

APPLICATION OF NON-THERMAL PLASMA TECHNOLOGY FOR DEVELOPING FAST SCR SYSTEM TO REMOVE NO_x

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ABSTRACT

Removal of NO by SCR system and combined plasma SCR system was investigated. The results indicate that overall NO conversion efficiency is improved by decreasing the ratio of NO/NO₂ via application of glass beads.

On the other hand, MnO_x-CeO₂/TiO₂ shows excellent performance for NO reduction at a temperature range of 100-200°C and NO removal efficiency can be significantly increased by the combination of plasma and SCR system. It is clear that NO removal efficiency depends on ratio of NO/NO₂. Overall, plasma can enhance NO removal achieved with the SCR system.

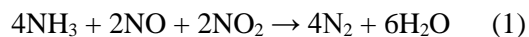
1. INTRODUCTION

Nitrogen oxides (NO_x) emitted from mobile and stationary sources are considered as one of the most dangerous air pollutants for their devastating effect on ecosystem, human health and atmosphere, such as acid rain, photochemical smog, deterioration of water quality and visibility [1]. Hence, how to effectively reduce NO_x emissions at a reasonable cost has become an emerging issue.

At present, several methods have been applied for NO_x removal [2]. Among them, selective catalytic reduction of NO_x by ammonia (NH₃-SCR) is a well-known and widely adopted process for NO_x emissions control [3]. In this method, V₂O₅, WO₃ or MoO₃ catalyst supported on TiO₂ is used as a catalyst, and NO_x is reduced by NH₃, urea or hydrocarbon as a reductant. However, SCR fails to address the most important problem, which is low reduction

performance at low temperatures of 373–573 K [4]. Hence, it has to be operated at higher temperature for good performance. Previous study indicates that Mn-Ce-based catalysts exhibited superior SCR activity in low temperature (<200°C) [5]. Therefore, we attempt to develop a fast SCR system by combining non-thermal plasma technology (DBD).

Application of non-thermal plasma (NTP) is a promising and effective idea for oxidizing NO. NTP generally induces chemical reactions with small energy, generating high energy charged particles by a high electric field without heating all the gas [6]. In NTP system, the collisions between neutral molecules and electrons produce active N and O species and OH radicals to react with the polluted gases and to ensure their oxidations. In the case of NO_x removal, the conversion of NO_x by NTP process consists of the oxidation of NO by O to NO₂ [7], which is the reactant we need in reaching fast SCR. The main reaction of fast SCR is shown in Reaction (1), and the reaction rate with equimolar amounts of NO and NO₂ is much faster than normal SCR [8].



In this hybrid system, non-thermal plasma is applied as a pre-treatment process for converting part of the NO into NO₂. As the ratio of NO/NO₂ is close at 1:1, it forms a fast SCR reaction for NO_x removal. MnO_x-CeO₂/TiO₂ catalyst is applied in SCR system. Due to the activation of the reactant by NTP and the capability of SCR, combination of plasma and SCR system is investigated to effectively reduce NO_x emissions at a reasonable cost.

2. EXPERIMENTAL

2.1 Reaction system measurement

Combined plasma SCR system can be divided into two parts, i.e., plasma treatment system for converting part NO into NO₂ and SCR reactor system. The layout of the entire system is presented in Fig. 1. For plasma treatment system, the feeding gas stream contained 1,000 ppm NO, with air as carrier gas. The total gas flow rate was controlled at 1.2 LPM by mass flow controllers. In addition, The reactor consisted of a glass tube (ID = 2 cm), a spiral stainless steel rod (OD = 0.3 cm) as the inner electrode, and a stainless steel wire mesh (L = 20 cm) as the outer electrode, additionally, glass beads were filled into discharge zone to enhance energy in the system for getting the appropriate ratio of NO/NO₂. The power source for plasma was a high voltage AC transformer, and voltage was controlled at value of 12-15 kV with a frequency of 100 Hz. The discharge power was determined by Lissajous diagram (V-Q plot), which was measured by a digital oscilloscope equipped with a high voltage probe and a voltage probe, and with a 1.0-μF capacitor connected to the reactor.

Both the gas stream after plasma treatment and 1,000 ppm NH₃ with N₂ as carrier gas are introduced into SCR system to conduct experiment. In SCR system, catalytic tests was performed in a fixed-bed quartz reactor (ID = 20 cm) containing 8 g catalysts. The total gas flow rate was controlled at 2 lpm, and it corresponded to GHSV of 20,000 h⁻¹. Finally, the operating temperature was varied from 100 to 200°C to evaluate the temperature effect. The concentrations of NO and NO₂ were analyzed before and after the reaction by using an NO_x detector [Testo 350]. Removal efficiency of NO is calculated by Equation (1):

$$\text{Removal efficiency of NO} = \left\{ \frac{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}} \right\} \times 100\% \quad (1)$$

Where [NO]_{in} and [NO]_{out} are NO concentrations measured before and after the reactor, respectively.

