International Journal of Smart Grid and Clean Energy

The performances of iron ore catalysts on low-temperature SCR of NO_x with NH_3

Shaochen Gu, Keting Gui*

Key Laboratory of Energy Thermal Conversion and Control of Ministry of Education, School of Energy and Environment, Southeast University, Nanjing, 210096, China.

Abstract

The effects of catalysts prepared from different calcined iron ores on low-temperature selective catalytic reduction of NO was studied in this paper. The research produced following two key findings: The active ingredient of the hematite is α-Fe_2O_3, and the NO conversion using this iron ore as catalyst is over 90% at 240-300 ℃. The main active ingredients of the calcined ferro-manganese ore are Mn_2O_3 and Fe_2O_3, and the NO conversation of this kind of catalyst calcined at 450 ℃ can maintain more than 97% at 90-270 ℃ and show high SO_2 durability for the SCR reaction. Hence, it is a new kind of catalyst with high efficiency and stable catalytic activity for low-temperature selective catalytic reduction of NO with NH_3.

Keywords: iron ore, selective catalytic reduction (SCR), low-temperature, SO_2

1. Introduction

Selective catalytic reduction (SCR) of NO_x with NH_3 is a widely used process for removing NOx from stationary sources, whereas most commercial catalysts for this process are V_2O_5/TiO_2 promoted by WO_3 or MoO_3. However, these vanadium-based catalysts are not environmental friendly as the vanadium is harmful to ecological environment. Moreover, high SCR reaction temperature range and high cost are also the disadvantages of these catalysts. Therefore, an urgent demand for developing environmentally-benign deNO_x catalysts with wide raw material sources, low cost and low SCR reaction temperature range is put forward. Gongshin Qi et al.[1] found that the reaction temperature of SCR could be decreased to 200-300 ℃ when a small amount of noble metal (Pt, Rh, or Pd) was added to the Fe-ZSM-5. The SCR activity follows the order Pt/FeZSM-5 > Rh/Fe-ZSM-5 > Pd/Fe-ZSM-5 at 250 ℃. On the Pt promoted Fe-ZSM-5, 90% NO conversion was obtained at 250 ℃ at GHSV = 1.1×10^5 h^{-1}. Panagiotis et al.[2] compared a series of TiO_2-, Al_2O_3-, and SiO_2-supported manganese oxide catalysts. They found that the SCR performance of the supported Mn catalysts decreased in the following order: TiO_2 (anatase, high surface area) > TiO_2 (rutile) > TiO_2 (anatase, rutile) > γ-Al_2O_3 > SiO_2 > TiO_2 (anatase, low surface area). Leonhard et al.[3], Siva et al.[4] reported that $Mn_{0.75}Fe_{0.25}/Al_2O_3$ and $Mn_{0.75}Fe_{0.25}/TiO_2$ catalysts prepared by deposition-precipitation had highly activity in the SCR reaction below the temperature of 300 ℃.

Various kinds of iron ore in the nature contain not only metallic element such as Fe, Mn, Cr, Al etc. but also non-metallic element such as Si, C, etc. Chemical composition and physical structure of different types of ores changes under the effects of the geological movements which brings the formation of the unique chemical property. Hence, to investigate the low-temperature SCR activity of iron ore catalysts, different kinds of iron ore including limonite, hematite and ferro-manganese ore were tested. The low

---

* Manuscript received December 2, 2017; revised July 10, 2019.

Corresponding author. Tel.: +86 18795857553; *E-mail address*: gsc187@126.com.

doi: 10.12720/sgce.8.5.522-528

temperature SCR performance, the effects of calcination temperature and the resistance of SO_2 of iron ore catalysts were assessed using a fixed-bed reactor system.

2. Experiments

2.1. Catalysts preparation

In order to prepare iron ore catalysts, some mine stone raw material, include limonite, hematite and ferro-manganese ore stone were selected and smashed by mechanical disruption. The smashed iron orestone were ground and sieved (35-60 mesh) to obtain homogeneous iron ore powder. Prior to the reaction studies, the iron ore powder was calcined in a muffle furnace at 350 ℃ in air for 3 h.

