Scr of No with Nh$_3$ over Fe$_2$o$_3$ Particles at Low Temperature

Xiaobo Wang[1, 2+], Keting Gui[3] and Lin Dong[1, 2]

[1] Key Laboratory of Mesoscopic Chemistry of MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, Jiangsu, China

[2] Jiangsu Key Laboratory of Vehicle Emissions Control, Center of Modern Analysis, Nanjing University, Nanjing 210093, Jiangsu, China

[3] Key Laboratory of Energy Thermal Conversion and Control of Ministry of Education, School of Energy and Environment, Southeast University, Nanjing 210096, Jiangsu, China

Abstract. Fe$_2$O$_3$ particles were used for selective catalytic reduction (SCR) of NO with NH$_3$ at low-temperature in a fixed bed reactor. M össbauer spectroscopy and H2-TPR were employed to characterize the Fe$_2$O$_3$ particles. It was found that Fe$_2$O$_3$ particles showed high activity in a wide temperature range of 150-270℃ and more than 95% of NO conversion could be obtained at 180℃. Moreover, the reaction order was found to be nearly 1, 0 and 0.42 with respect to NO, NH$_3$ and O$_2$, respectively. Apparent activation energy was calculated to be 28.8kJ/mol and lower than that for most of the catalysts reported by previous studies.

Keywords: Low-Temperature Scr, Fe$_2$o$_3$, M össbauer Spectroscopy, Kinetics, Apparent Activation Energy

1. Introduction

The selective catalytic reduction (SCR) of NOx by ammonia is one of effective post-treatments for the abatement of nitrogen oxide emissions from stationary sources [1-5]. The general reaction is as follows:

$4NO+4NH_3+O_2 \rightarrow 4NO+6H_2O$

Many catalysts have been reported to be active for the above NO-NH$_3$-O$_2$ reaction. The commercial catalysts for this SCR process are based on V$_2$O$_5$/TiO$_2$ mixed with WO$_3$ or MoO$_3$. Although the commercial catalysts are highly active and resistant to SO$_2$, there are also some disadvantages [1-5]. This catalyst shows high activity within a narrow temperature range of 300-400℃ and thus the SCR process is necessary to locate upstream of the desulphurization and particle removal in order to avoid the flue gas reheating. In addition, the formation of the N$_2$O is another drawback for the vanadium-based catalysts [2]. For the reasons above, there is strong interest to develop highly active SCR catalysts at low temperature. In this way, such a catalyst would show high catalytic activity at low temperature and thus the SCR system can be located downstream of the desulfurizer and the particulate-removal device without gas preheating.

Based on our previous study [6], we found that Fe$_2$O$_3$ particles were highly active for low temperature SCR of NO with NH$_3$ and the external magnetic field could improve low-temperature SCR activity of the Fe$_2$O$_3$ particles. Due to the fact that the reaction orders with respect to NO and NH$_3$ varied with the catalyst and the reaction conditions, it is important to understand the reaction kinetics of the NO-SCR over the catalyst. Consequently, more work should be done for the low-temperature SCR of NO with ammonia with Fe$_2$O$_3$ particles.

In this report, the catalytic property of the Fe$_2$O$_3$ particles was experimentally studied in a fixed bed. Experiments were also carried out to understand the reaction kinetics of NO-SCR over the Fe$_2$O$_3$ particles

---

[+] Corresponding author. Tel.: +86-25-83592290; fax: +86-25-83317761.
  E-mail address: winstonwell@126.com.

and calculate the apparent activation energy, which could be used to compare the performance of Fe_2O_3 particles with that of other catalysts at low-temperature.

