

## Investigation on Removal of Nitric Oxide from Flue Gas by Ammonia upon Prepared Catalysts

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**Abstract:** Selective catalytic reduction of NO with ammonia upon prepared platinum catalyst was investigated in this study. Experimental results showed that the catalyst had good activity on removal of NO in the used experimental conditions. Further investigation indicated that its selectivity could be improved when it was modified with La and Ce and its suitable compositions of the modified platinum catalyst had been obtained in this study. A pilot-scale study changed with 100 g catalyst in the fixed-bed reactor showed that the modified platinum catalyst had good activity, selectivity and stability in the used conditions. This implied that the modified platinum catalyst could be a promising catalyst to be used in the commercial application.

**Key words:** Selective catalytic reduction, platinum catalyst, modification, ammonia

### INTRODUCTION

It is usually difficult to remove nitric oxides from flue gas formed during coal burning industries such as in electric power and steam generation factories as the excess oxygen remaining in the exhaust gas<sup>[1-6]</sup>. Researchers reported that the method of Selective Catalytic Reduction (SCR) with hydrocarbon or ammonia as reductant has been considered as an effective method. Moreover, results showed that the method using ammonia to reduce nitric oxide in excess oxygen gases is particular effective as the technology for addition of ammonia to the exhaust gas in a controlled manner has been well reported<sup>[7-9]</sup>, which has been applied to both vehicular and stationary sources using vanadia-titania-based catalysts and the latter showed a high activity and selectivity between 270~350°C<sup>[9]</sup>. At the temperature higher than 350°C such materials would non-selectively catalyse the oxidation of ammonia leading to a loss in SCR activity<sup>[7]</sup>. Other results indicated that a wide range of metals and metal oxides such as Co, Cu, Ag and Pt also had good activities related to removal of nitric oxides using SCR methods while operated within narrow temperature range<sup>[10]</sup>. To facilitate applications on vehicular or stationary exhausts, there has been interest to develop catalysts which can operate over a wider temperature range in particular from 200 to 600°C. For example, flue gas temperature typically drops below 250°C soon after let off from the source. It therefore becomes necessary to reheat the flue gas to raise its temperature if the catalyst used has an operating temperature higher than 250°C wherein the operating costs would be increased. An alternative solution to this problem is to develop an inexpensive

low-temperature system with a catalyst that could be effective at such temperatures.

Several studies have focused on zeolite materials<sup>[11,12]</sup>, which were typically active over a relatively wide temperature range and also posed less of a disposal problem compared to the toxic vanadia-based materials. Ion-exchanged zeolites such as H-modernite and H-ZSM-5 were other materials used in this purpose<sup>[13-15]</sup>. Reports showed that the latter types were active both in the high temperatures and low temperatures<sup>[16-19]</sup> while their performance was found to be strongly dependent on the relative ratio of NO to NO<sub>2</sub> in the feed<sup>[20]</sup> and also instability<sup>[21]</sup>. Moreover, a desirable attribute of the catalysts applied at low temperatures is its stability in the presence of small amounts of SO<sub>2</sub><sup>[22-25]</sup>. This is because this constituent is likely to be present in such conditions. Given the potential benefit to be derived from NH<sub>3</sub>-SCR process operated at low temperature, it would be necessary to develop a catalyst active at lower temperatures and yet tolerant to sulfur compound.

This study reported on the original results on removal of nitric oxide upon prepared platinum-based catalysts within temperature range about from 150°C to 300°C. Based on laboratory studies, typical pilot-scale investigation was also investigated, which provided the basis for further study in a large scale.

### MATERIALS AND METHODS

**Experimental set-up:** Experiments were performed in a fixed-bed reactor system. An on-line gas analyzer was used to detect the concentrations of NO, O<sub>2</sub>, CO, CO<sub>2</sub> in the inlet and outlet. An off-line analyzer of 752 ultraviolet

spectrometer, a mass spectrometer (HP6890/5973) and a gas chromatograph (Shimadzu GC 8A) equipped with TCD (Thermal Conductivity Detector) and a column packed with Hysep Q-Porapac T were used to detect the concentrations of  $\text{NH}_3$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}_2$  and  $\text{SO}_2$  respectively. Similar method was used to calculate the conversion and selectivity in the NO catalytic reduction<sup>[26]</sup>. During experiment,  $\text{SO}_2$  was directly added in the gas mixtures of nitrogen and nitric oxide when investigating the effect of  $\text{SO}_2$  on catalyst performance. Reaction temperature was controlled with a temperature programmable controller and measured with a micro thermocouple inserted in its center through a small jacket tube.

