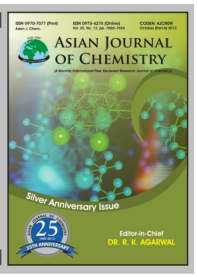
Asian Journal of Chemistry; Vol. 25, No. 18 (2013), 10572-10576

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.16092



Low-Temperature Selective Catalytic Reduction of NO with NH_3 Over Fe_xO_y/Carbon Nanotubes Catalyst

BINGNAN REN[1,*], QIAOWEN YANG[2] and JING GENG[3]

[1]Institute of Oceanology, SanYa University, Sanya, Hainan, P.R. China
[2]School of Chemical and Environment Engineering, China University of Mining and Technology (Beijing), Beijing 100083, P.R. China
[3]School of Tourism Managment, SanYa University, Sanya 572022, Hainan Province, P.R. China

*Corresponding author: Fax: +86 898 88386786; Tel: +86 15120679968; E-mail: renbingnan@126.com

(*Received*: 23 July 2013; *Accepted*: 27 November 2013) AJC-14450

The metal oxide catalyst was prepared by loading Fe_xO_y on carbon nanotubes with impregnation method. The catalyst was characterized by BET, TEM and XPS and the catalytic activity of the catalyst for selective catalytic reduction of NO was investigated. The results showed that the species of active components loaded on the catalyst was given priority to with Fe_2O_3. The NO conversion was improved with temperature increase under the range of 150-300 °C. The oxygen content had an outstanding influence on the NO conversion of catalysts at lower concentration range. Once the oxygen content was enhanced over 5 %, there was no significant increase. Increasing of NH_3/NO ratio could increase the NO conversion. When NH_3/NO ratio was continued to exceed 1.1, the NO conversion decreased. With the increasing of space velocity, the NO conversion was decreased under the reaction conditions.

Key Words: Carbon nanotubes, Catalyst, Low-temperature selective catalytic reduction.

INTRODUCTION

It is well known that NO_x is one of the most predominant pollutants. These pollutants can cause lung irritation and inhibit the body's ability to fight off diseases such as influenza and pneumonia. It takes about 10 times more nitrogen dioxide than ozone to cause significant lung irritation and inflammation. Long-term exposures to high concentrations of nitrogen dioxide can produce chronic damage to respiratory tract tissue that resembles the lung disease emphysema. In the dark, nitrogen dioxide can react with ozone and form a very reactive free radical. The free radical then can react with organic compounds in the air to form nitrogenated organic compounds, some of which have been shown to be mutagenic and carcinogenic. Further high levels of NO_x cause a variety of environmentally harmful effects such as acid rain and urban smog. They also contribute to the greenhouse effect. Therefore, it has become important to reduce the emission of nitrogen oxides from both stationary and mobile combustion technologies in order to keep the health of humans and protect environment.

Among various NO_x emission control techniques, selective catalytic reduction of NO with NH_3 in the presence of excess oxygen has been proven to be the most effective which is widely used. It has been proved that the catalyst being prepared through supported metallic oxides are with good catalytic performance. Various metal oxide based catalysts have been shown to possess some potential for low temperature application, including Fe_2O_3, CuO, Co_2O_3, Mn_2O_3, CeO_2, V_2O_5, *etc*.. Due to the carbon material with excellent surface properties, the carbon-supported catalysts have very good performance. Among the reported catalysts, metal oxides supported on carbon materials (activated carbon, activated coke, activated carbon fiber) have shown high activity. As a novel carbon material, carbon nanotubes (CNTs) have attracted much attention due to their unique electric, mechanical and structural characteristics. It has been widely studied in fields of high strength carbon fiber materials[1], hydrogen storage materials[2-4], new catalytic materials[4-8], *etc*. With the tunable pore structure and surface properties and the large specific surface area, carbon nanotubes have been regarded as the perfect supporting materials for catalysts. Meanwhile, due to one-dimensional tubular structure of carbon nanotubes, catalytic materials with specific properties can be prepared in the cavity of tubular. So as a new catalytic material, carbon nanotubes have caused attention of many researchers[9-12].