2. Experimental

2.1. Catalyst preparation

The particulate Fe_2O_3 particles was prepared by the Research Institute of Nanjing Chemistry Industry Group. The typically preparation of Fe_2O_3 particles was as follows: a solution of ammonia (1:1,*V/V*) was continuously added into the aqueous solutions of ferric sulfate and ferrous sulfate until the pH of the solution reached 8. After that, the resulting precipitate was washed several times with deionized water and separated by filtration under suction, followed by extrusion molding and evaporation to dryness at 120 ℃. At last, the particles were calcined at 300 ℃ in air for 3hr and collected in the diameters of 35-65 mesh by crushing and sieving. The bulk density of the Fe_2O_3 particles was 1.06 g/cm^3 and the BET surface area, pore volume, and pore size of the Fe_2O_3 particles were 90.79m^2/g, 0.2582cm^3/g and 11.38nm, respectively.

2.2. Catalyst characterization

Mössbauer spectroscopy was used to study the phases of iron presented in the Fe_2O_3 particles and the spectra were measured with a radioactive source of 57Co (Pd) moving in a constant acceleration mode at room temperature. The α-Fe foil was exploited as a reference and the experimentally observed Mössbauer spectra were curve-fitted by a least squares method, assuming Lorentzian line shapes. The corresponding Mössbauer parameters, i.e. isomer shift (IS), quadrupole splitting (QS), and magnetic hyperfine field (B_{hf}) were used for description of the individual iron species.

Temperature-programmed reduction (TPR) was carried out in a quartz U-tube reactor connected to a thermal conduction detector (TCD), under the following conditions: a hydrogen-argon mixture (7%H_2) at a flow rate of 60ml/min; a 50 mg sample; a heating rate of 10 ℃/min from room temperature to 600 ℃. The sample was pretreated in N_2 stream at 100 ℃ for 1h before reduction and then cooled to the room temperature.

2.3. Activity measurements

The SCR activity measurement was carried out in a fixed-bed quartz reactor. The reaction conditions were as follows: 500ppm NO, 500ppm NH_3, 3% O_2, balance N_2, 1500 ml/min or 1000 ml/min total flow rate. The feed gases were premixed in a glass chamber, but the NH_3 was fed directly into the reactor by passing the mixing chamber to avoid possible reaction before the reactor. All the data were obtained when the SCR reaction reached steady state, and the product components in the outlet gases were measured online by an online flue gas analyzer.

Steady-state kinetics studies were carried out in a fixed-bed quartz flow reactor (differential reactor). An amount of 0.65g of catalyst was placed in the reactor in this work. The flue gas was simulated by blending different gaseous reactants. The typical reactant gas composition was as follows: 500-2000ppm NO, 500-2000ppm NH_3, 0.5-5% O_2 and balance N_2. The total flow rate was 1500 ml/min (ambient conditions). The instrument is the same as for the catalytic activity measurement mentioned above.
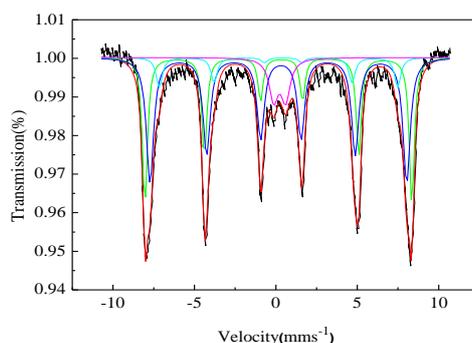

Fig. 1: Mössbauer spectra of the Fe_2O_3 particles

3. Results and Discussion

3.1. Catalyst characterization

The ^{57}Fe Mössbauer spectra of the Fe_2O_3 particles are shown in Fig. 1 and the Mössbauer parameters are summarized in Table 1. It can be seen from Fig. 1 that the ^{57}Fe Mössbauer spectra of the Fe_2O_3 particles were fitted with three sextets and one doublet. The values of IS calculated for the samples were characteristic of Fe^{3+} ions and near-zero values of QS for the sextets indicated the defect spinel structure for the samples [7, 8]. The IS of sub-spectrum 1 and sub-spectrum 2 were 0.271mms^{-1} and 0.249 mms^{-1} with B_{hf} of 51T and 49T, respectively, which could be assigned to γ-Fe_2O_3 [8-10]. The components described by IS=0.318 mm/s and B_{hf}= 45.56T were characteristic for α-Fe_2O_3 [11]. Based on the discussion above, the Fe_2O_3 particles mainly consisted of γ-Fe_2O_3 and α-Fe_2O_3. The γ form of Fe_2O_3 had the spinel structure and the cation vacancies were confined to the octahedral sites in the γ-Fe_2O_3 crystal, which could be written: $[Fe^{3+}]_T[Fe^{3+}_{5/3}\square_{1/3}]_O \ O_4$. The presence of vacancies could improve electron transfer on the Fe_2O_3 surface in the reaction and increase the catalytic performance of the catalysts.

