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

Fudong Liu, Hong He* and Changbin Zhang

Received (in Cambridge, UK) 4th January 2008, Accepted 25th January 2008
First published as an Advance Article on the web 20th February 2008
DOI: 10.1039/b800143j

An iron titanate catalyst with a crystallite phase, prepared by a co-precipitation method, showed excellent activity, stability, selectivity and SO_2/H_2O durability in the selective catalytic reduction of NO with NH_3 in the medium temperature range.

Nitrogen oxides (NO_x) have become a major source of air pollution which can result in photochemical smog, acid rain and ozone depletion and have strong respiratory toxicity endangering human health.[1] Stringent environmental legislation has been made worldwide to reduce NO_x emitted from mobile and stationary resources including vehicles and coal-fired power plants. Selective catalytic reduction of NO with NH_3 (NH_3-SCR) is an effective and economical method to remove NO and nowadays the most widely used catalyst system is V_2O_5–WO_3/TiO_2 or V_2O_5–MoO_3/TiO_2 with a relatively narrow temperature window of 350–400 °C.[2] The problems of this system are as follows: the low N_2 selectivity in the high temperature range because of N_2O formation and NH_3 over-oxidation; the toxicity of vanadium pentoxide to the environment; and high conversion of SO_2 to SO_3 with increasing vanadium amounts, which can result in catalyst deactivation.[3] Recently, many researchers have focused mainly on exploitation of new SCR catalysts with high activity in the low temperature range, such as amorphous MnO_x,[4] MnO_x–CeO_2 mixed oxides,[5] MnO_x loaded on TiO_2/Al_2O_3/SiO_2[6]/USY (ultrastable zeolite Y),[7] V_2O_5/AC (activated carbon)[8] and Fe–Mn based catalysts[9] which more or less have problems of low N_2 selectivity, H_2O and SO_2 deactivation and ammonium nitrate deposition, *etc.* Fe exchanged zeolite catalysts usually show good SCR activity in the high temperature range with remarkable H_2O and SO_2 durability, such as Fe-ZSM-5 by Ma and Grünert[10] and Fe–Ce-ZSM-5 by Carja *et al.*[11] Other Fe-based catalysts are mainly Fe_2O_3 loaded types such as Fe_2O_3–TiO_2 by Kato *et al.*[12] and Fe_2O_3–WO_3/ZrO_2 by Apostolescu *et al.*[13] with excellent SCR activity and H_2O/SO_2 durability in the medium temperature range. Based on the idea of combining the predominant SCR activity, thermal stability and N_2 selectivity of Fe-based catalysts and the excellent SO_2 durability of TiO_2, here we present a novel non-toxic catalyst using an iron titanate crystallite as the active component with a broad operation window in the medium temperature range (200–400 °C) under relatively high space velocities. NO conversion at 300 °C remaining at 100% in the presence of 10% H_2O and (or) 100 ppm SO_2 makes this catalyst a potential candidate for industrial applications.

The iron titanate catalysts were prepared by the conventional co-precipitation method using $Fe(NO_3)_3·9H_2O$ and $Ti(SO_4)_2$ as precursors (Fe : Ti = 1 : 1 in molar ratio) and 25 wt% $NH_3·H_2O$ as precipitator with subsequent filtration, washing, and drying at 100 °C overnight and calcination at 400, 500, 600, 700 °C for 6 h, respectively (signified by Fe_xTiO_y-400, 500, 600, 700 °C). Catalysts sieved with 20–40 mesh were used in the activity test experiments and the reaction conditions were as follows: 0.6 ml sample, 500 ppm NO, 500 ppm NH_3, 5% O_2, 100 ppm SO_2 (when used), 10% H_2O (when used), balance N_2, 500 ml min^{-1} total flow rate and gas hourly space velocity (GHSV) = 50 000 h^{-1}. The water vapor was injected with an accurate syringe pump equipped with an evaporator which was heated to 300 °C. The tubing of the activity test system was heated to 120 °C to avoid deposition of ammonium salts and water droplets. The effluent gas, including NO, NH_3, N_2O and NO_2 dried using $CaSO_4$ was continuously analyzed by an FTIR spectrometer (Thermo Nicolet Corporation Nexus 670, OMNIC Quantpad software) equipped with a heated, low volume multiple-path gas cell (2 m). The spectra were collected after 60–120 min when the SCR process reached a steady state.