Therefore, it can be an issue deserved intensive study to make use of carbon nanotubes to study the low-temperature selective catalytic reduction of NO with NH_3. This research reported the preparation of Fe_xO_y/carbon nanotubes catalyst through supported ferric oxide on the carbon nanotubes after

purification. We have investigated ferric oxide supported on the carbon nanotubes catalysts as low-temperature selective catalytic reduction catalysts.

EXPERIMENTAL

Catalyst preparation: The raw carbon nanotubes were purified by means of immersion in a 65 % of HNO_3 solution and refluxed at boiling point for 4-6 h. Then the sample was washed with distilled water till pH 6-7 and dried at 110 °C for 12 h. The supported Fe_xO_y/carbon nanotubes catalysts were prepared by impregnation method. The carbon nanotubes after purification was impregnated in different concentrations of ferric nitrate solution at room temperature for 24 h, then dried at 110 °C for 12 h. And after grinded, the carbon nanotubes were calcified at 500 °C under nitrogen atmosphere for 5 h.

Catalyst characterization: The specific surface area and pore volume of the carbon nanotubes and Fe_xO_y/carbon nanotubes catalysts were analyzed by an TRISTAR II 3020M which can be determined through N_2 absorption method. The pore volume was calculated using the BET method. A JEM-1200EX transmission electron microscope was used for TEM which acceleration voltage is 120 kv and magnification is 0-200000. XPS analysis was carried out by making use of AXIS Ultra-type X-ray photoelectron spectroscopy (England Kratos).

Catalytic activity tests: The catalytic activity tests were carried out in a fixed bed reactor made of stainless steel in the 150-300 °C temperature range. The gas composition was 450 ppm NO, 500 ppm NH_3, 5 % O_2 balanced by N_2. The total flow rate was 500 mL min^{-1}. The experimental apparatus of evaluation of the catalytic activity tests included sections of gas configuration, catalytic reaction and flue gas analysis, which was shown in Fig. 1. NO concentrations in the inlet and outlet gases were measured by flue gas analyzer (KM940, Kane). The NO conversion was calculated from the NO concentration at the inlet and outlet of the reactor. Before starting the activity measurements, the Fe_xO_y/carbon nanotubes catalysts were degasified under N_2 flow at 120 °C for 1 h. Afterwards, the activity tests were performed under isothermal conditions. Steady-state the NO conversion was observed when the NO concentration at the outlet of the reactor became steady, several hours after the reaction started.

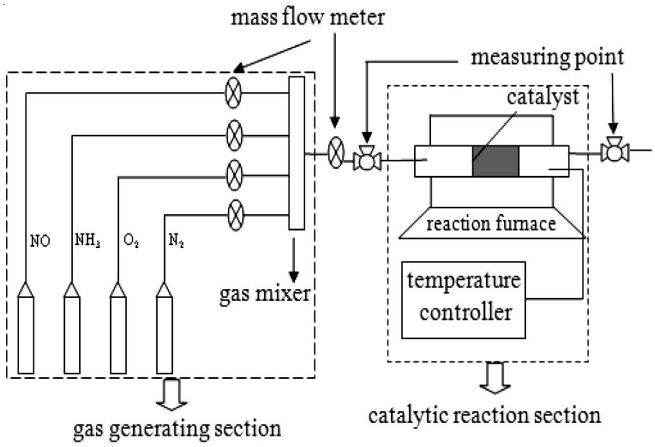


Fig. 1. Experimental apparatus for activity test

RESULTS AND DISCUSSION

The surface areas, pore volumes and pore sizes (inner diameters) of the raw carbon nanotubes, carbon nanotubes after purification and Fe_xO_y/carbon nanotubes catalyst were listed in Table-1.The surface area, pore volume and mean pore size of catalyst slightly decreased about 30 % compared with the data of carbon nanotubes after purification, which illustrated that the metallic oxide was loaded on the surface of carrier after impregnation and calcification. Due to the block of pore by metallic oxide, the surface area, pore volume and mean pore size all decreased. It can be proposed that the active component was already loaded on the carbon nanotubes.