Table 1: ^{57}Fe Mössbauer parameters at RT calculated for Fe_2O_3 particles

Sample	Sub-spectrum	Fitted spectrum	IS （mm/s）	QS （mm/s）	Γ （mm/s）	B_{hf} (T)	Relative Intensity （%）	Composition
Before reaction	S1	Sextet	0.271 ±0.008	-0.098 ±0.005	0.375	51.017 ±0.039	33.223	γ-Fe_2O_3[8,9]
	S2	Sextet	0.249 ±0.013	-0.079 ±0.006	0.538	49.063 ±0.069	50.090	γ-Fe_2O_3[10]
	S3	Sextet	0.318 ±0.037	-0.143 ±0.023	0.452	45.560 ±0.184	8.391	α-Fe_2O_3[11]
	S4	Doublet	0.253 ±0.028	-0.735 ±0.055	0.658		8.297	Fe(III)[8]

Key: IS = isomer shift given relative to α-Fe at RT; QS=quadrupole splitting; Bhf=hyperfine magnetic field; Γ=line width.

The redox property of the catalyst had an important influence on the SCR reaction. In particular, the redox property of the catalyst at low temperature with low activation energy had been shown to be the main factors for the SCR reaction [12]. In order to investigate the redox property of the Fe_2O_3 particles, H_2-TPR experiments were carried out and the results are shown in Fig. 2. It can be clearly seen from Fig. 2 that there were three reduction peaks at 231.9 ℃, 261.4 ℃ and 309.5 ℃ before 400 ℃, respectively, and an incomplete reduction peak after 400 ℃, showing a stepwise reduction of Fe_2O_3.It is generally accepted that the reduction of iron oxide involves a two-step process, with Fe_2O_3 first reduced to Fe_3O_4 (FeO Fe_2O_3) at low temperature (<400 ℃) and then to metallic Fe at high temperature (>350 ℃) [13-16]. Therefore, the reduction peaks observed before 400 ℃ might be attributed to the reduction of Fe_2O_3, while the incomplete reduction peak after 400 ℃ might be ascribed to the reduction of Fe_3O_4 (FeO Fe_2O_3).In addition, the reduction temperature of catalyst was proved to be closely correlated with the reaction temperature for SCR of NO. It can be seen from Fig. 2 that Fe_2O_3 particles were found to be reduced by H_2 at lower temperatures at around 150-300 ℃. Therefore, the lower reducible temperature of Fe_2O_3 particles may contribute to the higher activity of Fe_2O_3 particles at lower temperature.
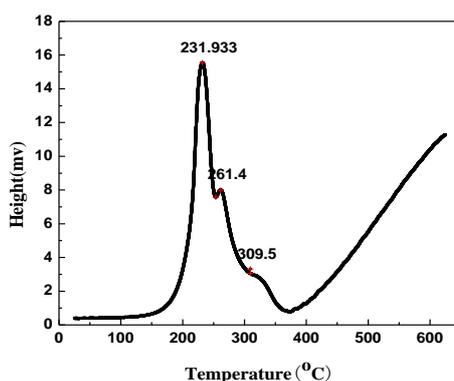

