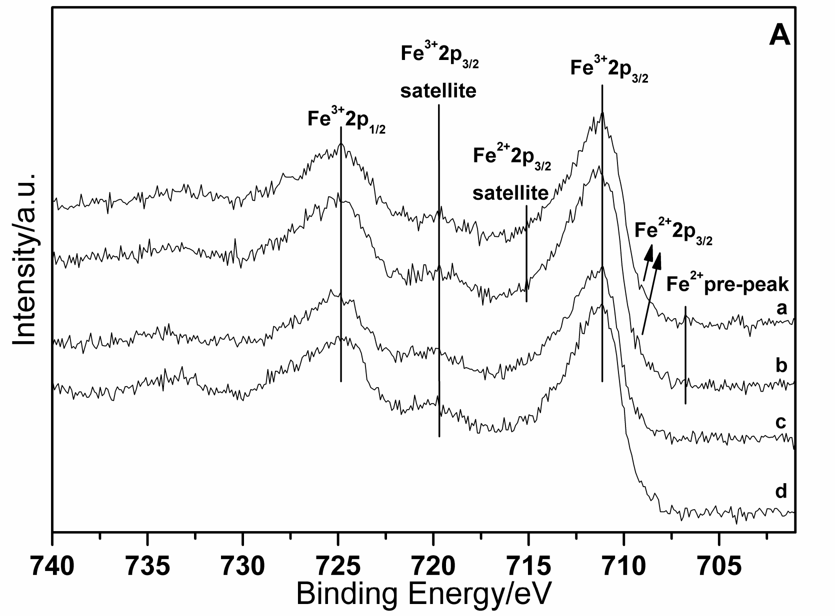


Fig.6 Specific activity per surface area of catalysts under different calcination temperature for 6 h: (a) 400 °C, (b) 500 °C, (c) 600 °C, (d) 700 °C.



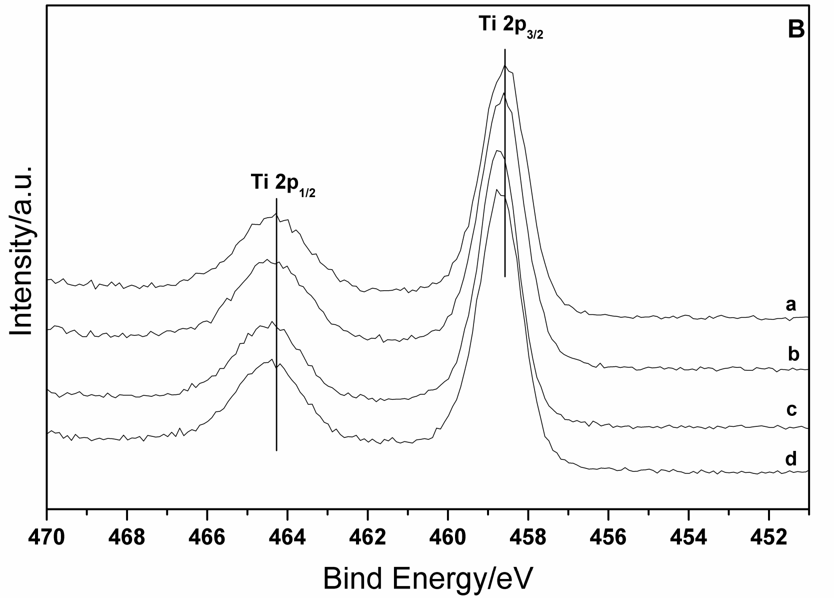


Fig.7 XPS results of catalysts under different calcination temperature for 6 h: (a) 400 °C, (b) 500 °C, (c) 600 °C, (d) 700 °C. A: Fe 2p; B: Ti 2p.

in situ DRIFTS study

In order to investigate the influence of SO_2 on the NH_3-SCR activity, we further carried out *in situ* DRIFTS experiments to observe the change of surface species after SO_2 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 (Fe_xTiO_y-400 °C) was pretreated at 400 °C in a flow of 20% O_2 + 80% N_2 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 N_2 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 ^oC may become more obvious, we chose 200 ^oC 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 ^oC, 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_2O 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.

