

## Effect of NO oxidation to NO<sub>2</sub> from diesel engine over Mn-Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst

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A series of Mn-Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by loading different amounts MnO<sub>x</sub>-CeO<sub>x</sub> on the sol-gel synthesized  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> mixed oxides. The activities of the catalysts for NO oxidation to NO<sub>2</sub> were evaluated in 500ppm NO and 10% O<sub>2</sub> (N<sub>2</sub> balance) based upon the simulation experiment. The results showed that NO conversion rate raised with the increase of the temperature, which reached up to the peak value at 300°C and reduced with the further increase in temperature. The steady time for the volume fraction and NO<sub>2</sub> was reduced with the increase of temperature. All the 6Mn10Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 8Mn10Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 10Mn10Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> exhibited high catalytic oxidation of NO to NO<sub>2</sub>, and NO conversion reached up to above 60%. Among all the catalysts, 6Mn10Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst showed the highest catalytic activity with 44% of NO conversion at the temperature below 200°C, which indicated that 6Mn10Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was benefit for oxidation NO to NO<sub>2</sub> at low temperature.

**Key words:** Diesel engine, NO oxidation, MnO<sub>x</sub>-CeO<sub>x</sub>, simulation experiment

### 1 INTRODUCTION

Nitrogen Oxides (NO<sub>x</sub>) emitted by automobiles often appears as a major source of air pollution, which is considered to be hazardous to environment and human health due to the formation of fine particles, ozone smog, acid rain and eutrophication [1,2]. NO<sub>x</sub> storage/reduction (NSR) is currently regarded as one of the most practical technologies for lean-burn gasoline and diesel vehicles and has also been extensively studied for NO<sub>x</sub> removal [3,4]. NSR catalysts are generally comprised of precious metals, NO<sub>x</sub> storage components and support metal oxides working under lean/rich conditions. Compared with NO as primarily components of NO<sub>x</sub>, NSR trapping materials more effectively sorb NO<sub>2</sub>, or NO<sub>2</sub> may be the required intermediate compound for NO<sub>x</sub> sorption. Then oxidation of NO to NO<sub>2</sub> will result in more efficient for NO<sub>x</sub> removal.

In general, Pt has been recognized as the best active catalyst for NO oxidation, while Pt-group metals are expensive and suffered by sulfate poisoning referring to sulfate oxidation with oxygen on the surface of the catalyst. Replace Pt with alternative materials or reduce loading of Pt with monolayer catalysts and electrocatalysts have attracted more concern to reduce the cost of catalysts in recent years [5,6,7,8].

MnO<sub>x</sub> based oxides present high active catalytic for NO<sub>x</sub> removal [9,10,11]. Mn/TiO<sub>2</sub> and Mn/ZrO<sub>2</sub> mixed oxides showed high oxidation of NO, which the peak value could reach up to 59% at 298°C and 78% at 270°C respectively [12]. It was found that CeO<sub>x</sub> metal oxides could storage Oxygen

through the transfer between Ce<sup>3+</sup> and Ce<sup>4+</sup>, which was benefit for improving the catalytic activity at low temperature [13,14,15,16]. Mn-Ce mixed oxides showed higher NO oxidation that was about 3-10 times more than that of with CeO<sub>2</sub> and MnO<sub>x</sub> at 200°C, indicating the interaction between Mn and Ce would enhance the oxidation activity of catalysts at low temperature [17].

In order to fully study the mechanism of NO oxidation to NO<sub>2</sub> over Mn-Ce mixed oxides catalysts, this report prepared a series of xMnyCe/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (x=4,6,8,10. y=10) catalysts by a sol-gel deposition method. The activities for NO oxidation to NO<sub>2</sub> were measured based upon the fixed bed reactor by simulation test, and the effect of temperatures on NO oxidation over Mn-Ce catalysts were also investigated to reveal the evolution process between NO and NO<sub>2</sub>.

### MATERIALS AND METHODS

#### Catalyst Preparation

Mn-Ce mixed oxides catalysts were synthesized by a sol-gel method. Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, C<sub>4</sub>H<sub>6</sub>MnO<sub>4</sub>·4H<sub>2</sub>O and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were dissolved in the solution containing deionized water, citric acid and polyethylene glycol, forming homogenous and transparent solution. After continuously stirring at 80°C until transparent gel was obtained, then dried at 110°C for 24h and then decomposed at 300°C for 1 h and calcined at 500°C for 5h under static air in a muffle to obtain the fresh catalyst samples.