Fig. 2: TPR profiles of the Fe_2O_3 particles

3.2. Catalytic activity of Fe$_2$O$_3$ particles

Catalytic activity of Fe$_2$O$_3$ particles as a function of temperatures is shown in Fig. 3. Compared the results of the NO conversion by SCR on Fe$_2$O$_3$ particles in the absence/ presence of O$_2$, it can be seen from Fig. 3 that the catalytic performance over Fe$_2$O$_3$ particles monotonically increased with temperature until 210 ℃, but the discrepancy of reactivity for catalysts under different O$_2$ concentration is obvious. More than 90%, 95.5% and 98.5 NO conversion could be achieved at 150 ℃, 180 ℃ and 210 ℃ over the Fe$_2$O$_3$ particles with 3% oxygen, respectively. Compared with that without oxygen, only 86.4%, 91.2% and 92% NO conversion could be obtained at 150 ℃, 180 ℃ and 210 ℃, respectively. Then NO conversion decreased with increasing temperatures. With the feeding of 3% oxygen, the NO conversion was increased from 91.2% to 95.5% and 92% to 98.5% at 180 ℃ and 210 ℃, respectively. The results in Fig. 3 showed that the Fe$_2$O$_3$ particles was highly active for the low-temperature SCR of NO with NH$_3$ in the presence of excess oxygen and the addition of oxygen caused enhancement of the catalytic activity.
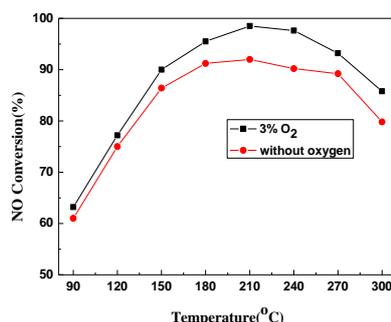

Fig. 3: NO conversion on the Fe$_2$O$_3$ particles in the absence/ presence of O$_2$. Reaction conditions: [NO]=[NH$_3$]=500ppm, [O$_2$]=3%, balance N$_2$, total flow rate 1500 ml/min, catalyst 12mL

3.3. Kinetics of the reaction and apparent activation energy

To determine the reaction orders with respect to NO, NH$_3$ and O$_2$, the differential reaction experiments were performed at 120, 150, 180 and 210 ℃, respectively. For calculating the reaction order with respect to NO, the concentration of NH$_3$ and O$_2$ was kept constant at 2000ppm and 3%, respectively, while the concentration of NO was varied between 500 and 2000ppm. Similar experiments were performed to determine the reaction orders with respect to NH$_3$ and O$_2$. The experimental results for the rate of NO conversion with the concentration of nitric oxide, ammonia and oxygen are presented in Fig. 4-6, respectively. As seen from Fig. 4-6, the rate of NO conversion increased with the increase of NO concentration, but it was nearly no change with the increase of NH$_3$ concentration (shown in Fig. 5). Fig. 6 showed the effect of oxygen on the reduction of NO by NH$_3$ at different temperatures. The Fe$_2$O$_3$ particles presented a low rate of NO conversion at different temperatures under a small concentration of O$_2$.However, when a higher concentration of O$_2$ was fed into the simulated flue gas, the NO conversion increased sharply.
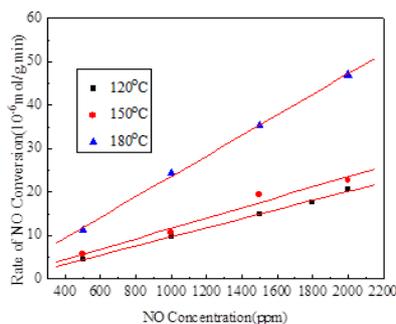

