

# Low-Temperature Catalytic Reaction over Manganese-Cerium Composite Oxide Supported on Titania

Rongzhi Zhao, Raorui Liang, Suqin Li\*, Cunyi Song

University of Science and Technology Beijing  
 lisuqin@metall.ustb.edu.cn

A series of catalysts of manganese-cerium (Mn-Ce) active components supported on TiO<sub>2</sub> prepared through sol-gel process were used for low-temperature catalytic reduction of NO with ammonia as reductant. The catalysts were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The results showed that the particle size of the catalysts is smaller and the active components are highly dispersed on the support. Doping Ce exhibited an inhibitory effect on the crystal transition of TiO<sub>2</sub> from anatase to rutile phase. Furthermore, the TiO<sub>2</sub> support got the entire anatase phase at 450°C, with an improved the property of the catalyst. The catalyst with the highest activity was obtained with a mass Ce(0.8)-Mn/TiO<sub>2</sub> ratio of 0.15, and calcinated at 450°C, providing 99.01% NO conversion at 140°C at a high space velocity of 67,000 h<sup>-1</sup>. With the increasing of Ce-Mn loading amount and Ce/Mn molar ratio, the NO conversion increased firstly and then decreased. With the increasing of NH<sub>3</sub>/NO molar ratio in inlet flue gas, NO conversion increased firstly and then tended to be stable.

## 1. Introduction

NO<sub>x</sub> (nitrogen oxides) is one of the main pollutants in the atmosphere, which on atmospheric pollution caused by the main influence is NO and NO<sub>2</sub>. More than 95% of NO<sub>x</sub> is NO in atmosphere, NO<sub>2</sub> accounts for the proportion to be very small. 90% of NO<sub>x</sub> in flue gas is NO (Chen et al., 2010). So, the removal of NO is the most important in the prevention and treatment of nitrogen oxides. Selective catalytic reduction method refers to the NH<sub>3</sub> and other reducing agents restore the NO<sub>x</sub> to N<sub>2</sub> selectively under the action of certain temperature and catalyst. At present, the most mature commercial catalyst in the SCR method of industrial application is to add a certain amount of MoO<sub>3</sub> or WO<sub>3</sub> (Jung and Grange, 2001) on the basis of the V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>, so as to carry out the modification of the catalyst.

However, the temperature of catalyst activities between 350°C and 400°C Celsius, so that the SCR device must be placed before the air pre heater, which will cause the high sulfur and high sulfur dust in the flue gas have a huge impact on catalyst activity and catalyst life (Shen et al., 2006). However, with the successful industrialization of Calcium-Based Semi-Dry Method of Sintering Flue Gas Desulphurization Technology, the flue gas outlet temperature of sintering flue gas is about 80~150°C. Therefore, it has become a hot spot and key point of the Study on denitrification of sintering flue gas to seek the catalyst of high efficiency at low temperature, especially in the temperature range of 80~150°C.

In recent years, researchers at home and abroad have carried out a lot of research on the low temperature SCR catalyst carrier and catalyst active constituent. The catalyst with transition metal was found to have good catalytic performance in low temperature and the better one is Mn oxide (Park et al., 2001; Gong and Ralph, 2003; Imen et al., 2016; Pragma and Vasanthakumari, 2016). Studies showed that Ce can transfer electrons and ions in the catalytic reaction because of its oxygen storage, so that the active component of Ce-Mn which is obtained after doping as an auxiliary agent displayed out better catalytic activity (Gong and Ralph, 2003; Liu et al., 2006; Shen et al., 2010). Because the anatase TiO<sub>2</sub> has a larger specific surface area and active site, which the stability of sulfate on the surface of is much lower than the other metal oxides. So TiO<sub>2</sub> is difficult to happen sulfation reaction and its curing is reversible (Boningari and Panagiotis, 2011; Leonardo et al., 2014). Other studies have indicated that the vulcanization of TiO<sub>2</sub> can enhance the catalytic activity, so it not only has a strong ability to anti sulfur poisoning, but also can play a protective role of the active component of the load

(Saur et al., 1986). Therefore, many scholars use anatase  $\text{TiO}_2$  as a carrier to load other metal oxides which mixed Mn as catalysts for selective catalytic reduction at low temperature. In addition,  $\text{MnO}_x\text{-TiO}_2$ ,  $\text{CeO}_2\text{-MnO}_x\text{-TiO}_2$  and  $\text{V}_2\text{O}_5\text{-MnO}_x\text{-TiO}_2$  catalysts prepared by sol gel method were reported. The addition of Ce and V could inhibit the transformation of  $\text{TiO}_2$  from anatase to rutile. With the addition of the active component, the specific surface area of the catalyst and the pore volume will increase. Through the activity tests showed that the catalytic effect has been greatly improved (Wu et al., 2011).