2.2. Activity measurement

The catalytic activity measurement for the reduction of NO by ammonia (NH_3-SCR) with oxygen was carried out at atmospheric pressure in a fixed bed reactor as illustrated in Figure 1. The fixed-bed reactor was manufactured by a stainless steel tube in 20 mm internal diameter and 800mm in long. The typical reactant gas composition was as follows: 500 ppm NO, 500 ppm NH_3, 200ppm SO_2 (when used), 3 vol% O_2 and N_2 as balance. The reaction was carried out in the temperature range of 100-350 ℃ at a heating rate of 1 ℃/min. The concentrations of NO, NO_2 and NO_x in the outlet streams of the reactor were monitored using an online nitrogen oxides analyzer (Ecom-J2KN, Germany).

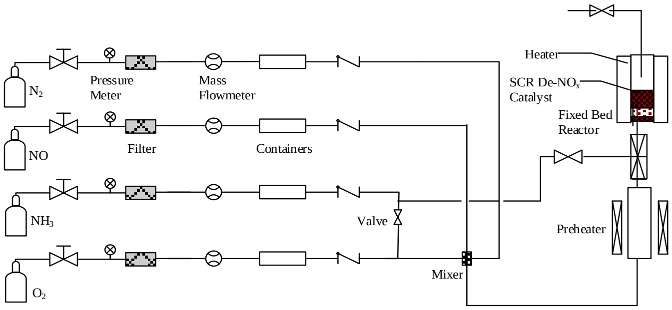

Fig. 1. Schematic diagram of experiment devices.

The NOx conversion is defined as follows:

$$\text{NO conversion \% } (x_{NO} \%)=\frac{(C_{in}-C_{out})}{C_{in}}\times 100 \qquad (1)$$

In Eq. (1), C_{in} and C_{out} denoted the inlet and outlet gas concentrations of NO, respectively.

2.3. Catalyst characterization

Specific surface areas of the catalysts were determined using a Micromeritics ASAP 2020 M Instrument, through nitrogen adsorption at liquid nitrogen temperature (-196 ℃) after standard evacuation at 300 ℃ for 3 h.

The crystal phase structure of the catalysts were determined by the XRD spectra (RIGAKU, D/Max-ⅢA, Japan). Cu Kα radiation was employed and the X-ray tube was operated at 40 kV and 30 mA. The XRD spectra were recorded in the 2h range of 20-100 ° at 0.02 ° intervals. The identification of the phases was confirmed with the ICDD cards (International Centre for Diffraction Data).

Thermogravimetric analysis (TG) was carried out to investigate the thermal stability of sulfate species over the iron ore catalysts. TG experiments were carried out in a static N_2 atmosphere, using a Setsys Evolution 16 instrument (Setarma France). For each experiment, 12-15 mg of each catalyst was analyzed between 35 and 1000 ℃ at a rate of 20 ℃/min.

3. Results and Discussion

3.1. SCR activity of different iron ore catalysts

Figure 2 shows the NH_3-SCR activity of three kinds of iron ore catalysts (hematite, limonite and ferro-manganese ore). The hematite catalyst and the limonite catalyst exhibit the same variation trend that the NO conversion increased below 300 ℃.The ferro-manganese ore catalyst shows different NO conversion characteristics. It is higher than 90% from 120 to 230 ℃, and the top NO conversion is 99% at 170 ℃. This characteristics indicates that ferro-manganese ore catalyst possesses better low temperature catalytic activity to NO conversion than other two kinds of iron ore catalysts.