Fig. 4: Dependence of NO conversion rate on NO concentration over Fe$_2$O$_3$ particles at different temperatures. Reaction conditions: [NO]=500-2000ppm, [NH$_3$]=2000ppm, [O$_2$]=3%, balance N$_2$, total flow rate 1500 ml/min, catalyst 0.65g.
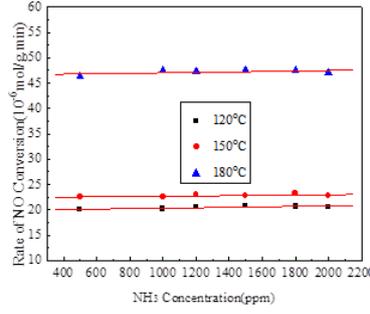
Fig. 5: Dependence of NO conversion rate on NH$_3$ concentration over Fe$_2$O$_3$ particles at different temperatures. Reaction conditions: [NO]=2000ppm, [NH$_3$]=500-2000ppm, [O$_2$]=3%, balance N$_2$, total flow rate 1500ml/min, catalyst 0.65g.
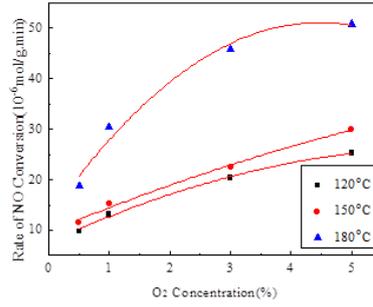

Fig. 6: Effect of O$_2$ concentration on NO conversion rate over Fe$_2$O$_3$ particles at different temperatures. Reaction conditions: [NO]=[NH$_3$]=2000ppm, [O$_2$]=0.5-5%, balance N$_2$, total flow rate 1500ml/min, catalyst 0.65g.

The reaction rate of NO conversion as a function of reactant concentrations can be expressed simply as follows [1]:

$$R_{NO}=-k[NO]^{\alpha} [NH_3]^{\beta}[O_2]^{\gamma} \tag{1}$$

Where, R_{NO} is the SCR reaction rate, k is the apparent rate constant, α and, β, and γ are the reaction orders for NO, NH$_3$ and O$_2$, respectively.

The SCR reaction order with respect to NO, NH$_3$, O$_2$ was calculated to be nearly 1, 0, and 0.42, respectively. Then the SCR reaction rate of NO conversion was expressed simply as:

$$R_{NO}=-k[NO][O_2]^{0.42} \tag{2}$$

In this system, only when the oxygen partial pressure was below approximately 0.5at%, this rate equation can be established [2]. Based on the experimental conditions used (the partial pressure of O$_2$ was all 0.03atm), the Eq. (3) could be used as the rate equation.

$$R_{NO}=-k[NO] \tag{3}$$

The amount of oxygen was in excess during SCR reaction, the relationship between apparent rate constant (k) and NO conversion (x) could be given as follows:

$$k = -F_0 \frac{\ln(1-x)}{[NO_0]w} \tag{4}$$

where F$_0$ was the molar NO feed rate (mol/min), [NO]$_0$ was the molar NO concentration at the inlet (mol/L) and W was the amount of catalyst(g).

The relationship between ln(1-x) and [NO]$_0$ W /F_0 was shown in Fig. 7. And the value of the apparent rate constant (k) at different temperatures had been calculated and a summary comparison made for the Fe$_2$O$_3$ particles with other reported excellent catalysts is listed in Table 2.
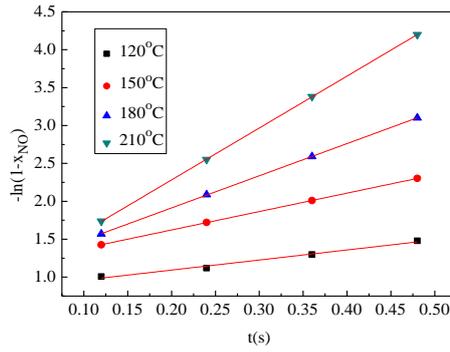
Fig.7: First-order plots with respect to NO with different gas flow rate at different temperatures.