TABLE-1
SURFACE AREA AND PORE STRUCTURE ANALYSES OF CARBON NANOTUBES (CNTs)

Samples	S_{BET} (m^2/g)	S_{meso} (m^2/g)	Pore volume (cm^3/g)	Mean pore size (nm)
CNTs after purification	145.1517	123.4085	0.776334	23.7064
Fe_xO_y /CNTs catalyst	102.1253	86.9504	0.520621	21.2912

Fig. 2 showed the TEM image of carbon nanotubes-after purification and Fe_xO_y/carbon nanotubes catalyst, in which the HNO_3 treatment made most of the carbon nanotubes open

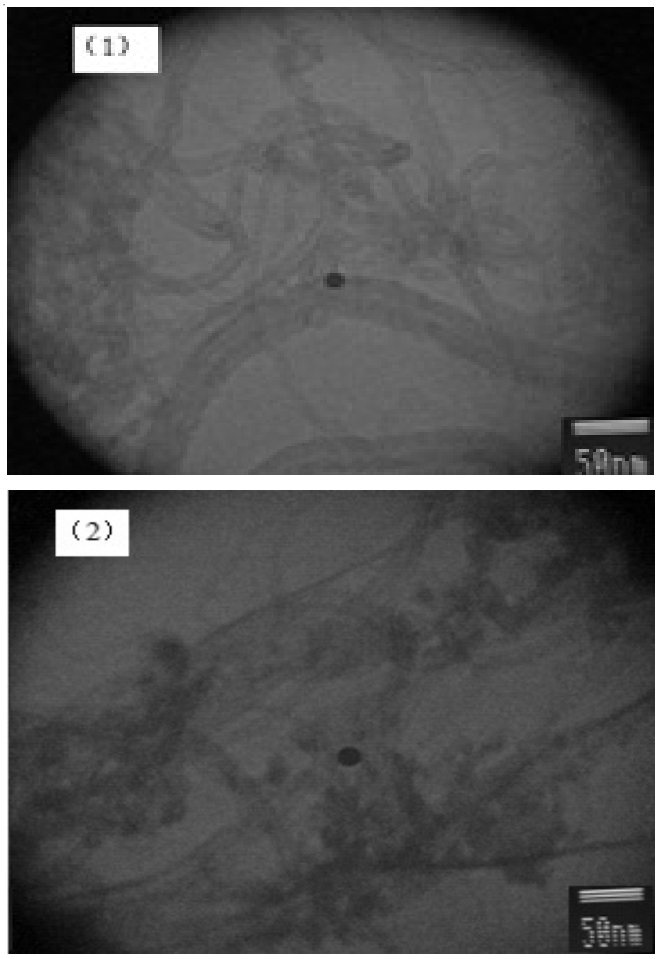


Fig. 2. TEM image of carbon nanotubes:(1) after oxidized by nitrate acid; (2) 10 % Fe_xO_y /carbon nanotubes

(Figs. 2 and 1), which leads to an increase of the surface areas. For Fe_xO_y/carbon nanotubes catalyst, Fe_xO_y particles were located on the wall of the tubes (Figs. 2 and 2). But the metal oxide particles loaded on the carbon nanotubes was not evenly on the surface of the carrier. Future researches should be worthy to be carried out to improve the metal oxide particle dispersion.

Fig. 3 illustrated the surface element concentration of Fe_xO_y/carbon nanotubes catalyst by XPS spectra, in which (a), (b) and (c) were separately Fe_xO_y/carbon nanotubes catalyst spectra, Mn(2p) spectra and O(1s) spectra, respectively. The catalyst XPS spectra showed three obvious peaks, the peak of 710 eV was the absorption peak of iron; the binding energy in the middle peak was 530 eV, which was the absorption peak of oxygen; peak with the biggest binding energy was 284 eV, which was the absorption peak of carbon. The surface element concentrations of Fe_xO_y/carbon nanotubes catalyst sample measured by XPS were 95.39 % of C, 2.96 % of O, 1.6 % of Fe. It can be seen from Fig. 3(b) that the large absorption peak was 710.1 eV corresponded to Fe_2O_3. Therefore, the combination form of metallic oxide was given priority to with Fe_2O_3.