**Laboratory tests:** In order to investigate prepared catalyst activity and selectivity, experiments were performed at temperatures ranged from about  $150^\circ\text{C}$  to  $300^\circ\text{C}$  and different space velocities and gas compositions. The mixtures containing NO and  $\text{SO}_2$  were controlled using mass flow controllers and stainless steel pipelines were used to reduce the incidence of reactions caused by the corrosive gases. The mass balance of gaseous components in terms of inlet and outlet was done in advance when the reactor loaded with quartz and catalyst under selected operation conditions. Experiment results showed that the mass balance differences were within the experimental acceptable ranges. Catalytic reductions were initiated by introducing gas mixtures to the fixed-bed reactor packed with 1.0 g prepared catalyst.

**Pilot-scale investigation:** Based on laboratory studies loaded with small amount of catalyst, a pilot-scale experiment charged with 100g catalyst was investigated in the fixed bed reactor at the following conditions. Reaction temperature  $160\sim 250^\circ\text{C}$ , space velocity  $2500\text{h}^{-1}$ , gas compositions (v/v%)  $3.5\text{H}_2\text{O}+(0.003\sim 0.08)\text{NO}+0.002\text{SO}_2+0.1\text{CO}+12.0\text{CO}_2+9.8\text{O}_2$  balanced with  $\text{N}_2$ , the concentration of ammonia added in the system was varied within  $800\sim 1000\text{ppm}$ . Other conditions were similar in the laboratory test introduction.

**Catalyst preparation:** The precious catalyst was prepared by impregnating  $\text{Al}_2\text{O}_3$  support with 27.7 mM aqueous solution of  $\text{H}_2\text{PtCl}_6$  at room temperature. The precursor was then oven-dried overnight at  $80^\circ\text{C}$  under vacuum and subsequently calcined in a muffle furnace at  $600^\circ\text{C}$  for 6 h. To prepare series of Pt-La-Ce-O/ $\text{Al}_2\text{O}_3$  catalysts, the support was first impregnated by the aqueous solution in which contained desired amounts of lanthanum and cerium nitrate. The impregnation process was lasted for 4 hours at room temperature. It was then filtered and dried overnight at  $80^\circ\text{C}$  under vacuum and calcined in a muffle furnace at  $600^\circ\text{C}$  for 6 h.

**Characterization:** The surface properties of fresh and used catalysts were determined using  $\text{N}_2$  adsorption-desorption on a Micromeritics ASAP2010 BET apparatus. The acidities of those samples were determined with  $\text{NH}_3$ -TPD method. In addition, NO-TPD method was used in this study by the following procedure. 100 mg catalyst was charged in quartz microreactor and reduced with mixture of hydrogen and nitrogen lasted 1 h under  $450^\circ\text{C}$ . The reactor was purged with pure nitrogen lasted 1 h under  $550^\circ\text{C}$  and then cooled to  $50^\circ\text{C}$ . After that, 8-15 mL pure NO was injected with impulse method and purged with pure nitrogen about half one hour to remove the unadsorbed NO from the system. Finally, the system was raised to  $800^\circ\text{C}$  at  $20^\circ\text{C min}^{-1}$  rate and an on-line MS-GC was used to detect the desorbed products. X-Ray Diffraction (XRD) for identification of the catalyst crystalline phases was performed with a Rigaku D/Max-rA instrument using  $\text{CuK}\alpha$  radiation, 40 kV tube voltage and 100 mA tube current. The fresh and used catalyst surface profiles were investigated with a S-3200N HITACH Scanning Electron Microscope (SEM). The catalyst compositions were determined with an inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7500, US) instrument. TG data were obtained using a PCT-1A instrument.

## RESULTS AND DISCUSSION

**Platinum catalyst:** Our previous studies showed that supported Cu and Cr catalyst had good activity at lower space velocity when the temperature was lower than  $300^\circ\text{C}$ , while its selectivity was not satisfied as using this technology in the process of producing pure carbon dioxide. This study firstly studied the performance of platinum supported catalyst on removal of NO at the following conditions used in the supported Cu and Cr catalysts, catalyst weight 1.0 g, reaction temperature  $240^\circ\text{C}$  space velocity of gas volume  $2500\text{h}^{-1}$ , 1.0:1.2 molar ratio of NO to  $\text{NH}_3$ , gas composition (v/v%)  $0.08\text{NO}+0.015\text{CO}+12.0\text{CO}_2+9.8\text{O}_2$  balanced with  $\text{N}_2$ . Experimental results indicated that platinum catalyst had good activity and selectivity compared with nonnoble catalyst. Moreover, results showed that the former had bifunctional performance. The added  $\text{NH}_3$  firstly selectively reduced NO in the presence of catalyst and then the excess  $\text{NH}_3$  was catalytically oxidized to  $\text{N}_2$  and  $\text{H}_2\text{O}$ .