The conversions of NO over catalysts under different calcination temperatures are reported in Fig. 1 as a function of reaction temperature from 150–400 °C. Fe_xTiO_y-400 °C showed the best

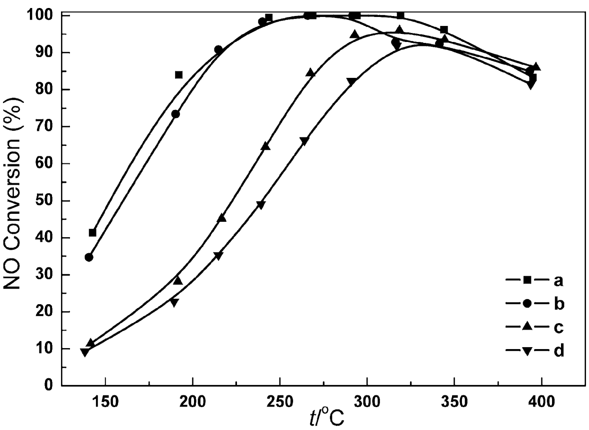

Fig. 1 NO conversions over catalysts under different calcination temperatures for 6 h: (a) 400 °C, (b) 500 °C, (c) 600 °C, (d) 700 °C.

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

† Electronic supplementary information (ESI) available: Catalyst preparation, reactant quantification, comparison with Mn- and Cu-based catalysts, preliminary experiments on active component determination and an *in situ* DRIFTS study. See DOI: 10.1039/b800143j

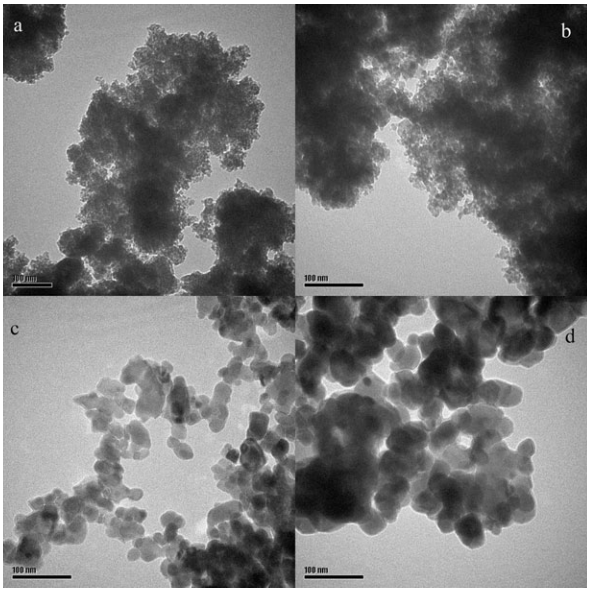

Fig. 2 TEM images of catalysts under different calcination temperatures for 6 h: (a) 400 °C, magnification 200 k; (b) 500 °C, magnification 300 k; (c) 600 °C, magnification 300 k; (d) 700 °C, magnification 300 k.

activity, with NO conversion above 95% from 225 °C to 350 °C and the N_2 selectivity was always above 94% even at 400 °C. Fe_xTiO_y-500 °C had similar activity to the one calcined at 400 °C. The BET surface areas of these four catalysts are 245.3, 150.6, 48.3 and 28.1 $m^2\ g^{-1}$, respectively. The TEM and XRD results are shown in Fig. 2 and 3. Comparing these results, we can see that with an increase in calcination temperature, the BET surface area had a sharp decrease along with an obvious growth in catalyst particle size (from 7–8 nm to 50–60 nm) which was one possible reason for the activity decline. The catalyst calcined at 400 °C for 6 h showed no obvious sharp X-ray diffraction peaks besides some broad bumps, implying that under this preparation condition the Fe_xTiO_y was mainly in a crystallite phase (maybe $FeTiO_3$ crystallite according to JCPDS-791838 and Fe_2TiO_5 crystallite). XRD patterns of pseudobrookite Fe_2TiO_5 appeared with increasing calcination temperature and rutile TiO_2 appeared after 600 °C, 700 °C calcination for 6 h resulting in the decrease of $FeTiO_3$ and Fe_2TiO_5 crystallites which were considered as active components.