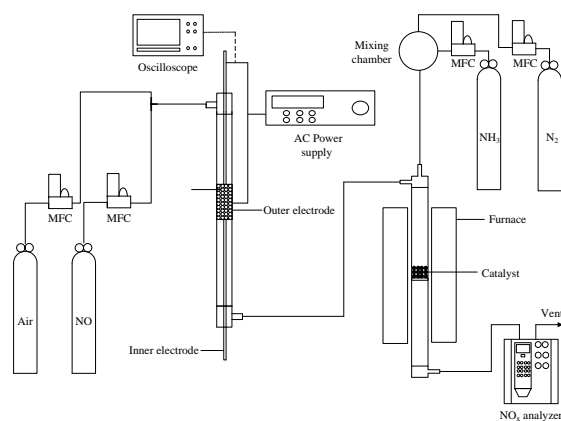


Fig. 1 Illustration of combination of plasma and SCR system

2.2 Catalyst preparation and analysis

MnO_x-CeO₂/TiO₂ catalyst was prepared by wet impregnation method. The manganese nitrate (Mn(NO₃)₂ · 4H₂O, Acros) and cerium nitrate (Ce(NO₃)₃ · 6H₂O, Acros) were used as the sources of manganese and cerium for the catalyst, respectively. The titanium oxide powder (TiO₂, P25, Degussa) was used as support material to prepare the catalyst. The mole ratios of metal oxides adopted for MnO_x-CeO₂/TiO₂ catalyst was 0.4/0.13/1. Briefly, the cerium nitrate, manganese nitrate, deionized water and TiO₂ powder were mixed in appropriate ratio under vigorous stirring for 30 min. Then, the excess water was slowly evaporated on water bath with continuous stirring at 70°C. The resulting material was dried at 110°C overnight, then calcined at 500°C for 4 hour in air atmosphere and was finally sieved to obtain homogeneous powder. Additionally, properties of catalyst were analyzed with Brunauer Emmett Teller (BET), X-ray diffraction (XRD) and scanning electron microscopy (SEM).

3. RESULTS AND DISCUSSION

3.1 Physicochemical properties of catalyst

Fig. 2 shows the XRD patterns of MnO_x-CeO₂/TiO₂, and the result indicates that there are only two crystallite phases for TiO₂ and CeO₂, respectively. It is clear that these two phases are independent of the manganese oxide. On the other hand, the manganese oxide species peaks are not observed in the XRD patterns, implying that manganese oxide species may be well dispersed on the surface of catalyst. The finding was consistent with previous study [9].

The catalyst morphology is presented in Fig. 3, and indicates that MnO_x-CeO_2/TiO_2 is of granular structure. Moreover, the specific surface area of MnO_x-CeO_2/TiO_2 is $42.1 \text{ m}^2/\text{g}$. The specific surface area of MnO_x-CeO_2/TiO_2 is lower than that of pure TiO_2 described in previous studies. This could be attributed to the blocking of TiO_2 support micropores by deposited CeO_2 .

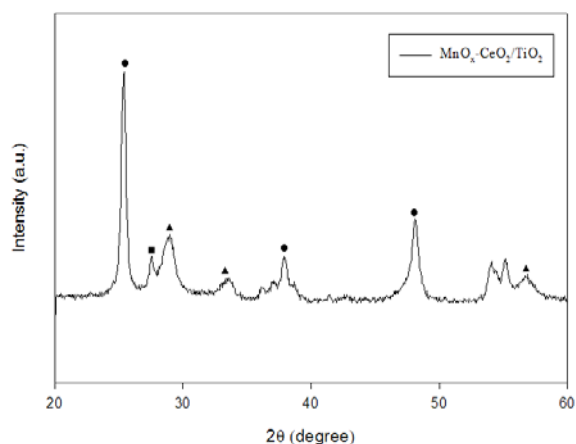


Fig. 2 X-ray diffraction pattern of MnO_x-CeO_2/TiO_2 calcined in air at 500°C (■: TiO_2 rutile, ▲: CeO_2 , ●: TiO_2 anatase)

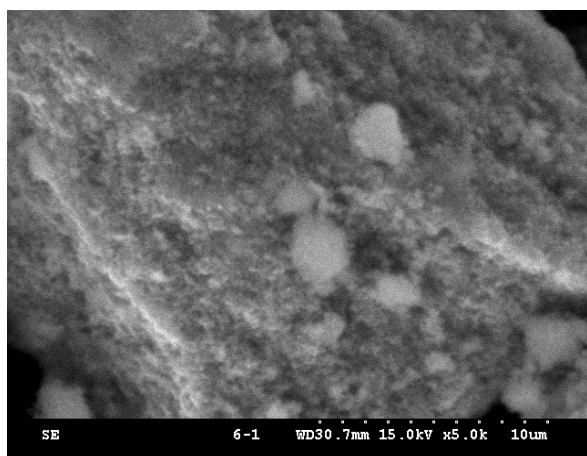


Fig. 3 SEM photographs of MnO_x-CeO_2/TiO_2 .