The operation cost would be obviously decreased if the noble catalyst could be used at higher space velocity from commercial view and also provided the basis to further improve its performance. Figure 1 was the experimental results of platinum catalyst on removal of NO at different reaction temperatures and  $5000\text{h}^{-1}$  space

velocity. The other reaction conditions were same as the previous mention. Results showed that the platinum catalyst performance on removal of NO was slightly increased with reaction temperature at used experimental conditions. Considering NO conversion ratio and selectivity together with exit concentration of N<sub>2</sub>O, it indicated that the suitable reaction temperature for the platinum catalyst to be used in the process would be from 220;æ to 240;æ. It also showed that it was necessary to modify the platinum catalyst to further improve its performance on removal of NO from the flue gas.

**Modified platinum catalysts:** Lanthanum and cerium were used in this study to improve platinum catalyst performance. Experimental studies showed that the modified catalyst had good performance when molar ratio of Pt: La: Ce reached to 1.0: 3.78: 3.56. Figure 2 showed platinum and modified catalyst performance on removal of NO at different reaction temperatures and the other conditions listed below, catalyst weight 1.0g, space velocity of gas volume 15000 h<sup>-1</sup>, 1.0:1.2 molar ratio of NO to NH<sub>3</sub>, gas composition (v/v%) 0.08NO+ 0.002SO<sub>2</sub>+ 0.015CO+12.0CO<sub>2</sub>+9.8O<sub>2</sub>+balanced with N<sub>2</sub>. It indicated that the activity of modified platinum catalyst was almost same as the platinum catalyst while the selectivity of the former was improved very much compared with the latter, which would further decrease the concentration of N<sub>2</sub>O in the exit.

**Characterization :** Basic characterization such as using XRD, SEM, TPD, ICP and TG has been done in order to reveal the reason why the performance of modified platinum catalyst could be improved in the experimental conditions. Here we only gave the NO-TPD results performed on Al<sub>2</sub>O<sub>3</sub> support, Pt/Al<sub>2</sub>O<sub>3</sub> and Pt-La-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts, respectively. Results showed that there were two characterized desorption peaks both for NO and N<sub>2</sub>O on Pt/Al<sub>2</sub>O<sub>3</sub> and Pt-La-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts, while only one peak appeared for NO and N<sub>2</sub>O on Al<sub>2</sub>O<sub>3</sub> support, respectively, shown in Fig. 3. The higher desorption temperatures occurring on Pt/Al<sub>2</sub>O<sub>3</sub> and Pt-La-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts were lower than that occurring on Al<sub>2</sub>O<sub>3</sub> support, which might be resulted by the adsorbed NO because the existence of Pt, La and Ce would benefit NO desorption from the support. In addition, characterization showed that NO was easily desorbed and decomposed on Pt-La-Ce/Al<sub>2</sub>O<sub>3</sub> catalyst while difficult on Al<sub>2</sub>O<sub>3</sub> support. This could be the reason that Pt/Al<sub>2</sub>O<sub>3</sub> property was improved by addition of La and Ce on it.

**Pilot-scale tests:** Based on laboratory tests, a pilot-scale experiment was investigated in order to further check the

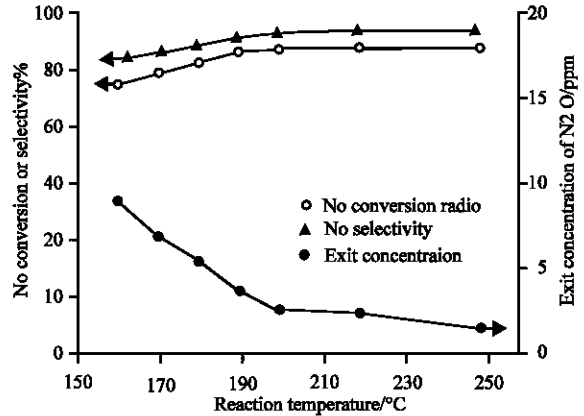


Fig. 1: Performance of platinum catalyst on removal of NO at various reaction temperatures