In this paper, the reaction temperature is set at  $80\sim 140^\circ\text{C}$  according to the semi dry sintering flue gas desulfurization process exit temperature.  $\text{TiO}_2$  carrier was prepared by gel sol method, and the active component of Ce-Mn was prepared by impregnation method. Evaluation of the catalytic activity of NO by low temperature catalytic reduction of  $\text{NH}_3$ , and research for the impact of the catalyst poisoning and activity about the high oxygen and high humidity condition of sintering flue gas. .

## 2. Experimental section

### 2.1 Catalyst Preparation

Cerium ( $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ ) and manganese acetate ( $4\text{H}_2\text{O}\cdot\text{C}_4\text{H}_6\text{MnO}_4$ ) were used as precursors in the preparation of active components. The mixing of the solution and the carrier was mixed, and the heating type magnetic mixer was used for stirring for one hour at the temperature of 60 degrees Celsius, so that the active component could be fully contacted with the carrier and the active component was adhered to the surface of the carrier. In the drying oven in  $105^\circ\text{C}$  dried in the muffle furnace roasting to  $450^\circ\text{C}$  holding 3 h to obtain the Ce-Mn/ $\text{TiO}_2$  supported catalyst:  $\text{X}\%\text{Ce}(\text{Y})\text{-Mn}/\text{TiO}_2$ , Where X% was Ce-Mn/ $\text{TiO}_2$ , Mn, Ce elements of the quality of the sum, said the size of the load Ce-Mn; Y was Ce/Mn molar ratio, which indicated the ratio of cerium and manganese in the catalyst.

### 2.2 Characterization of catalysts

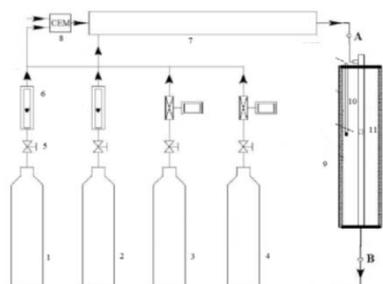
The micro morphology of the catalyst was characterized by the EVO ZEISS 18 scanning electron microscope, and the amplification factor of the scanning electron microscope was 5000 times.

The Japanese sample the DMAX-RB kW rotating anode X-ray diffraction phase analysis. Using a copper target (wavelength 0.15406 nm), at 40 kV accelerating voltage, 150 Ma of current intensity, to 10 degrees per minute speed scanning, the scanning range is  $2\theta = 10 \sim 100^\circ$ .

The specific surface area and pore structure parameters of the catalyst were tested by static nitrogen physical adsorption method using SI QuadraSorb type specific surface and micro hole analyzer.

### 2.3 Catalyst activity test.

The prepared catalyst was used as catalyst, and the particle size of  $60\sim 100$  was selected as the catalyst for the experiment. 0.5 g samples were used to test the catalytic activity. Test device as shown in *Figure 1*, the quartz reaction tube diameter of 9 mm, was composed of a vertical pipe type heating furnace, the simulated flue gas composition 0.1%NO, 0.1% $\text{NH}_3$ , 10% $\text{O}_2$ ,  $\text{N}_2$  balance, gas flow for 600 ml according to  $\text{min}^{-1}$ , space velocity of  $67000 \text{ H}^{-1}$ , reaction temperature was  $80 \sim 140^\circ\text{C}$ .



1- $\text{N}_2$  Gas Cylinders; 2- $\text{O}_2$  Gas Cylinders; 3-NO Gas Cylinders; 4- $\text{NH}_3$  Gas Cylinders; 5-Pressure Relief Valve; 6-Flowmeter; 7, 8-Liquid Mixing Heating Device; 9-Preheating Box Type Resistance Furnace; 10-thermometer; 11- Quartz Tube Reactor.