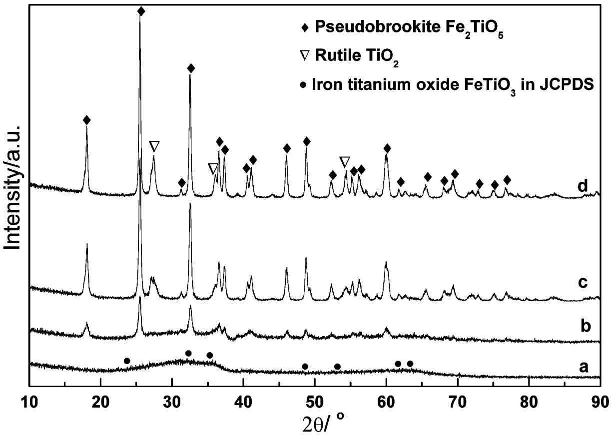

Fig. 3 XRD patterns of catalysts under different calcination temperatures for 6 h: (a) 400 °C, (b) 500 °C, (c) 600 °C, (d) 700 °C.

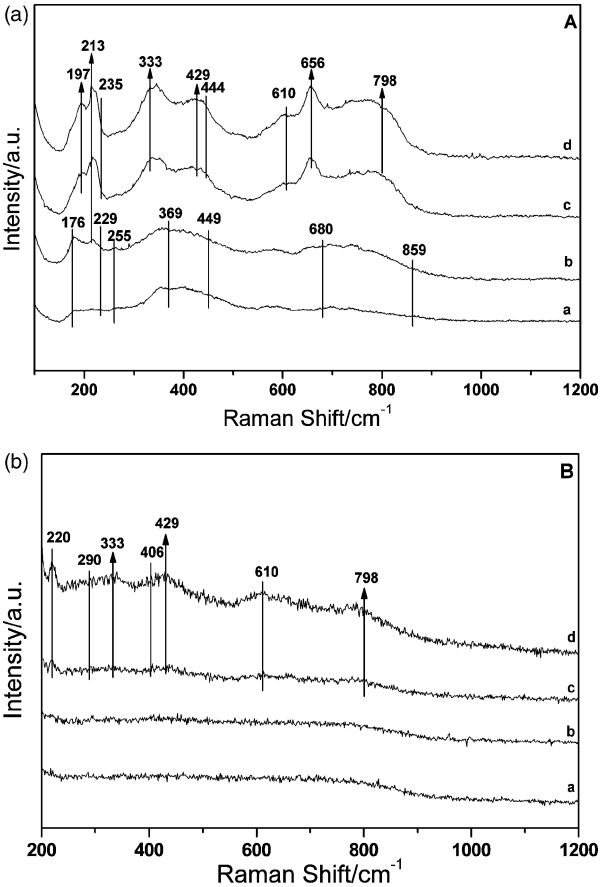

Fig. 4 (A) Vis-Raman spectra (λ_{ex} = 532 nm) and (B) UV-Raman spectra (λ_{ex} = 325 nm) of catalysts under different calcination temperatures for 6 h: (a) 400 °C, (b) 500 °C, (c) 600 °C, (d) 700 °C.

We also carried out Vis-Raman and UV-Raman spectrum experiments to find out the actual active phase, and these are shown in Fig. 4. Titanium oxide usually has strong absorption in the UV region, so UV-Raman spectroscopy is more surface-sensitive in these catalysts.[14] Vis-Raman spectroscopy can be used to reveal the components in bulk phase which can also be associated with the XRD results. In the Vis-Raman spectra, the catalysts calcined at 400 °C and 500 °C showed several broad bands which could be attributed to $FeTiO_3$ crystallite (176, 229, 255, 369, 449, 680 and 859 cm^{-1})[15] and we could also see that Fe_2TiO_5 crystallite (bands with arrowheads)[16] formed in Fe_xTiO_y-500 °C. After high temperature calcination, Fe_2TiO_5 had better crystallization and rutile TiO_2 (235, 444 and 610 cm^{-1}) separated out due to non-stoichiometry of Fe and Ti. This result had a good accordance with the XRD patterns. In the UV-Raman spectra, there was no obvious Raman band for Fe_xTiO_y-400 °C and 500 °C, which was due mainly to the strong absorption of UV light. Fe_2TiO_5 (bands with arrowheads) and hematite Fe_2O_3 (290, 406 and 610 cm^{-1}) could be detected on the surface of Fe_xTiO_y-600 °C and 700 °C implying that rutile TiO_2 was not the only oxide separated out during high temperature calcination. Hematite Fe_2O_3 mainly aggregated on the surface of catalyst, and rutile TiO_2 formed in the bulk phase.