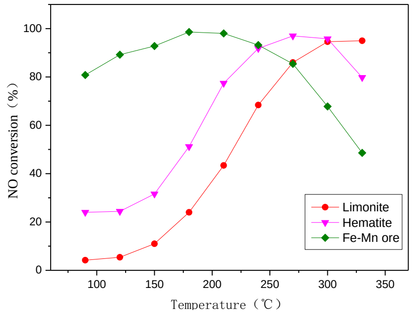

Fig. 2. NO conversion over three kinds of iron ore catalysts with 1.5 L/min gas flow, GHSV=7500h^{-1}, $NO=NH_3=0.05$ ppm and $O_2=3$ vol%.

3.2. X-ray diffraction

The XRD patterns of hematite, limonite and ferro-manganese ore catalyst calcined at 350 ℃ are shown in Figure 3. The most diffraction peaks of hematite and limonite catalysts can be attributed to α-Fe_2O_3, while that of ferro-manganese ore catalyst are respectively indexed to SiO_2, Mn_2O_3 and Fe_2O_3. These XRD patterns indicate that α-Fe_2O_3 is in a more highly dispersed amorphous state on the surface of hematite catalyst than that of limonite catalyst, which resulted in a higher NO conversion[5-7]. Otherwise, it has been proved that Mn oxide has an excellent activity in the low-temperature NH_3-SCR process, and the N_2 selectivity of Mn_2O_3 is the highest in all Mn oxides[8]. Moreover, the low temperature catalytic activity to NO conversion of Mn-Fe mixed oxide is superior that of single metal oxides in ferro-manganese ore catalyst[9-12]. This is due to the geological process in nature caused the change of material structure and surface properties of manganese ores, promoted the synergistic effect between Mn, Fe, and Al metal oxides. Hence, the ferro-manganese ore catalyst exhibits excellent low-temperature SCR catalytic activity to NO conversion.

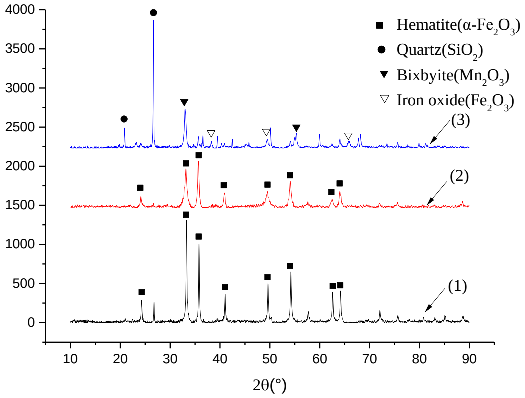

Fig. 3. XRD of three kinds of iron ore catalyst: (1) limonite, (2) hematite, (3) ferro-manganese ore.

3.3. Influence of calcination temperature

The calcination temperature has a great influence on its physical and chemical properties. Figure 4 shows the NO conversion of NH_3-SCR with the aid of the ferro-manganese ore catalyst calcined at 350 ℃, 450 ℃ and 550 ℃, respectively. It is obvious that the NO conversion of the ferro-manganese ore catalyst calcined at 450 ℃ keeps above 97% from 90 to 270 ℃, while the ferro-manganese ore catalyst calcined at 550 ℃ exhibits lower activity at the whole temperature range. When calcined at 350 ℃, the reaction temperature window to obtain high NO conversion is 150 - 210 ℃ which is narrow compared to that calcination at 450 ℃.

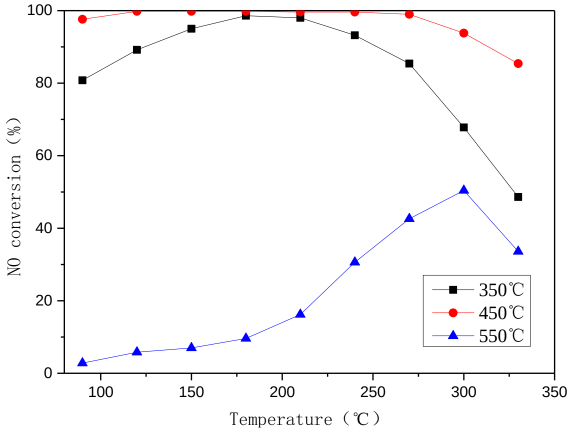

Fig. 4. NO conversion on ferro-manganese ore catalysts calcined at different temperatures with 1.5 L/min gas flow, GHSV=7500h^{-1}, NO=NH_3=0.05 ppm and O_2=3 vol%.