*Figure 1: Schematic profile of SCR reaction experimental apparatus*

Determined NO concentration in import and export using KM900 handheld flue gas analyzer in UK Kane company. Taking into account the adsorption of the catalyst itself on the gas, the initial experiment to the reactor through the NO, to be stable when the outlet concentration, and then through the  $\text{NH}_3$  to export NO concentration reached a stable after reading the data. Considering gas flow, oxygen and other nonadjustable parameters. When the influence of process parameters on the conversion of NO was studied, these

parameters were taken as fixed values, and the effect of the adjustable process parameters on the conversion of NO was studied.

### 3. Experimental results and discussion

#### 3.1 Effects of different preparation conditions on the catalytic reduction reaction.

##### 3.1.1 Effect of active component loading on catalytic reduction reaction.

The experiment, to ensure that other conditions unchanged, selected 80°C, 100°C, 120°C, 140°C four flue gas temperatures, and NO conversion rate and the relationship between the catalyst load was shown in Fig.2.

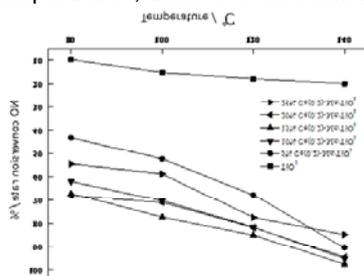


Figure 2: Effect of the catalyst loading on the NO conversion

Table 1: The specific surface area and pore volume of the different loading catalysts

Sample	Surfacearea/( $\text{m}^2 \cdot \text{g}^{-1}$ )	Pore volume/( $\times 10^{-2} \text{cm}^3 \cdot \text{g}^{-1}$ )	Average pore diameter $l$ /(nm)
TiO <sub>2</sub>	49	8.17	6.1
5%Mn-Ce(0.2)/TiO <sub>2</sub>	51	10.25	5.7
15%Mn-Ce(0.2)/TiO <sub>2</sub>	48	12.96	4.0
20%Mn-Ce(0.2)/TiO <sub>2</sub>	36	5.85	6.5
25%Mn-Ce(0.2)/TiO <sub>2</sub>	35	5.74	6.5

The effect of different active component loading on the conversion of NO was demonstrated in Fig.2. The catalyst loading amount was 0, 5%, 10%, 15%, 20% and 25%, and the Ce/Mn molar ratio was 0.2. The specific surface area and total pore volume of the catalyst increases first and then decreases with the increase of catalyst loading, while the average pore size shows the opposite trend in Table 1. It can be seen from the figure that the TiO<sub>2</sub> carrier has a certain catalytic performance, at 140°C to about 20%, the load Ce-Mn active component, and the reaction activity is greatly improved. With the increase of the reaction temperature, the catalyst activity of each load is improved, and the maximum amount is over 95%. But when the load capacity reaches 25%, the conversion rate of NO is significantly lower, and the activity is reduced to about 140 at 80%. Analysis shows that the active load increases the catalyst ratio surface area, and corresponding also increases the number of active sites for the surface of the carrier, but load increases to a certain extent, will cause the active sites overlap mutual shading, but the catalytic activity could not be further improve even compared to the previous decreased. This experiment results show that 15% Mn-Ce (0.2) /TiO<sub>2</sub> catalyst has the best performance in the test temperature range. The conversion rate of NO is 97.8% at 140°C. So this experiment determines the load of X% is 15%.

##### 3.1.2 Effect of Ce/Mn active components on catalytic reduction reaction.

The relationship between the NO conversion rate and the Ce/Mn molar ratio in the catalyst is shown in Figure 3. This part of the experiment is to confirm the effect of the doping modification of Ce on the catalytic performance of the catalyst.