Fig. 4 presented the NO conversion of Fe_xO_y/carbon nanotubes catalyst at different temperature. The result indicated that all catalysts reached to the highest NO conversion rate at 300 °C. The NO conversion of catalyst prepared with different impregnation concentrations increased rapidly with the rise of temperature under the temperature range of 150-300 °C. During the process of the selective catalytic reduction, rising temperature would lead to the reaction rate of the NO conversion increased. The consumption of NH_3 was mainly for NO reduction reaction and NO conversion rate increased rapidly. After that, continue to rise the reaction temperature, NO reaction would be restricted for the occurrence of NH_3 oxidation reaction because rising temperature made the NH_3 oxidation reaction easily occurred.

Fig. 5 showed the effect of oxygen content on selective catalytic reduction activity of Fe_xO_y/carbon nanotubes catalyst. The result showed that the NO conversion increased with

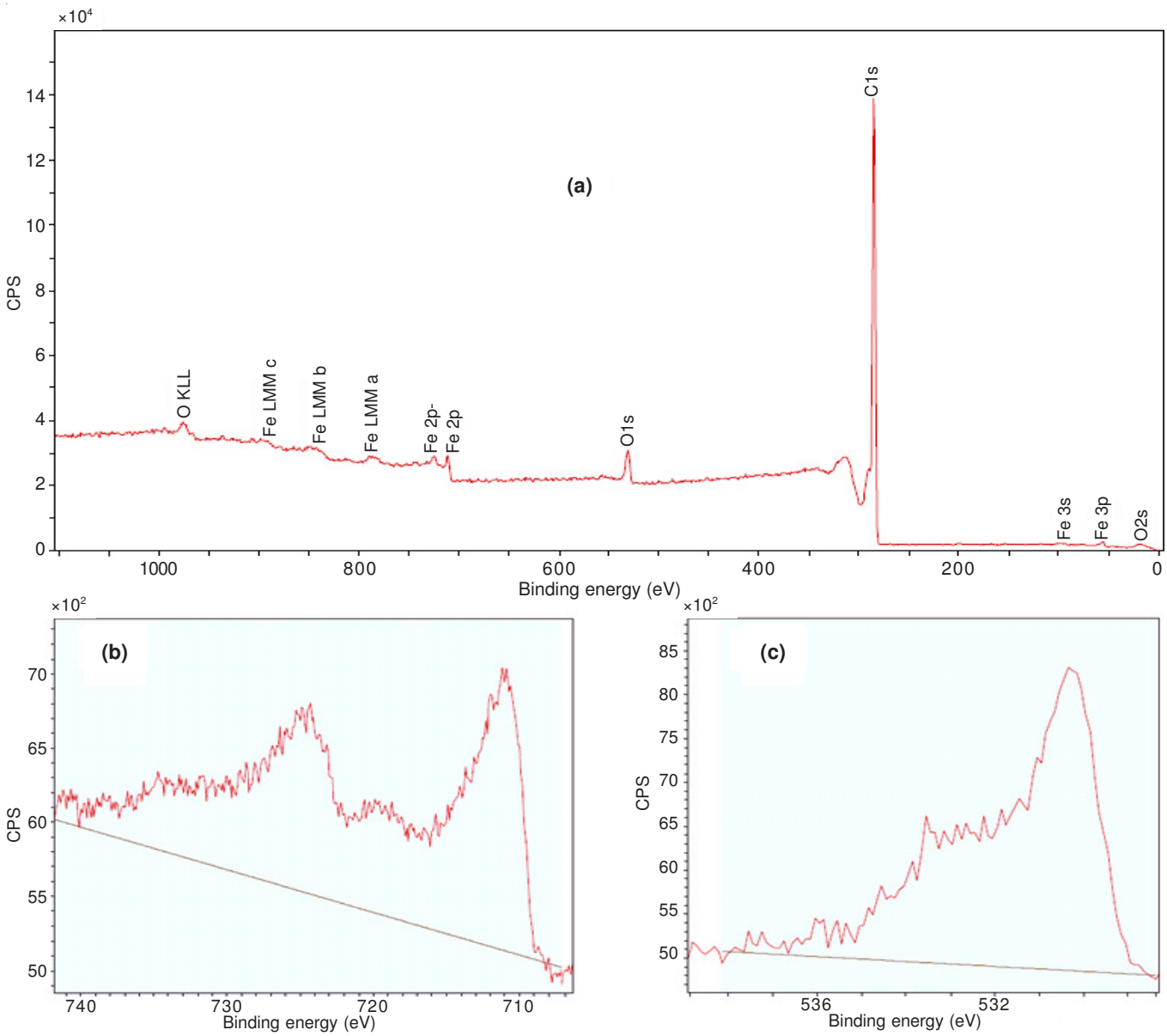


Fig. 3. XPS spectra of the Fe_xO_y/carbon nanotubes: (a) Fe_xO_y/carbon nanotubes, (b) Fe(2p), (c) O(1s)

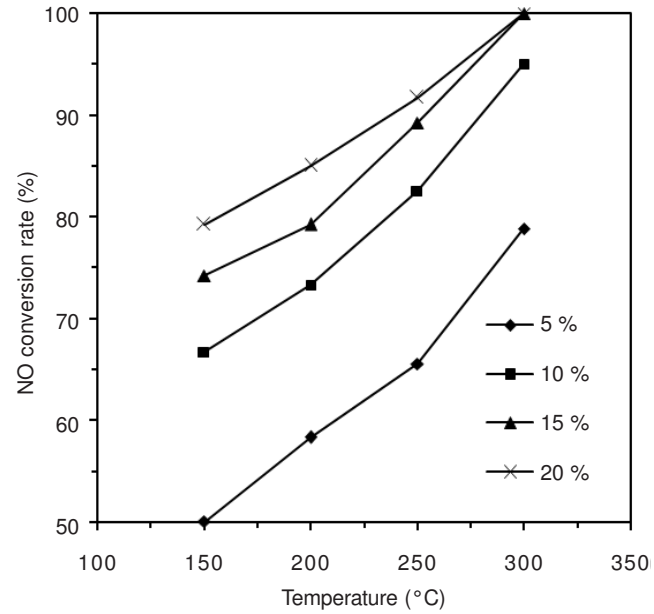


Fig. 4. Effect of reaction temperature on the activity of Fe_xO_y/carbon nanotubes

increasing of oxygen content at different temperature. With increasing oxygen content from 1 to 5 %, the NO conversion increased rapidly. At 250 °C, the NO conversion increased rapidly from 54 to 100 %. However, no obvious change was observed when the O_2 concentration exceeded 5 %. The NO conversion remained stable basically. This indicated that O_2 played a significant promoting role in the selective catalytic reduction. Gas phase oxygen and adsorbed oxygen species achieved a balanced state when the O_2 concentration reached 5 %.