The results of the XRD analysis of ferro-manganese ore catalysts calcined at 350 ℃, 450 ℃ and 550 ℃ are shown in Figure 5. It can be seen that Fe_2O_3 and Mn_2O_3 showed a stronger diffraction peak, indicating that stable crystalline oxide catalyst was formed after calcination 350 ℃. However, the oxide diffraction peaks of catalysts after calcination at 450 ℃ become weak. This result can be analyzed by combined with the surface characterization expressed in Table 1. It can be found that the crystal structure properties changed greatly, a several fold increased in the specific surface area and a half reduce produced in pore size. This illustrates that the Fe, Mn oxide in catalysts exist in amorphous crystalline form after calcination at 450 ℃[13-16]. However, the temperature of 550 ℃ to the calcination of catalyst causes the amorphous crystalline of Fe and Mn oxides crystallization and Mn_2O_3 transforms to Mn_3O_4[17-19]. So the NO conversion of the catalysts decreased largely. In summary, all analysis mentioned above confirms that 450 ℃ calcination temperature can promote the performance of the ferro-manganese ore catalyst significantly.

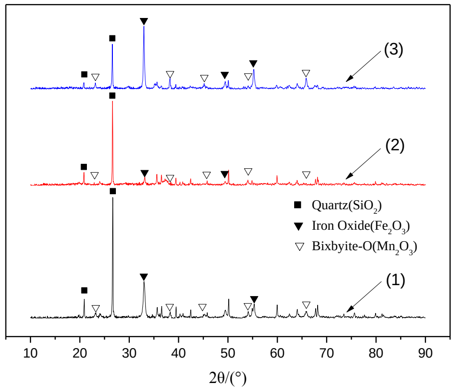

Fig. 5. XRD of ferro-manganese ore catalysts calcined at different temperatures.

Table 1. The physical characteristics of manganese ore catalyst calcined at different temperatures: (1) 350 ℃, (2)450 ℃ and (3)550 ℃.

Catalyst	Surface area (m^2g^{-1})	Pore volume (cm^3g^{-1})	Average pore size (nm)
1	6.57	0.0191	11.63
2	66.44	0.1018	6.13
3	7.98	0.037	18.57

3.4. Influence of SO_2

The effects of SO_2 on the NO conversion efficiency of SCR with the aid of the ferro-manganese ore catalyst were studied for 8 h at 180 ℃ and 270 ℃ in the presence of 200 ppm SO_2, as shown in Figure 6. When SO_2 was introduced under 180 ℃, the activity decreased rapidly (about 60-65%) and then kept stable. The SCR activity still kept at an extreme low level even if SO_2 was cut off at 350 min. But when under 270 ℃, the activity decreased slightly (about 15%) and above 70% of NO was achieved when it kept stable. In addition, the NO conversion recovered to 83% when SO_2 were removed.

The inhibitory effect of SO_2 on the removal of NOx is mainly due to the forming of ammonium sulfate substances on the surface of catalysts after the reaction of ammonia and SO_2, thereby blocking the surface of the catalyst pore [20]. In addition, Fe, Mn and other metal elements in active ingredients change to metal sulfate after sulfuration [21, 22]. On the other hand, the decomposition of ammonium sulfate has been increased at high temperature (270 ℃), so as to inhibit the deposition of ammonium sulfate and blocking of the active site on the catalyst surface [23, 24]. Therefore, the sulfur resistance of the catalyst at 270 ℃ is better than that of the lower reaction temperature (180 ℃).