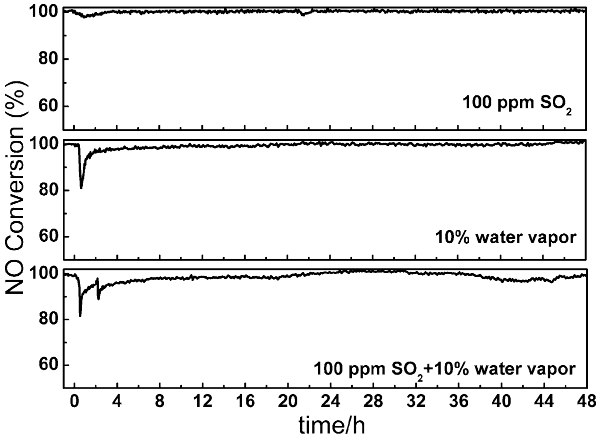

Fig. 5 NO conversion as a function of time at 300 °C over Fe_xTiO_y-400 °C in the presence of SO_2/H_2O.

This is another reason for the activity decrease. XPS results also showed that there is Fe^{2+} in the catalysts calcined at low temperature, implying the existence of $FeTiO_3$. The binding energy of Ti shifted from 458.6 eV to 458.8 eV resulting in a decrease of redox ability in the SCR reaction (see ESI†).

Since the combustion exhaust usually contains SO_2 and water vapor, we further chose the best catalyst Fe_xTiO_y-400 °C to study its SO_2/H_2O durability. As the deactivation effect of these two components (especially SO_2) needs a long time to achieve steady state, which makes it meaningless to test the activity by changing the reaction temperature, we chose a fixed temperature point (300 °C) to investigate their influence. The results are given in Fig. 5. As we can see, when 100 ppm SO_2 was added at 0 min, a slight decrease in NO conversion occurred after 1–2 h and then the conversion recovered to 100% and held up until 48 h. In the case of 10% H_2O, NO conversion dramatically decreased to 80% after 0.5 h and then it also recovered to 100%. Interestingly, 100 ppm SO_2 along with 10% H_2O made NO conversion decrease twice. Comparing the times when the lowest conversions were reached, we can see that: the first decrease occurring after 0.5 h was caused mainly by water vapor; the second decrease, occurring after 2 h, was much sharper than the first one and this may be caused by the synergistic poisoning effect of SO_2 and H_2O which needs to be verified in future work.

To investigate the influence of sulfation on the SCR activity across the whole temperature range, we also did the SCR ($NO + NH_3 + O_2$), NO oxidation ($NO + O_2$) and NH_3 oxidation ($NH_3 + O_2$) experiments, respectively over Fe_xTiO_y-400 °C after 100 ppm SO_2 sulfation for 48 h at 300 °C and the results are given in Fig. 6. After sulfation, the SCR activity decreased between 150 °C and 250 °C, however it was promoted above 250 °C to a certain extent. Results of separate NO oxidation and NH_3 oxidation experiments showed that: the sulfation could cause deactivation of NO oxidation to NO_2 which was possibly the reason for activity loss in the relatively low temperature range where the "fast SCR" was important to the reaction;[17] decrease of non-selective oxidation of NH_3 to nitrogen oxides in the relatively high temperature range was possibly responsible for the activity promotion.

In conclusion, the iron titanate catalyst with a crystallite phase, prepared by a conventional co-precipitation method, showed excellent NH_3-SCR activity, N_2 selectivity and SO_2/H_2O durability in a broad medium temperature range. Even after 48 h sulfation, the catalyst still showed NO conversion above 90% from 250 °C to 400 °C. Studies concerning the mechanism of SCR reaction on this catalyst and SO_2/H_2O deactivation effect are under way.