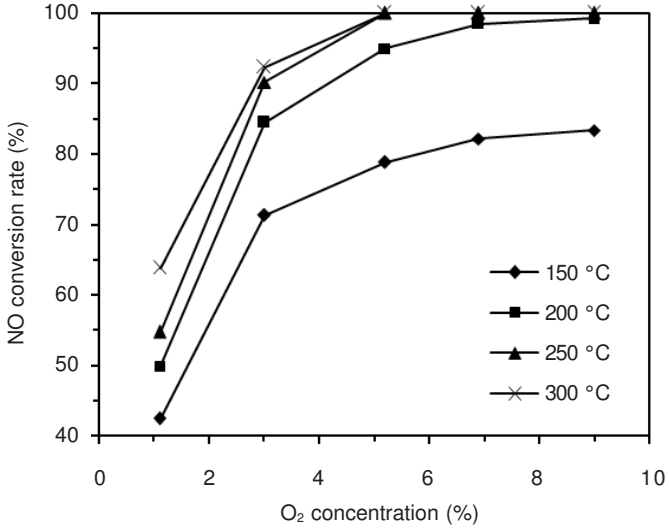


Fig. 5. Effect of O_2 concentration on NO removal over Fe_xO_y/carbon nanotubes

Figure 6 illustrated the influence of NH_3/NO ratio on NO reduction at different temperatures (150-300 °C). The result showed that the NO conversion increased with increasing of NH_3/NO ratio in the range of ratios from 0.7 to 1.1. When NH_3/NO ratio continued to exceed 1.1, the NO conversion decreased. For NH_3/NO < 1.1, increasing of NH_3/NO ratio could increase the unit mass of NH_3 adsorption quantity on the catalyst. So the selective catalytic reduction reaction rate was accelerated. But excessive NH_3 cannot be adsorbed on catalyst. NH_3 was reacted with NO, which could lead to the decease of the NO conversion.

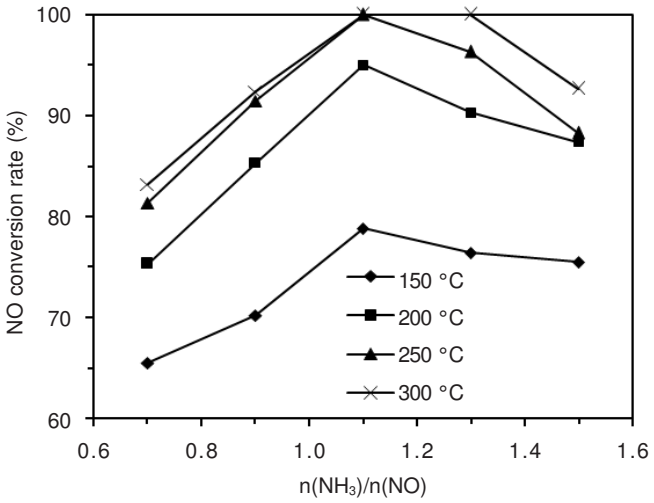


Fig. 6. Effect of $n(NH_3)/n(NO)$ on NO removal over Fe_xO_y/carbon nanotubes

Figure 7 presented the effect of space velocity on the NO conversion at different temperatures (150-300 °C). The NO conversion all tended to decrease with the increase of space velocity under all the experimental temperatures. However, when reaction happened in 150 °C, the NO conversion decreased rapidly with the increase of space velocity. While the NO conversion remained unchanged and then decreased slowly under the temperature range of 150-300 °C. Which illustrated that higher reaction temperature can weaken the effect of space velocity on the NO conversion. Furthermore, the NO conversion increased constantly with the rising of temperature under each space velocity. The higher the space velocity was, the shorter time the reactant gas stayed on catalyst. At a high space velocity, the decrease in the NO conversion may result from insufficient contact time between the reactants and the catalyst or from insufficient amounts of active sites to react.

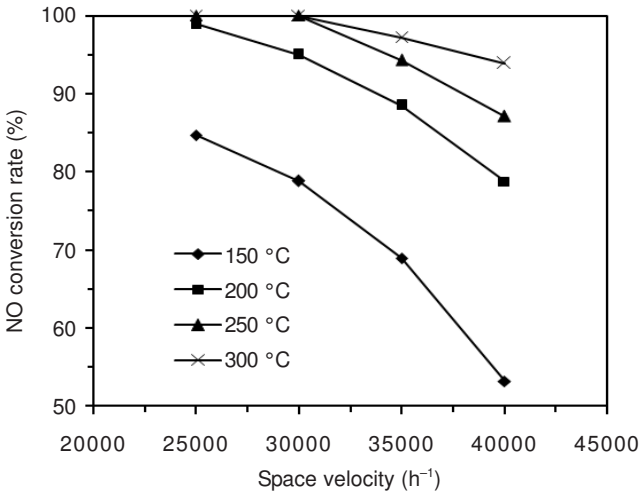


Fig. 7. Effect of space velocity on NO removal over FexOy/carbon nanotubes

Conclusion

Carbon nanotubes after purification was impregnated in different concentrations of ferric nitrate solution. The metallic oxide was loaded on the surface of carbon nanotubes after impregnation and calcification. Due to the block of pore by metallic oxide, the surface area, pore volume and mean pore size all decreased. But the metal oxide particles loaded on the carbon nanotubes was not evenly on the surface. Future researches should be worthy to be carried out to improve the metal oxide particle dispersion.