Table 2: Performance of the Fe_2O_3 particles for low-temperature SCR of NO with NH_3

Sample	Reaction conditions	t(℃)	x_{NO}（%）	$k(cm^3g^{-1}s^{-1})$
Fe₂O₃[this work]	[NO]=[NH₃]=500ppm,O₂=3%, balance N₂, total flow rate 1500 ml/min, catalyst 12mL	120	77.2	1.33
		150	90	2.43
		180	95.5	4.25
		210	98.5	6.85
MnOx/Al₂O₃ [17]	[NO]= 500ppm, [NH₃]=550ppm, O₂=2%, SV(cm³ g⁻¹ h⁻¹)=24000	150	63	9.40
10%Mn-14%Ce /USY [2]	[NO]= [NH₃]=1000ppm, O₂=2%, SV(cm³ g⁻¹ h⁻¹)=30000	80	50	6.84
		100	59	9.31

It is well known that apparent activation energy of a reaction is a significant parameter to evaluate the performance of catalyst. The apparent activation energy could be obtained by using Arrhenius equation:

$$k = k_0 e^{\frac{-Ea}{RT}} \tag{5}$$

where E_a is the apparent activation energy.

When ln$k$ was plotted vs 1/T, the activation energy and the pre-exponential factor for SCR reaction could be obtained by the slope and intercept (as shown in Fig. 8). The activation energy for Fe_2O_3 in SCR process was calculated to be 28.8kJ/mol. This is consistent with our previous study and is lower than values obtained by other researchers, such as MnOx/TiO$_2$ [1](38kJ/mol), H-ZSM-5 [18](55kJ/mol), V$_2$O$_5$/TiO$_2$ [19] (85kJ/mol) and Fe-ZSM-5 [20](68kJ/mol). It indicated that less energy was needed for activation than other catalysts in the reaction. Therefore the Fe_2O_3 particles would be substantially more active than all other catalysts at low temperature.
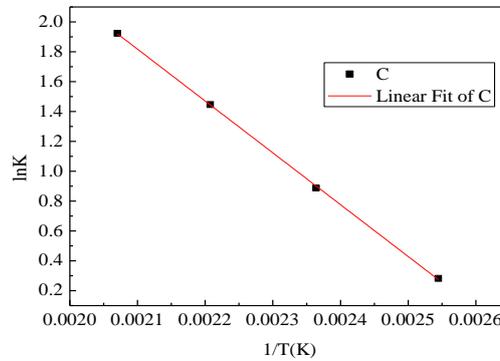

Fig. 8: Arrhennius plots of the NO-NH₃-O₂ reaction on Fe₂O₃ particles

4. Conclusion

Based on the above results, it can be concluded that the Fe_2O_3 particles were highly active for the selective catalytic reduction of NO with NH_3 in the presence of excess oxygen at low temperatures. More

than 90% NO conversion was obtained over a broad temperature range of 150-270 ℃ under the conditions used. The reaction order of NO, NH_3, O_2 was determined to be nearly 1, 0, and 0.42, respectively. And the apparent active energy of the reaction was calculated to be 28.8kJ/mol, which was consistent with our previous study and was lower than the values obtained by other researchers.

5. Acknowledgments

6. References

[1]   Z. Wu, B. Jiang, Y. Liu, W. Zhao, B. Guan. Experimental study on a low-temperature SCR catalyst based on MnO_X/TiO_2 prepared by sol-gel method. *J. Hazard. Mater.*2007, 145:488-494.

[2]   G. Qi, R. T. Yang, R. Chang. Low-temperature SCR of NO with NH_3 over USY-supported manganese oxide-based catalysts. *Catal. Lett.* 2003, 87:67-71.

[3]   X. Tang, J. Hao, H. Yi, H. Li. Low-temperature SCR of NO with NH3 over AC/C supported manganese-based monolithic catalysts. *Catal. Today.* 2007, 126(3-4):406-411.

[4]   G. Qi, R. T. Yang. Low-temperature selective catalytic reduction of NO with NH_3 over iron and manganese oxides supported on titania.*Appl Catal B-Environ.*2003, 44:217-215.

[5]   M. Kang, E. D. Park, J. M. Kim, J. E. Yie. Cu-Mn mixed oxides for low temperature NO reduction with NH_3.Catal. *Today.*2006, 111:236-241.