The thermal stability of the sulfate species on the ferro-manganese ore catalyst after the reaction under 270 ℃ was evaluated in the TG experiment. As shown in Fig. 7, the TG curve presents three major weight losses and the DTG curve displays three corresponding valleys. The first one appeares at approximately 100 ℃, which is due to the evaporation of water. The other apparent DTG valley emerges at 600 ℃ and 800 ℃, which is the decomposition of iron and manganese compound. The TG curve doesn't show obvious weight losses at the decomposition temperatures of $(NH_4)_2SO_4$ (230 ℃) and NH_4HSO_4 (350 ℃) as reported in the literature [25, 26], which indicates that fewer sulfate species are adsorbed on the surface of ferro-manganese ore catalyst after the reaction under 270 ℃. This finding explains the reason of the favorable SO_2 resistance under 270 ℃ reaction temperature.

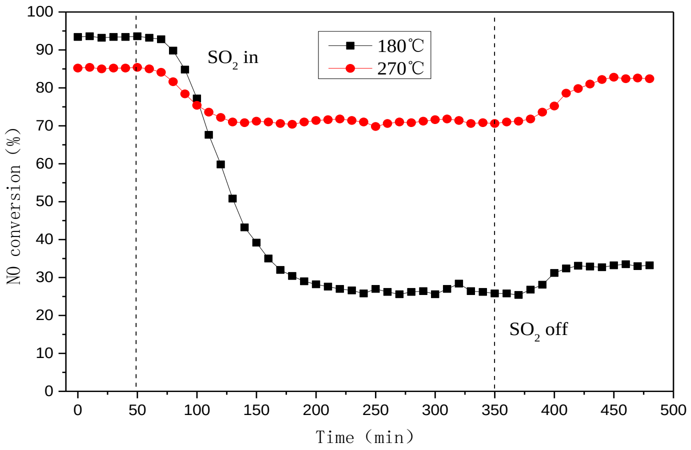

Fig. 6. SO_2 toerance under different reaction temperature with 1.5 L/min gas flow, NO=NH_3=500 ppm，SO_2=200 ppm，O_2=3 vol%， GHSV=$7500h^{-1}$.

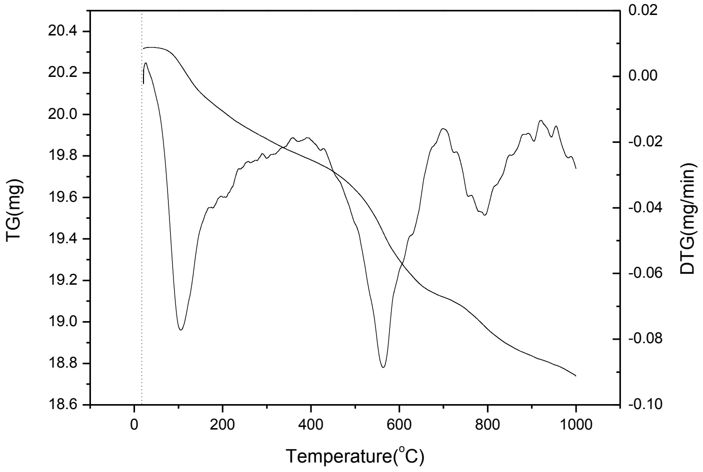

Fig. 7. TG analysis after reaction with 270 ℃ reaction temperature, 1.5 L/min gas flow，$NO=NH_3=500$ ppm，$SO_2=200$ ppm，$O_2=3$ vol%，$GHSV=7500h^{-1}$.

4. Conclusions

Ferro-manganese ore catalyst for SCR of NOx is developed in this article. It achieves over 97% NO convention at 90 ℃ to 270 ℃. The XRD patterns shows that Mn_2O_3 and Fe_2O_3 are the major component in ferro-manganese ore catalyst and are in a highly dispersed amorphous state. The calcination temperature of 450 ℃ enlarges the surface areas and total pore volumes, provides porous structure and promotes the performance of the ferro-manganese ore catalyst significantly. The catalyst showed a much better SO_2 tolerance under 270 ℃ reaction temperature than 180 ℃. TG experiment indicated that fewer sulfate species were adsorbed on the surface of ferro-manganese ore catalyst after the reaction under 270 ℃. The NH_3 and NO adsorption characteristics of ferro-manganese ore catalyst will be clarified to explain the SCR reaction mechanism in the further study.