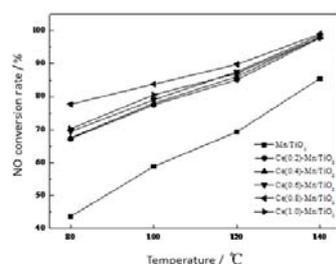


Figure 3: Effect of Ce/Mn(molar ratio) in catalyst on the NO conversion

Fig. 3 shows the effect of different Ce/Mn molar ratio on the conversion of NO. Under the condition of operating conditions, when the amount of Ce doped in 0.2~1.0 (Ce/Mn molar ratio), all the catalysts in the reaction temperature range of low temperature catalytic reduction activity compared to the Mn/TiO<sub>2</sub> catalyst has been greatly improved. Ce (0.8) -Mn/TiO<sub>2</sub> catalyst at 80°C NO removal rate is close to 80%, and all of the Ce doped catalyst at 140°C, the catalytic activity was about 95%. The low temperature catalytic reduction activity of this series of catalysts modified by Ce was from low to high: Mn/TiO<sub>2</sub><Ce(0.2)-Mn/TiO<sub>2</sub><Ce(0.4)-Mn/TiO<sub>2</sub><Ce(0.6)-Mn/TiO<sub>2</sub><Ce(1.0)-Mn/TiO<sub>2</sub><Ce(0.8)-Mn/TiO<sub>2</sub>. Therefore, combined with the best parameters of the load before, and the best Ce/Mn molar ratio of Y=0.8 in this stage, the best catalyst is determined to form 15%Ce (0.8) -Mn/TiO<sub>2</sub>.

### 3.1.3 Effect of calcinations temperature on catalytic reduction reaction.

In this phase, 15%Ce (0.8) -Mn/TiO<sub>2</sub> is selected to study the effect of different calcination temperatures on the catalytic activity, crystal form and morphology of the catalyst. The relationship between NO conversion rate and catalyst calcination temperature is shown in Figure 4. Fig. 5 XRD spectra of different calcination temperatures. The scanning electron microscopic morphology of the catalysts at different calcination temperatures was shown in Figure 6.

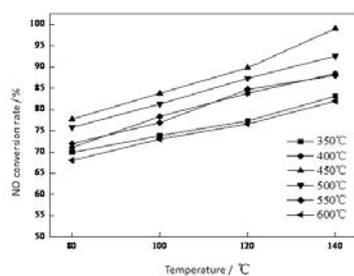


Figure 4: Effect of calcination temperature in catalyst on the NO conversion

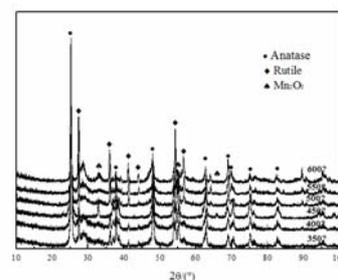


Figure 5: XRD patterns of different calcination temperatures

The activity of 15%Ce (0.8) -Mn/TiO<sub>2</sub> catalyst at different calcination temperatures is observed to increase with the increase of the reaction temperature. The best catalytic activity is achieved at 450°C, and the reaction temperature is 140°C, and the activity is as high as 99.01%. The effect of different calcination temperature on the crystal form of TiO<sub>2</sub> carrier and active group is analyzed with figure 5, and the reasons for the formation of this result are also explained. From Figure 5 XRD spectra can see catalyst to 450°C calcining TiO<sub>2</sub> carrier ( $2\theta=25.3^\circ, 37.8^\circ, 48.1^\circ, 53.9^\circ, 55.0^\circ, 62.7^\circ, 68.7^\circ, 70.3^\circ$ ) (JCPDS 21-1272) are sharp diffraction peak of anatase and a high degree of crystallization, grain is fine, and no rutile peaks, anatase type TiO<sub>2</sub> as catalyst provides rich active bit. When TiO<sub>2</sub> was used as catalyst, Karakitsou (Fang, 2006) was proved to produce hydrogen at a rate of 7 times the rate of rutile. So it is in favor of low temperature catalytic reduction reaction activity of ascension. And other calcination temperatures are rutile type structure ( $2\theta=27.44^\circ, 36.08^\circ, 41.22^\circ$ ) (JCPDS 21-1276) and the ability of adsorption of hydrogen on the surface of rutile TiO<sub>2</sub> particles is much weaker than that of anatase TiO<sub>2</sub>, so the catalytic activity of the catalyst will have a certain impact. XRD results still  $2\theta=32.9^\circ, 55.0^\circ, 65.7^\circ$  (JCPDS 24-0508) about Mn<sub>2</sub>O<sub>3</sub> diffraction peak, but the basic for crystal peak is weak and diffraction peak wide phase structure, shows that the crystallization degree is not high, Mn<sub>2</sub>O<sub>3</sub> is uniformly dispersed on the surface of the carrier. And from the figure is not observed in the Ce oxide phase, the analysis shows that the Ce doping highly dispersed on the surface of the carrier, is no fixed form (Xu et al., 2009), and the addition of Ce can restrain TiO<sub>2</sub> from anatase to rutile transformation, to enhance the catalytic effect to promote (Chen et al., 2010; Lin et al., 2008; Tang et al., 2007).