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### Catalyst characterization

X-ray diffraction patterns used to investigate the phase structure and phase composition of catalysts were measured on a Bruker D8 ADVANCE X-ray diffractometer with a Ni-filtered Cu K $\alpha$  ( $\lambda = 0.154068$  nm) radiation source at 40 kV and 40 mA. The catalyst samples were scanned at  $2\theta$  ranging from  $20^\circ$  to  $80^\circ$  with a scanning velocity of  $7^\circ\text{min}^{-1}$ .

### Catalytic Measurements

The catalytic test were carried out in a continuous fixed-bed quartz tubular microreactor with an inside diameter of 10 mm at atmospheric pressure, as shown in Figure 1. The oxidation of NO to NO<sub>2</sub> activity was measured at the temperatures in the range of 150-450°C. 0.3ml catalyst powder was packed in the reactor bed. The reactant gas mixture (500ppm NO, 10%O<sub>2</sub>,N<sub>2</sub> balance) was fed to the reactor with a total flow rate of 100ml/min, corresponding to a gas hour space velocity (GHSV) of  $50000\text{h}^{-1}$ . NO and NO<sub>2</sub> concentration were analyzed by a Thermo 42iHL NO<sub>x</sub> gas analyze (America). The NO conversion ( $X_{\text{NO}}$ ) is defined as:

$$X_{\text{NO}} = \frac{\text{NO}_{2\text{ out}}}{\text{NO}_{\text{ in}}} \times 100\%$$

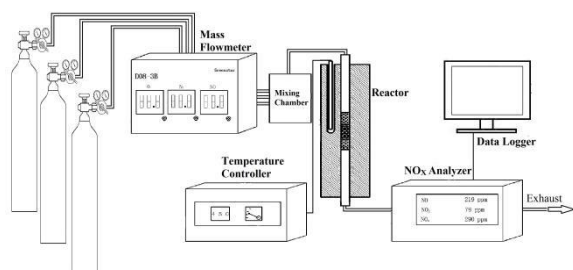


Fig. 1. Schematic diagram of catalyst activity test

## RESULTS AND DISCUSSION

### XRD Analysis

The XRD pattern of  $x\text{Mn}10\text{Ce}/\gamma\text{-Al}_2\text{O}_3$  ( $x=4,6,8,10$ ) catalysts are shown in Figure 2. As can be seen in Figure 2, all the samples exhibit characteristic peaks of  $\gamma\text{-Al}_2\text{O}_3$  (JCPDS:PDF 48-0366). The main diffraction peaks at  $2\theta=28.5^\circ$ ,  $33.1^\circ$ ,  $47.5^\circ$  and  $56.3^\circ$ , attributed to the (111), (200), (220) and (311) planes of cubic fluorite CeO<sub>2</sub> (JCPDS:PDF 43-1002) [18]. Other two diffraction peaks at  $2\theta=31.8^\circ$  and  $56.3^\circ$  (which are overlapped with the peaks of CeO<sub>2</sub>) are identified as the phase of MnO<sub>2</sub> (JCPDS:PDF 65-7467). According to Scherrer's formula, the crystalline size of CeO<sub>2</sub> is calculated as 26 nm. Moreover, the diffraction peaks of CeO<sub>2</sub> shifted to lower

degrees, and the main reason is that a part of Ce<sup>4+</sup> ions are replaced by Mn<sup>4+</sup> and Mn<sup>3+</sup> to form solid solution, which is benefit for oxygen vacancies forming and then improve the active catalytic of catalysts.