Acknowledgements

Financial support for this project from the National Nature Science Foundation of China (51276039) and the Research Subject of Environmental Protection Department of Jiangsu Province of China (2015008) are gratefully acknowledgment.

References

[1] Qi G, Yang RT. Low-temperature SCR of NO with NH_3 over noble metal promoted Fe-ZSM-5 catalysts. *Catal. Lett.*, 2005; 100(3-4): 243-246.

[2] Smirniotis PG, Sreekanth PM, Peña DA, Jenkins RG. Manganese oxide catalysts supported on TiO_2, Al_2O_3, and SiO_2: A comparison for low-temperature SCR of NO with NH_3. *Ind. Eng. Chem. Res.*, 2006; 45(19): 6436-6443.

[3] Schill L, Putluru SSR, Jensen AD, Fehrmann R. $MnFe/Al_2O_3$ catalyst synthesized by deposition precipitation for low-temperature selective catalytic reduction of NO with NH_3. *Catal. Lett.*, 2015; 145(9): 1724-1732.

[4] Putluru SSR, Schill L, Jensen AD, Siret B, Tabaries F, Fehrmann R. Mn/TiO_2 and $Mn-Fe/TiO_2$ catalysts synthesized by deposition precipitation—promising for selective catalytic reduction of NO with NH_3 at low temperatures. *Applied Catalysis B: Environmental*, 2015; 165: 628-635.

[5] Yang S, Li J, Wang C, Chen J, Ma L, Chang H, Chen L, Peng Y, Yan N. Fe-Ti spinel for the selective catalytic reduction of NO with NH_3: Mechanism and structure-activity relationship. *Applied Catalysis B: Environmental*, 2012; 117-118: 73-80.

[6] Liu F, He H, Zhang C, Shan W, and Shi X. Mechanism of the selective catalytic reduction of NO_x with NH_3 over environmental-friendly iron titanate catalyst. *Catal. Today*, 2011; 175(1): 18-25.

[7] Yang S, Wang C, Li J, Yan N, Ma L, Chang H. Low temperature selective catalytic reduction of NO with NH3 over Mn-Fe spinel: Performance, mechanism and kinetic study. Applied Catalysis B: Environmental, 2011; 110: 71-80.

[8] Smirniotis PG, Pena DA, Uphade BS. Low-temperature selective catalytic reduction (SCR) of NO with NH_3 by using Mn, Cr, and Cu oxides supported on Hombikat TiO_2. *Angew. Chem. Int. Edit.*, 2001; 40(13): 2479.

[9] Wu Z, Jiang B, Liu Y. Effect of transition metals addition on the catalyst of manganese/titania for low-temperature selective catalytic reduction of nitric oxide with ammonia. *Applied Catalysis B: Environmental*, 2008; 79(4): 347-355.

[10] Qi G, Yang RT. Low-temperature selective catalytic reduction of NO with NH_3 over iron and manganese oxides supported on titania. *Applied Catalysis B: Environmental*, 2003; 44(3): 217-225.

[11] Long RQ, Yang RT, Chang R. Low temperature selective catalytic reduction (SCR) of NO with NH_3 over Fe-Mn based catalysts. *Chem. Commun.*, 2002; (5): 452-453.

[12] Huang HY, Yang RT. Removal of NO by reversible adsorption on Fe-Mn based transition metal oxides. *Langmuir*, 2001; 17(16): 4997-5003.