Fig. 6 is the SEM pattern of the catalyst with different calcination temperatures. The scanning electron microscopy analysis shows that the grain size of supported catalysts prepared by sol gel method and impregnation method is small. From the figure can be observed under 450°C of the catalyst calcined grain is fine and active group points evenly distribution on the surface of the carrier, and the morphology before and XRD characterization results coincide. Therefore, this system preparation conditions of catalytic activity better provides the basis. After observation can also be found in more than 550°C calcination temperature, catalyst particles to the sintering phenomenon, serious aggregation to cover up the activity of the surface of the carrier, also affected the active component of the uniform distribution, reduces the probability of contact between reactant and the catalyst activity, thereby reducing the catalyst performance (Jin et al., 2010; Tian et al., 2011). Through the analysis, we can get the best roasting temperature is 450°C, the next phase of the experiment are used to prepare the catalyst.

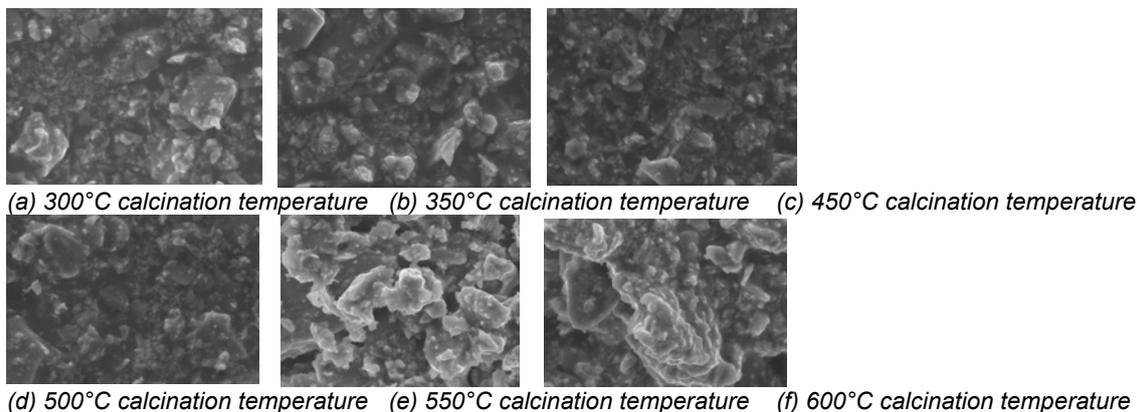


Figure 6: SEM pattern of the catalyst with different calcination temperatures

### 3.2 Effect of different process parameters on catalytic reduction reaction.

In this phase, the 15%Ce (0.8) -Mn/TiO<sub>2</sub> catalyst is selected and the other conditions are unchanged. The relationship between the NO conversion rate and the NH<sub>3</sub>/NO molar ratio of the inlet flue gas is shown in Figure 7.

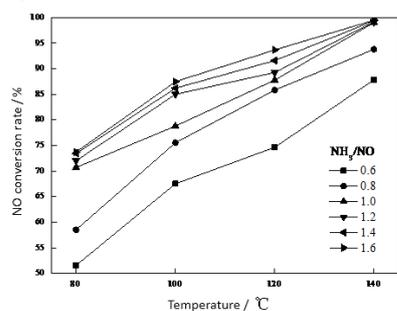


Figure 7: Effect of the NH<sub>3</sub>/NO (molar ratio) in inlet flue gas on the NO conversion