4. FURTHER GUIDELINES

3.2 Effect of input voltage on NO conversion efficiency with DBD-alone

Fig. 4 shows the NO conversion efficiency and NO/NO_2 ratio with DBD-alone at various input voltages. The results indicate that NO conversion efficiencies increase with increasing input voltage for both cases of without and with filling glass beads. For the case with glass beads, the NO conversion efficiency increases from 28 to 33%, while NO conversion efficiencies achieved

without glass beads are between 21 to 25% at 12 to 15 kV. It indicates that NO conversion efficiency can be significantly increased by adding glass bead into reactor. This result can be explained by the increase of reduced field (E/N) in the system due to glass beads, because adding glass beads changes the gap of discharge in the reactor. The ratio of NO/NO_2 gradually decreased with increasing input voltage. Total NO_x ($NO+NO_2$) concentration is maintained at 1,000 ppm with various input voltages. Namely, the NO consumed are all converted into NO_2 . Specifically, the ratio of NO/NO_2 achieved with filling glass beads can reach 1.9.

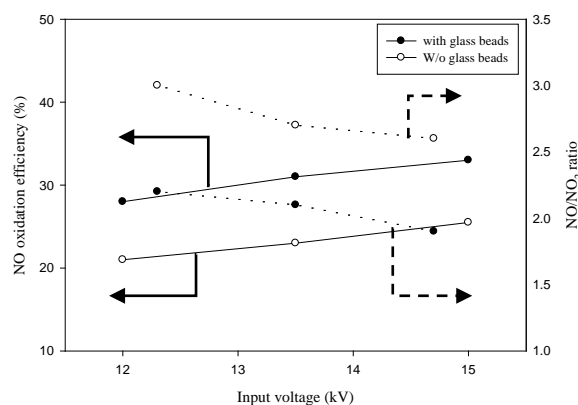


Fig. 4 Conversion efficiency of NO and ratio of NO/NO_2 with NTP-alone at various input voltages ($C_{NO} = 1,000 \text{ ppm}$, total flow rate = 1.2 L/min , frequency = 100 Hz)

3.2 Effect of temperatures on NO conversion efficiency for SCR-alone system and combination of plasma and SCR system

NO removal efficiencies of NO achieved with SCR-alone system and combination of plasma and SCR system at various temperatures (100°C , 150°C and 200°C) are presented in Fig. 5. The results indicate that NO removal efficiencies increase monotonously with increasing temperature for both systems. In the SCR-alone system, NO removal efficiency are 53, 82, 97%, respectively. NO removal efficiency can be increased to 70, 94, 100% by combination of plasma system. Obviously, NO removal efficiency depends on ratio of NO/NO_2 . Previous study [8] indicates that NO removal efficiency can be significantly increased as the ratio of NO/NO_2 is close to 1, as shown in Reaction (1). On the other hand, few NO_2 is produced in SCR system, but this situation can be excluded in combined plasma SCR system.

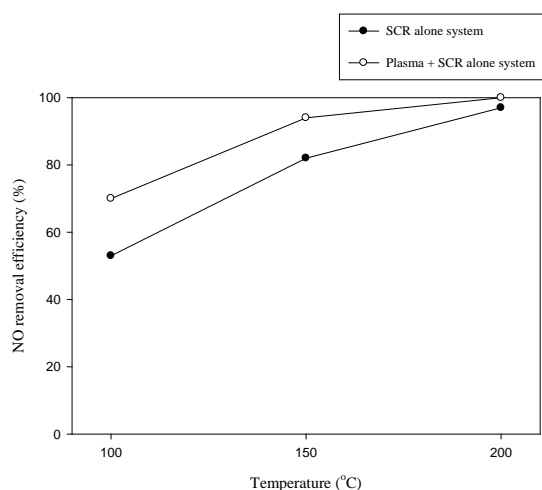


Fig. 5 Removal efficiency of NO for SCR alone system and combination of plasma and SCR system at various temperature ($C_{NO} = 1,000$ ppm $C_{NH_3} = 1,000$ ppm, total flow rate = 2 L/min)

4. CONCLUSIONS

This work demonstrates, respectively, that MnO_x-CeO_2/TiO_2 has excellent performance for NO reduction, and its removal efficiency for NO can reach 97% at 200°C. Furthermore, the ratio of NO/NO₂ can be significantly decreased by passing through the reactor filling with glass beads for NTP-alone system.

For combination of plasma and SCR system, NO removal efficiencies achieved are significantly higher than that of SCR-alone system. NO removal efficiencies are in the range of 70-100% at 100-200°C. Indeed, a strong correlation was observed between the removal efficiencies of NO and ratio of NO/NO₂. Overall, the combination of plasma and SCR process is eco-friendly, and cost-effective.

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