[6]   G. Yao, F. Wang, X. Wang, K. Gui. Magnetic Field Effects on Selective Catalytic Reduction of NO by NH_3 over Fe_2O_3 Catalyst in a Magnetically Fluidized Bed.*Energy.*2010, 35:2295-2300.

[7]   C. Sudakar, T. R. N. Kutty. Structural and magnetic characteristics of cobalt ferrite-coated nano-fibrous γ-Fe_2O_3. *J.Magn. Magn. Mater..*2004, 279:363-374.

[8]   E. Tabor, K. Závěta, N. K. Sathu, Z. Tvarůžková, Z. Sobalḱ. Characterization of iron cationic sites in ferrierite using Mӧssbauer spectroscopy.*Catal Today.*2011, 169:16-23.

[9]   M. Jeleńska, A. Hasso-Agopsowicz, B. Kopcewicz. Thermally induced transformation of magnetic minerals in soil based on rock magnetic study and Mӧssbauer analysis. *Phys Earth Planet In.*2010, 179:164-177.

[10] D. Ortega, J. S. Garitaonandia, C. Barrera-Solano, M. Ram�́rez-del-Solar, E Blanco, M Domínguez. γ-Fe_2O_3/SiO_2 nanocomposites for magneto-optical applications: Nanostructural and magnetic properties.*J. Non-Cryst. Solids.*2006, 352:2801-2810.

[11] C. V. Cromphaut, V. G. Resende, E. D. Grave, A. V. Alboom, R. E. Vandenberghe, G. Klingelhӧfer. Characterisation of the magnetic iron phases in Clovis Class rocks in Gusev crater from the MER Spirit Mӧssbauer spectrometer.*Geochim. Cosmochim. Ac.*2007, 71:4814-4822

[12] D. W. Kwon, K. H. Park, S. C. Hong. The influence on SCR activity of the atomic structure of V2O5/TiO2 catalysts prepared by a mechanochemical method. *Appl. Catal. A-Gen.*2013, 451:227-235.

[13] K. Li, H. Wang, Y. Wei, M. Liu. Preparation and characterization of Ce1-xFexO2 complex oxides and its catalytic activity for methane selective oxidation. *J. Rare. Earth.*2008, 26:245-249.

[14] M. Liang, W. Kang, K. Xie. Comparison of reduction behavior of Fe_2O_3, ZnO and $ZnFe_2O_4$ by TPR technique. *J.Nat. Gas. Chem.*2009, 18:110-113.

[15] G. Munteanu, L. Ilieva, D. Andreeva.Kinetic parameters obtained from TPR data for α-Fe_2O_3 and Au/α-Fe_2O_3 systems .*Thermochimica. Acta.*1997, 291:171-177.

[16] P. S. Lambrou, A. M. Efstathiou. The effects of Fe on the oxygen storage and release properties of model Pd-Rh/CeO2-Al2O3 three-way catalyst .*J. Catal.* 2006, 240(2):182-193.

[17] L. Singoredjo, R. Korver, F. Kapteijn, J. Moulijn. Alumina supported manganese oxides for the low-temperature selective catalytic reduction of nitric oxide with ammonia. *Appl. Catal. B-Environ.*1992, 1:297-316.

[18] S. A. Stevenson, J. C. Vartuli, C. F. Brooks. Kinetics of the Selective Catalytic Reduction of NO over HZSM-5. *J. Catal.* 2000, 190:228-239.

[19] M. D. Amiridis, J. P. Solar. Selective catalytic reduction of nitric oxide by ammonia over V_2O_5/TiO_2, $V_2O_5/TiO_2/SiO_2$, and V_2O_5-WO_3/TiO_2 Catalysts: Effect of vanadia content on the activation energy. *Ind. Eng. Chem. Res.* 1996, 35(3): 978-981.

[20] M. Iwasaki, K. Yamazaki, H. Shinjoh. Transient reaction analysis and steady-state kinetic study of selective catalytic reduction of NO and NO + NO2 by NH3 over Fe/ZSM-5.*Appl. Catal. A-Gen*.2009, 366:84-92.