Observed in Figure 7, when the NH<sub>3</sub>/NO ratio within the range of 0.6~1.6 and NH<sub>3</sub>/NO ratio is less than 1, with increasing ratio of ammonia nitrogen, NO conversion rate is improved obviously. The reason is that in sintering flue gas in the oxygen rich environment, under the low NH<sub>3</sub>/NO ratio, NO conversion to NO<sub>2</sub>. When NH<sub>3</sub>/NO is 0.6 and 80°C, although the conversion rate of NO is only 51.57%, the utilization rate of NH<sub>3</sub> in the reaction is very high, which is close to 90% at low temperature. The results indicates that the low-temperature catalytic reduction in the process of promoting NO to NO<sub>2</sub> conversion is very important, With the increase of reaction temperature, the catalyst activity increases, and the conversion rate of NO is greatly increased. When the NH<sub>3</sub>/NO is greater than 1, the NO conversion rate is not different, and the highest NO conversion rate is about 95%. This is because the amount of NH<sub>3</sub> at this time is no longer the main factor to determine the conversion rate of NO, and excess NH<sub>3</sub> is consumed by the side effects (Qi and Yang, 2003; Kijlstra et al., 1996; Huang et al., 2010). In this stage of the experiment, taking into account the conversion rate of NH<sub>3</sub>/NO, the NO is set to 1 for the next stage of the other process parameters. In the actual denitrification project, not only to achieve maximum efficiency of denitrification, but also need to take into account the economic and environmental benefits, to prevent the two pollution caused by ammonia escape.

## 4. Conclusion

(1) TiO<sub>2</sub> carrier is prepared by sol-gel method, and the Ce-Mn/TiO<sub>2</sub> catalyst is obtained by the Ce-Mn active component of the impregnation method, and the catalyst has good catalytic activity. When the reaction temperature is 80~140°C and 10%O<sub>2</sub>, the conversion rate of NO increases with the increase of the reaction temperature. With the increase of Ce-Mn loading and the increase of Ce/Mn molar ratio, the conversion rate of NO shows a trend of first increasing and then decreasing. The optimum load and Ce/Mn molar ratio are 15% and 0.8, respectively.

(2) Through the XRD spectrum and SEM morphology analysis, the catalyst is obtained by the 450°C calcination temperature, and the catalyst is smaller in size and homogeneous in the anatase structure. The catalyst under the optimum preparation condition is 15%Ce (0.8)-Mn/TiO<sub>2</sub>. The best calcination temperature is 450°C, and the optimum NO conversion rate is 99.01% at 140°C.

(3) With the increase of NH<sub>3</sub>/NO mole ratio of inlet flue gas, when the NH<sub>3</sub>/NO is less than 1, the conversion of NO is improved obviously, and the best NH<sub>3</sub>/NO is 1. The conversion rate of NO in the temperature range of 80~120°C is 70.71%, 78.78%, 87.78% and 99.01% respectively.