[13] Zhu L, Zhong Z, Yang H, Wang C. NH_3-SCR performance of Mn-Fe/TiO_2 catalysts at low temperature in the absence and presence of water vapor. *Water, Air, & Soil Pollution*, 2016; 227(12):

[14] Cao F, Su S, Xiang J, Wang P, Hu S, Sun L, Zhang A. The activity and mechanism study of Fe-Mn-Ce/γ-Al_2O_3 catalyst for low temperature selective catalytic reduction of NO with NH_3. *Fuel*, 2015; 139: 232-239.

[15] Cao F, Xiang J, Su S, Wang P, Hu S, Sun L. Ag modified Mn-Ce/γ-Al_2O_3 catalyst for selective catalytic reduction of NO with NH_3 at low-temperature. *Fuel Process. Technol.*, 2015; 135: 66-72.

[16] Schill L, Putluru SSR, Fehrmann R, Jensen AD. Low-temperature NH_3-SCR of NO on Mesoporous $Mn_{0.6}Fe_{0.4}/TiO_2$ prepared by a hydrothermal method. *Catal. Lett.*, 2014; 144(3): 395-402.

[17] Wang Y, Ge C, Zhan L, Li C, Qiao W, Ling L. MnO_x-CeO_2/Activated Carbon Honeycomb Catalyst for Selective Catalytic Reduction of NO with NH_3 at Low Temperatures. *Ind. Eng. Chem. Res.*, 2012; 51(36): 11667-11673.

[18] Wu Z, Jiang B, Liu Y, Wang H, Jin R. DRIFT study of manganese/titania-based catalysts for low-temperature selective catalytic reduction of NO with NH_3. *Environ. Sci. Technol.*, 2007; 41(16): 5812-5817.

[19] MARBAN G. Mechanism of low-temperature selective catalytic reduction of NO with NH_3 over carbon-supported Mn_3O_4 Role of surface NH_3 species: SCR mechanism. *J. Catal.*, 2004; 226(1): 138-155.

[20] Zhang L, Qu H, Du T, Ma W, Zhong Q. H_2O and SO_2 tolerance, activity and reaction mechanism of sulfated Ni-Ce-La composite oxide nanocrystals in NH_3-SCR. *Chem. Eng. J.*, 2016; 296: 122-131.

[21] Sheng Z, Hu Y, Xue J, Wang X, Liao W. SO_2 poisoning and regeneration of Mn-Ce/TiO_2 catalyst for low temperature NO_x reduction with NH_3. *J. Rare Earth.*, 2012; 30(7): 676-682.

[22] Shu Y, Aikebaier T, Quan X, Chen S, Yu H. Selective catalytic reaction of NO_x with NH_3 over Ce-Fe/TiO_2-loaded wire-mesh honeycomb: Resistance to SO_2 poisoning. *Applied Catalysis B: Environmental*, 2014; 150-151: 630-635.

[23] Wang X, Wu S, Zou W, Yu S, Gui K, Dong L. Fe-Mn/Al_2O_3 catalysts for low temperature selective catalytic reduction of NO with NH_3. *Chinese J. Catal.*, 2016; 37(8): 1314-1323.

[24] Qiu L, Wang Y, Pang D, Ouyang F and Zhang C. SO_4^{2-}-Mn-Co-Ce supported on TiO_2/SiO_2 with high sulfur durability for low-temperature SCR of NO with NH_3. *Catal. Commun.*, 2016; 78: 22-25.

[25] Jin R, Liu Y, Wang Y, Cen W, Wu Z, Wang H and Weng X. The role of cerium in the improved SO_2 tolerance for NO reduction with NH_3 over Mn-Ce/TiO_2 catalyst at low temperature. *Applied Catalysis B: Environmental*, 2014; 148-149: 582-588.

[26] Lu X, Song C, Jia S, Tong Z, Tang X and Teng Y. Low-temperature selective catalytic reduction of NO_x with NH_3 over cerium and manganese oxides supported on TiO_2−graphene. *Chem. Eng. J.*, 2015; 260: 776-784.