During the selective catalytic reduction reaction process of Fe_xO_y/carbon nanotubes catalyst, rising temperature would lead to the reaction rate of the NO conversion increased. Continue to rise the reaction temperature, NH_3 oxidation reaction would happen, the reduction reaction of NO would be restrained, the NO conversion rate started to slow down. Oxygen played a significant promoting role in the selective catalytic reduction reaction. The NO conversion increased with increasing of oxygen content at each reaction temperature. The oxygen content caused a prominent affect on catalyst at lower oxygen content. Once the O_2 concentration exceeded 5 %, the NO conversion remained stable basically. For NH_3/NO ratio < 1.1, increasing of NH_3/NO ratio could increase the unit mass of NH_3 adsorption quantity on the catalyst. The NO conversion increased. When the NH_3/NO ratio continued to exceed 1.1, the NO conversion decreased. The NO conversion all tended to decrease with the increase of space velocity under all the experimental temperatures. Higher reaction temperature can weaken the effect of space velocity on the NO conversion. The higher the space velocity was, the shorter time the reactant gas stayed on catalyst.

ACKNOWLEDGEMENTS

The authors gratefully acknowledged the financial support by the Natural Science Foundation of Hainan Province of China (413128), the Scientific Research Foundation of the Higher Education Institutions of the Education Department of Hainan Province (Hjkj2012-48), the Academy-Locality Cooperation Project of Sanya (2012YD50).

REFERENCES

1. P. Poncharal, Z.L. Wang, D. Ugarte and W.A. de Heer, *Science*, **283**, 1513 (1999).
2. A.C. Dillon, K.M. Jones, T.A. Bekkedahl, C.H. Kiang, D.S. Bethune and M.J. Heben, *Nature*, **386**, 377 (1997).
3. Y. Ye, C.C. Ahn, C. Witham, B. Fultz, J. Liu, A.G. Rinzler, D. Colbert, K.A. Smith and R.E. Smalley, *Appl. Phys. Lett*., **74**, 2307 (1999).
4. C. Liu, Y.Y. Fan, M. Liu, H.T. Cong, H.M. Cheng and M.S. Dresselhaus, *Science*, **286**, 1127 (1999).
5. J.M. Planeix, N. Coustel, B. Coq, V. Brotons, P.S. Kumbhar, R. Dutartre, P. Geneste, P. Bernier and P.M. Ajayan, *J. Am. Chem. Soc*., **116**, 7935 (1994).
6. B. Coq, J. Marc Planeix and V. Brotons, *Appl. Catal. A*, **173**, 175 (1998).
7. Y. Zhang, H.B. Zhang, G.D. Lin, P. Chen, Y.Z. Yuan and K.R. Tsai, *Appl. Catal. A*, **187**, 213 (1999).
8. C. Liang, Z. Li, J. Qiu, C. Li and C. Li, *J. Catal*., **211**, 278 (2002).
9. H. Zhang, J. Qiu, C. Liang, Z. Li, X. Wang, Y. Wang, Z.C. Feng and C. Li, *Catal. Lett*., **101**, 211 (2005).
10. K.P. De Jong and J.W. Geus, *Catal. Rev., Sci. Eng*., **42**, 481 (2000).
11. P. Serp, M. Corrias and P. Kalck, *Appl. Catal. A*, **253**, 337 (2003).
12. G.G. Wildgoose, C.E. Banks and R.G. Compton, *Small*, **2**, 182 (2006).