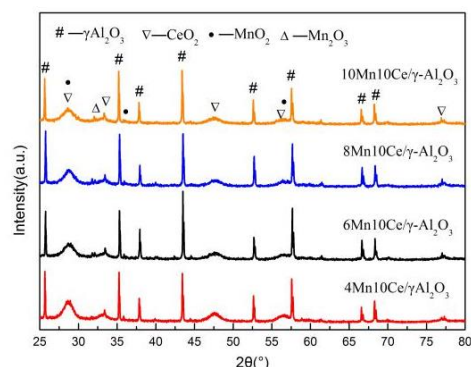
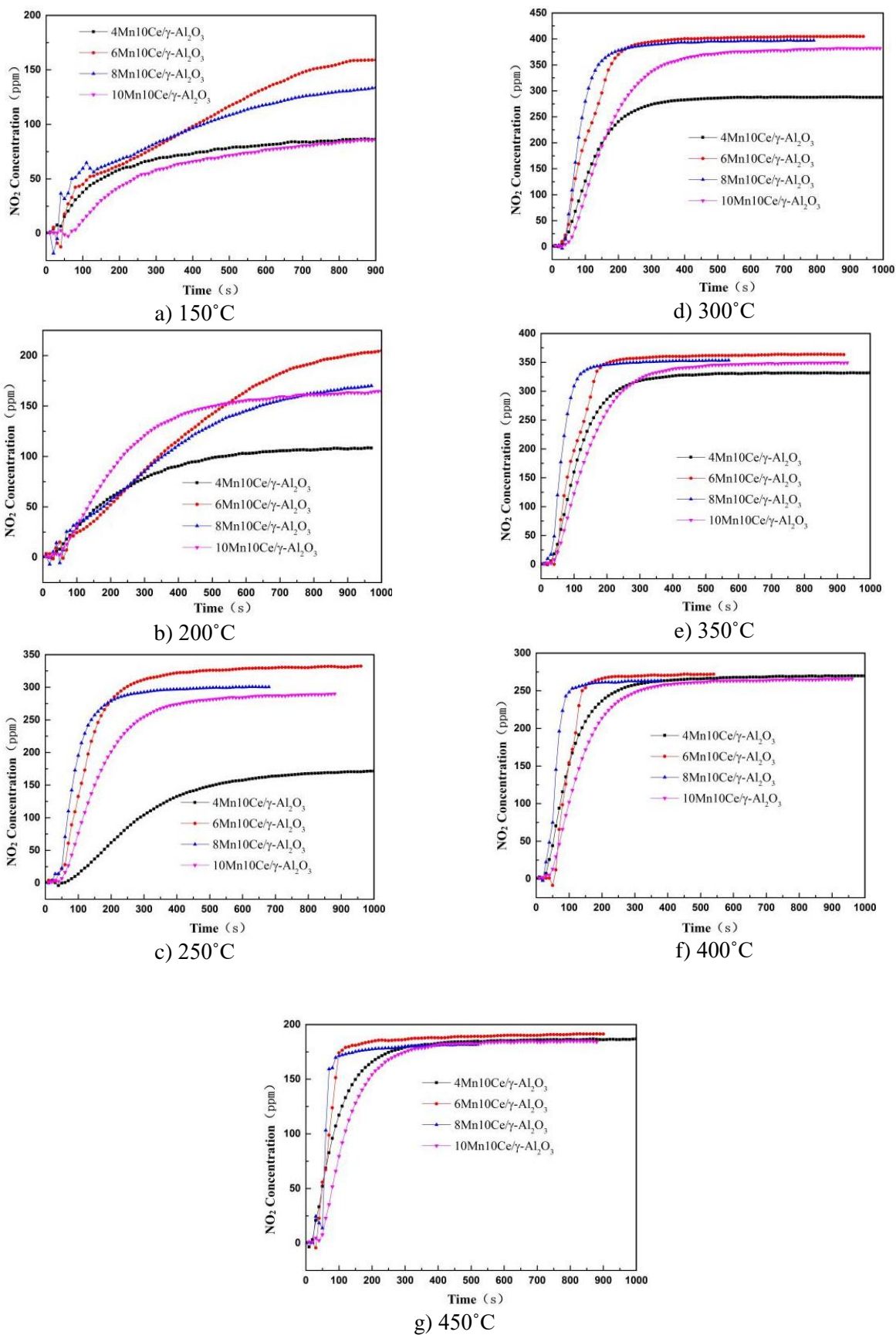


Fig. 2. XRD pattern of  $x\text{Mn}10\text{CeO}/\gamma\text{-Al}_2\text{O}_3$  catalysts

### Oxidation activity

NO and NO<sub>2</sub> concentration as a function of time at the temperature ranging from 150°C to 450°C over  $x\text{Mn}10\text{Ce}/\gamma\text{-Al}_2\text{O}_3$  ( $x=4,6,8,10$ ) catalysts are shown in Figure 3. It can be found that NO<sub>2</sub> concentration first sharp increases and then reduces with the rise of temperature. In the range of 150°C to 300°C, the stabilized NO<sub>2</sub> concentration increases as the temperature is increased and reaches up to the most high value at 300°C. With the further increase in temperature, NO<sub>2</sub> concentration decrease occurs. The time that from reaction began to NO<sub>2</sub> concentration got stabilized decreases as the temperature increases in the range of 150°C to 450°C. Among all the catalysts, the stabilized times for 6Mn10Ce/ $\gamma\text{-Al}_2\text{O}_3$  and 8Mn10Ce/ $\gamma\text{-Al}_2\text{O}_3$  catalysts are significantly shorter than that of 4Mn10Ce/ $\gamma\text{-Al}_2\text{O}_3$  and 10Mn10Ce/ $\gamma\text{-Al}_2\text{O}_3$  catalysts, which indicates that 6Mn10Ce/ $\gamma\text{-Al}_2\text{O}_3$  and 8Mn10Ce/ $\gamma\text{-Al}_2\text{O}_3$  catalysts have better oxidation catalytic. The stabilized time of NO<sub>2</sub> over 6Mn10Ce/ $\gamma\text{-Al}_2\text{O}_3$  catalyst is shorter than that of 8Mn10Ce/ $\gamma\text{-Al}_2\text{O}_3$  catalyst below 200°C, while the later will get more shorter above 250°C.