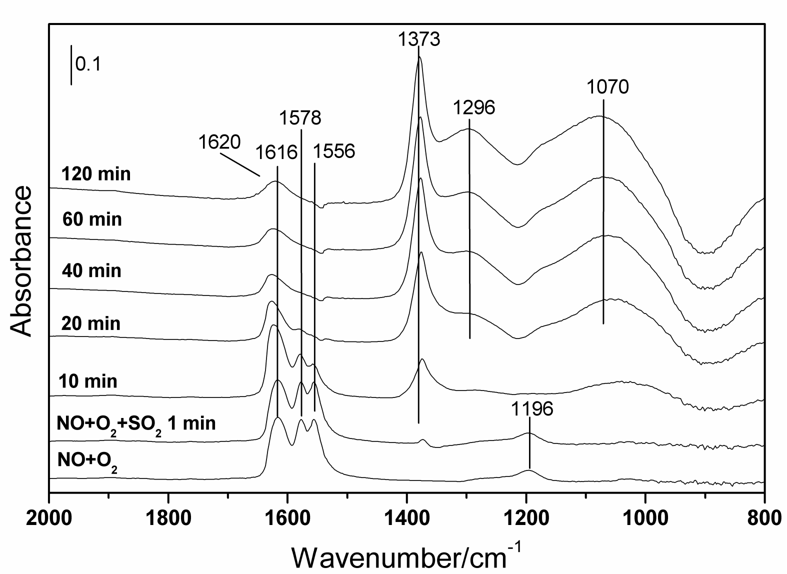


Fig.8 *in situ* DRIFTS spectra of adsorbed species on Fe_xTiO_y after SO_2 addition in a flow of $NO+O_2$ at 200 ^oC.

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.

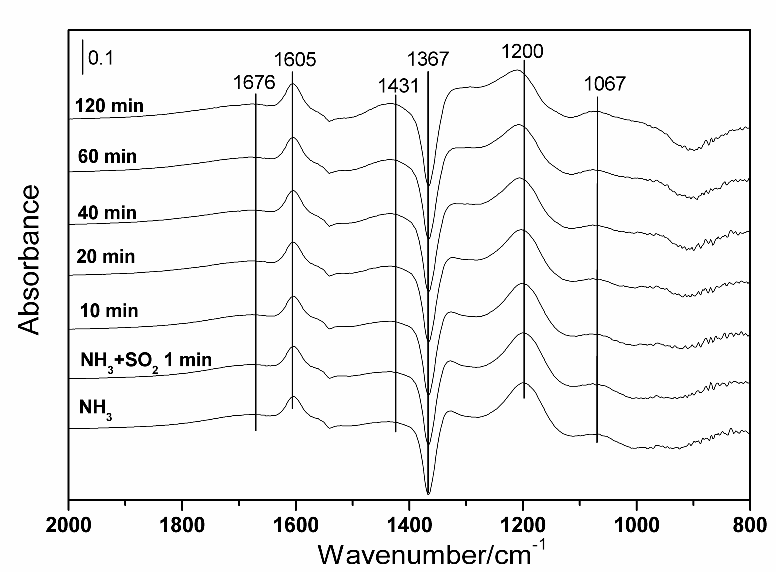


Fig.9 *in situ* DRIFTS spectra of adsorbed species on Fe_xTiO_y after SO_2 addition in a flow of NH_3 at 200 °C

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.

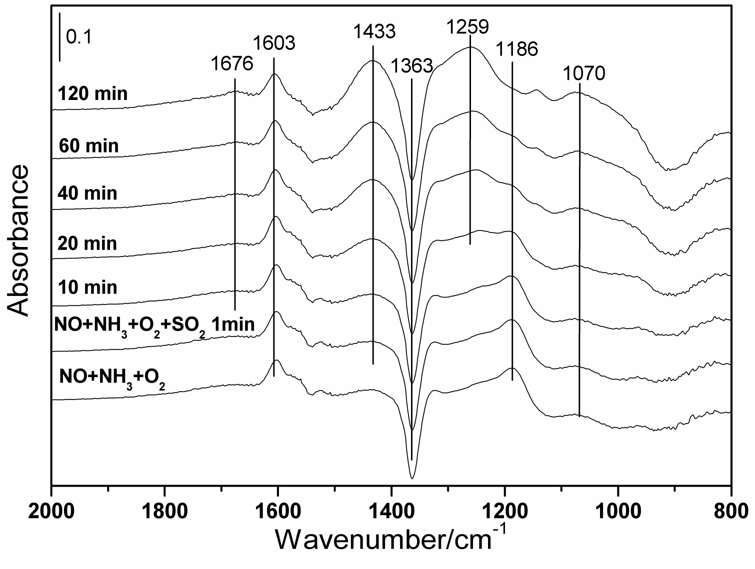


Fig.10 *in situ* DRIFTS spectra of adsorbed species on Fe_xTiO_y after SO_2 addition in a flow of NO+NH_3+O_2 at 200 °C