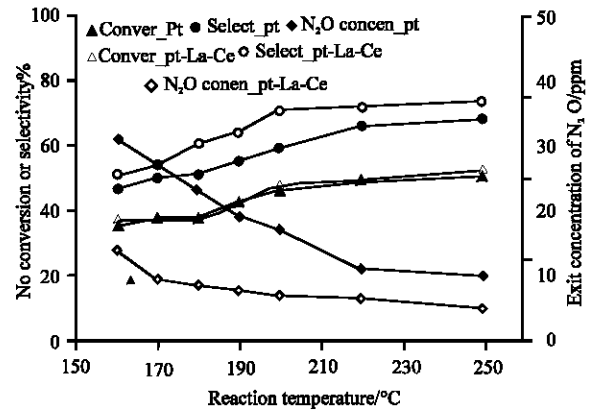


Fig. 2: Performance comparison of platinum with modified platinum catalysts on removal of NO at various reaction temperatures

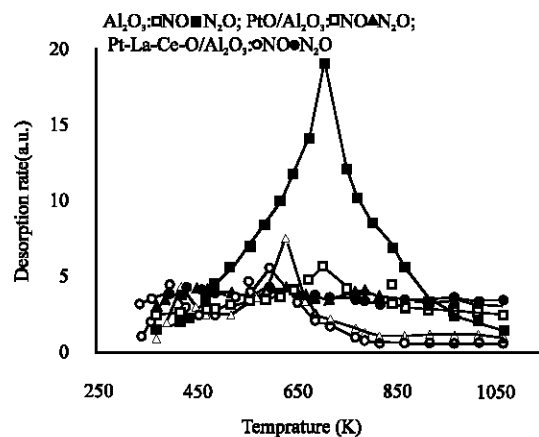


Fig. 3: TPD spectra of NO and N<sub>2</sub>O from Al<sub>2</sub>O<sub>3</sub> support and catalysts of PtO/Al<sub>2</sub>O<sub>3</sub> and Pt-La-Ce-O/Al<sub>2</sub>O<sub>3</sub> absorbed with NO

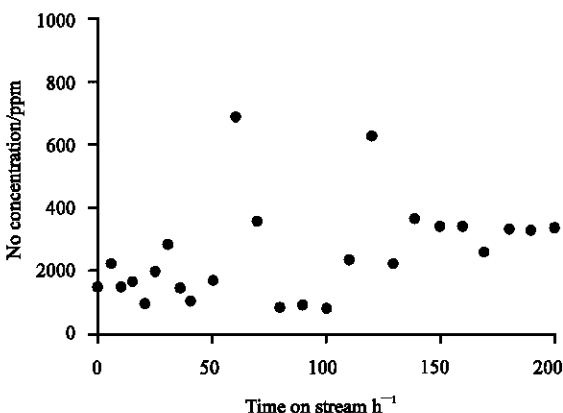


Fig.4: Variation of NO concentration during the tests

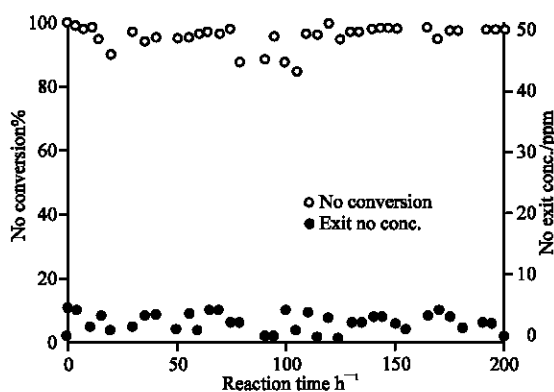


Fig.5: NO conversion and exit concentration in the used experimental conditions at pilot-scale test

modified catalyst performance and also its possibility to be used in the commercial application. The test was lasted for 200 h in which the temperature of fixed-bed reactor was varied among 160~250°C. The practical NO concentration in the feed was shown in Fig. 4, which showed that the NO concentration during the test was varied from 60 to 700 ppm. The modified catalyst performance on removal of NO from the gas mixture was shown in Fig. 5. It indicated that the modified catalyst (Pt-La-Ce) had higher NO conversion ratio. The concentration of NO in the exit was lower than 5 ppm in the used experimental conditions. Analytical results also showed that the N<sub>2</sub>O and ammonia could not be detected in the pilot-scale study, which indicated that the modified platinum catalyst could be a promising catalyst to be used in the commercial application.

### CONCLUSION

This study showed that the prepared platinum catalyst had good activity on removal of NO using

ammonia in the used experimental conditions. Further study showed its selectivity could be improved when it was modified with La and Ce and the suitable composition of the latter for the molar ratio of Pt: La: Ce would be 1.0: 3.78: 3.56 in the used experimental conditions. Based on laboratory tests, a pilot-scale study changed with 100g catalyst in the fixed-bed reactor showed that the modified platinum catalyst had good activity, selectivity and stability. This study provided the basis for further test in a large scale considering the commercial application.

### ACKNOWLEDGEMENT

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