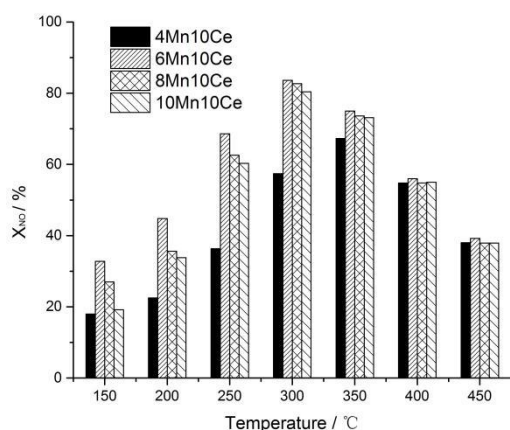
NO conversion as a function of temperature over  $x\text{Mn}10\text{Ce}/\gamma\text{-Al}_2\text{O}_3$  ( $x=4,6,8,10$ ) catalysts is shown in Fig.4. It can clearly be found that NO conversion presents the trend of increasing gradually and then reducing as the rise of temperature. Compared with 4Mn10Ce/ $\gamma\text{-Al}_2\text{O}_3$  catalyst, 6Mn10Ce/ $\gamma\text{-Al}_2\text{O}_3$ , 8Mn10Ce/ $\gamma\text{-Al}_2\text{O}_3$  and 10Mn10Ce/ $\gamma\text{-Al}_2\text{O}_3$  catalysts shows obviously higher catalytic activity for oxidation NO to NO<sub>2</sub>, especially at the temperature below 300°C.



**Fig. 3.** NO and NO<sub>2</sub> concentration as the function of time over xMn10Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>(x=4,6,8,10) catalysts at different temperature



For example, NO conversion reaches up to 22% at 200°C over 4Mn10Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, while more than 44%, 35% and 33% NO conversion are achieved over the other three catalysts respectively. It is interesting to find that NO conversion over different catalyst get closer in the range of 400°C to 450°C, and that means the key important effect on catalytic activity is the temperature at that range but not the molar ratio of Mn/Ce in catalysts. All the catalysts show the best NO conversion at 300°C except for example, NO conversion can reach up to 83% over 6Mn10Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. It is also important to note that NO conversion decreases with the further increase of the temperature. The main reason is that NO oxidation to NO<sub>2</sub> is an exothermic reversible reaction and is limited by the thermodynamic equilibrium at high temperatures, and NO<sub>2</sub> can dissociate into NO and O<sub>2</sub> if it comes in contact with the Mn-Ce mixed oxidation catalyst at high temperature, as like that in the range of 400°C to 450°C.



**Fig. 4.** NO conversion as the function of temperature over xMn10Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (x=4,6,8,10) catalysts.

## CONCLUSION

1. Mn in the xMn10Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (x=4,6,8,10) catalysts is mainly in the form of MnO<sub>2</sub> and Mn<sub>2</sub>O<sub>3</sub>. And part of the Ce<sup>4+</sup> ions will be replaced by Mn cation upon the incorporation of Mn<sup>4+</sup> and Mn<sup>3+</sup> cation into the CeO<sub>2</sub> lattice, which can lead to form more oxygen vacancies and then improve the NO to NO<sub>2</sub> oxidation activity of Mn-Ce mixed oxides catalysts.

2. The reaction time of stabilized NO<sub>2</sub> concentration will reduced gradually as the temperature increase. Among all the xMn10Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts, NO<sub>2</sub> concentration up to the steady value after sharp increase is the shortest under the treatment of 6Mn10Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst below 200°C, while the strong activity for the NO oxidation could be observed over 6Mn10Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst

above 250°C.

3. NO conversion presents first increase and then decrease trend as the rise of temperature. All the xMn10Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts show the most high oxidation catalytic at 300°C except the 4Mn10Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. Among the xMn10Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts, 6Mn10Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> shows the best oxidation activity for NO converting to NO<sub>2</sub>. The high temperature is benefit for improving the oxidation activity of xMn10Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts, while it will also lead to NO<sub>2</sub> dissociate into NO and then reduce the NO conversion.

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