## Reference

- Chen Y., Li C.T., Zeng G.M., Fan X.P., 2010, Research of low-temperature selective catalytic reduction for NO by Ce-Fe/ACF catalyst, *Chinese Journal of Environmental Engineering*, 4, 625-628.
- Boningari T, Panagiotis G.S., 2011, Co-doping a metal (Cr, Fe, Co, Ni, Cu, Zn, Ce, and Zr) on Mn/TiO<sub>2</sub> catalyst and its effect on the selective reduction of NO with NH<sub>3</sub> at low-temperature, *Applied Catalysis B: Environmental*, 110, 195.
- Chen L., Li J.H., Ge M.F., 2010, DRIFT study on cerium-tungsten/titania catalyst for selective catalytic reduction of NO<sub>x</sub> with NH<sub>3</sub>, *Environ.Sci.Technol*, 44, 9590.
- Fang M., 2006, Preparation, Structure and Property of Anatase Crystalline Sol, Zhejiang University, Hangzhou.
- Huang H.F., Zhang F., Lu H.F., Chen Y.F., 2010, Effect of preparation methods on structures and performance of MnO<sub>x</sub>/TiO<sub>2</sub> catalyst for low-temperature NH<sub>3</sub>-SCR, *Journal of the chemical industry and engineering society of China*, 61, 80-85.
- Imen M., Ahmed M., Mohamed A.A., Ahmed O., 2016, LBM Simulation of Heat Transfer in Solid Oxide Fuel Cell. *International Journal of Heat and Technology*, 34(3), 351-356. DOI: 10.18280/ijht.340301.
- Jin R.B., Liu Y., Wu Z.B., Wang H.Q., Gu T.T., 2010, Low-temperature selective catalytic reduction of NO with NH<sub>3</sub> over Mn-Ce oxides supported on TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>: A comparative study, *Chemosphere*, 78, 1160-1166.
- Jung S.M., Grange P., 2001, Characterization and reactivity of V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub> supported on TiO<sub>2</sub>-SO<sub>4</sub><sup>2-</sup> catalyst for the SCR reaction, *Applied Catalysis B*, 32, 123.
- Kijlstra W.S., Daamen J.C., Graff J.M., 1996, Inhibiting and deactivating effects of water on the selective catalytic reduction of nitric oxide with ammonia over MnO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>, *Applied Catalysis B: Environmental*, 337.
- Leonardo V., Jose L.C.K., Joulia L., Palminio R., Pedro S., 2014, Ferromagnetismo a temperatura ambiente en mezclas de perovskitas de CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> CON ZnO Y TiO<sub>2</sub>. *Revista de la Facultad de Ingeniería*, 29(4), 137-142
- Lin T., Zhang Q.L., Li W., 2008, Monolith manganese-based catalyst supported on ZrO<sub>2</sub>-TiO<sub>2</sub> for NH<sub>3</sub>-SCR reaction at low temperature, *Acta Physico-Chimica Sinica*, 24, 1129-1131.
- Liu W., Tong Z.Q., Luo J., 2006, Low-temperature selective catalytic reduction of NO with NH<sub>3</sub> over Ce-Mn/TiO<sub>2</sub> catalyst, *Acta Scientiae Circumstantiae*, 26, 1240.
- Park T.S., Jeong S.K., Hong S.H., Hong S.C., 2001, Selective catalytic reduction of nitrogen oxides with NH<sub>3</sub> over natural manganese ore at low temperature, *Ind.Eng.Chem.Res*, 40, 4491-4495.
- Pragya and Vasanthakumari., 2016, Boundary Layer Flow Of Silver and Titaniumoxide Nanofluids over Vertical Stretching Sheet. *International Journal of Heat and Technology*, 34(3), 371-376. DOI: 10.18280/ijht.340304.
- Qi G.S., Yang R.T., 2003, Low-temperature selective catalytic reduction of NO with NH<sub>3</sub> over iron and manganese oxides supported on titania, *Applied Catalysis B: Environmental*, 44, 217.
- Qi G.S., Yang R.T., 2003, Performance and kinetics study for low-temperature SCR of NO with NH<sub>3</sub> over MnO<sub>x</sub>-CeO<sub>2</sub> catalyst, *Journal of Catalysis*, 217, 434.
- Saur O., Bensitel M., Mohammed A.B.S., 1986, The structure and stability of sulfated alumina and titania, *J.Catal*, 99, 104.
- Shen B.X., Liang C., Guo B.B., 2006, Present status and perspectives of low temperature SCR of flue gas denitrification technology, *Environmental Protection of Electric Power*, 22, 37.
- Shen B.X., Liu T., Zhao N., Yang X.Y., Deng L.D., 2010, Iron-doped Mn-Ce/TiO<sub>2</sub> catalyst for low temperature selective catalytic reduction of NO with NH<sub>3</sub>, *Journal of Environmental Sciences*, 22, 1447.
- Tang X.L., Hao J.M., Xu W.G., 2007, Low temperature selective catalytic reduction of NO<sub>x</sub> with NH<sub>3</sub> over amorphous MnO<sub>x</sub> catalysts prepared by three methods, *Catalysis Communication*, 8, 329-334.
- Tian W., Yang H.S., Fan X.Y., Zhang X.B., 2011, Catalytic reduction of NO<sub>x</sub> with NH<sub>3</sub> over different-shaped MnO<sub>2</sub> at low temperature, *Journal of hazardous materials*, 188, 105-109.
- Wu X.D., Si Z.C., Li G., Weng D., Ma Z.R., 2011, Effects of cerium and vanadium on the activity and selectivity of MnO<sub>x</sub>-TiO<sub>x</sub> catalyst for low-temperature NH<sub>3</sub>-SCR, *Journal of rare earths*, 29, 64.
- Yu Y.B., 2009, Deactivation of a Ce/TiO<sub>2</sub> catalyst by SO<sub>2</sub> in the selective catalytic reduction of NO by NH<sub>3</sub>, *J.Phys.Chem.C*, 113, 4426.