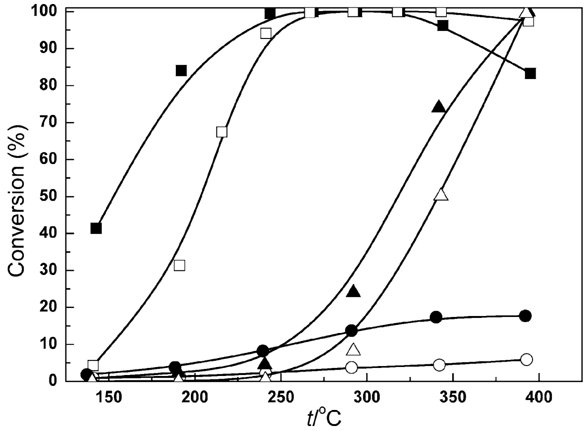

Fig. 6 Comparison of SCR, separate NH_3 oxidation and separate NO oxidation activities over catalyst before and after sulfation: ■, □ NO conversion in SCR before and after sulfation; ▲, △ NH_3 conversion in NH_3 oxidation before and after sulfation; ●, ○ NO conversion in NO oxidation before and after sulfation.

We sincerely appreciate the help from Professor Can Li and Zhaochi Feng with respect to the Raman spectrum experiments in the Dalian Institute of Chemical Physics, Chinese Academy of Sciences. This work was financially supported by the National Natural Science Foundation of China (20425722, 20621140004) and the Ministry of Science and Technology, China (2006AA060304).

Notes and references

1 H. Bosch and F. Janssen, *Catal. Today*, 1988, **2**, 369.
2 G. Busca, L. Lietti, G. Ramis and F. Berti, *Appl. Catal., B*, 1998, **18**, 1.
3 J. P. Dunn, P. R. Koppula, H. G. Stenger and I. E. Wachs, *Appl. Catal., B*, 1998, **19**, 103.
4 X. L. Tang, J. M. Hao, W. G. Xu and J. H. Li, *Catal. Commun.*, 2007, **8**, 329.
5 G. Qi, R. T. Yang and R. Chang, *Appl. Catal., B*, 2004, **51**, 93.
6 P. G. Smirniotis, P. M. Sreekanth, D. A. Peña and R. G. Jenkins, *Ind. Eng. Chem. Res.*, 2006, **45**, 6436.
7 G. Qi, R. T. Yang and R. Chang, *Catal. Lett.*, 2003, **87**, 67.
8 Z. G. Huang, Z. P. Zhu, Z. Y. Liu and Q. Y. Liu, *J. Catal.*, 2003, **214**, 213.
9 R. Q. Long, R. T. Yang and R. Chang, *Chem. Commun.*, 2002, 452.
10 A. Z. Ma and W. Grünert, *Chem. Commun.*, 1999, 71.
11 G. Carja, G. Delahay, C. Signorile and B. Coq, *Chem. Commun.*, 2004, 1404.
12 A. Kato, S. Matsuda, F. Nakajima, M. Imanari and Y. Watanabe, *J. Phys. Chem.*, 1981, **85**, 1710.
13 N. Apostolescu, B. Geiger, K. Hizbullah, M. T. Jan, S. Kureti, D. Reichert, F. Schott and W. Weisweiler, *Appl. Catal., B*, 2006, **62**, 104.
14 J. Zhang, M. J. Li, Z. C. Feng, J. Chen and C. Li, *J. Phys. Chem. B*, 2006, **110**, 927.
15 A. L. Wang, K. E. Kuebler, B. L. Jolliff and L. A. Haskin, *Am. Mineral.*, 2004, **89**, 665.
16 P. H. C. Camargo, G. G. Nunes, G. R. Friedermann, D. J. Evans, G. J. Leigh, G. Tremiliosi-Filho, E. L. de Sá, A. J. G. Zarbin and J. F. Soares, *Mater. Res. Bull.*, 2003, **38**, 1915.
17 M. Koebel, M. Elsener and G. Madia, *Ind. Eng. Chem. Res.*, 2001, **40**, 52.