Dielectric barrier discharge plasma-assisted catalytic reduction of NOx over Mn-Cu catalyst

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Abstract. Manganese-copper bimetal oxide catalysts supported on ZSM5 were produced by incipient wetness impregnation for selective catalytic reduction of NO with dielectric barrier discharge plasma. The significant enhanced activity of catalysts was exhibited with the increasing calcination temperature from 350°C to 550°C, especially in the higher discharge power. NO removal efficiency reached 95% with the manganese-copper bimetal oxide catalyst of 550°C at 18W. The catalysts samples were characterized by XRD and BET. This results show that the Cu-Mn/ZSM-5 catalyst possesses more NO reduction activity with the adding calcination temperature.

Introduction

Emissions of Nitrogen oxides (NO_x) from large quantities fuel combustion in power plants and cars have been one of the major problems that lead to the formation of acid rain and the precursor of ground level ozone. In the field of NO_x pollutants controlling, selective catalytic reduction (SCR) processes have been well used in power plant. However, problems like huge investment cost, high activation temperature of catalyst limit the applications of SCR. Recently, dielectric barrier discharge (DBD) combined with catalyst has been utilized for treatment of nitrogen oxides, Co-OMS-2 calcined at 300°C [1], Ce-Ti at 500°C [2], $SG/\gamma-Al_2O_3$ at 550°C [3] result in high NO removal efficiency. Herein, temperature is a mainly factor in nitrogen oxides removal. The experiment was carried out at different catalyst calcination temperature, investigating the discharge characteristics and NO removal.

Experimental

Experimental Setup

The schematic layout of the Mn-Cu/ZSM5 catalyst with plasma is presented in Fig.1. There are 500 ppm NH_3, 500 ppm (parts per million) NO as the feeding gas composition and 6% O_2, and N_2 as the carrier gas. The overall flow rate is 2 L/min and gas hourly space velocity of 30000 h^{-1} in the dielectric barrier discharge reactor, separately.

To maintain the designated gas temperature, we put the NO removal reactor into the furnace, the reactor contain two glass tubes with a height of 850 mm to form the dielectric barrier wall. The outer tube which cover with copper wire mesh had a diameter of 20 mm and a thicknesses of 1.5 mm. The inner tube had a diameter of 5 mm and a thicknesses of 1 mm.

Catalyst preparation

In the typical synthesis of Mn-Cu catalyst, incipient wetness impregnation of ZSM5 was used. In this step, $CuSO_4 \cdot 3H_2O$ solutions was added to $Mn(NO_3)_2$ solutions, then put the mixed solutions through ultrasonic treatment for 2 h, the mixture was dried at 110°C for 24h. The catalysts was calcined at 350°C, 450°C and 550°C for 4 h, which owned the same Cu and Mn lodings : 12 wt.% Cu and 16 wt.% Mn.

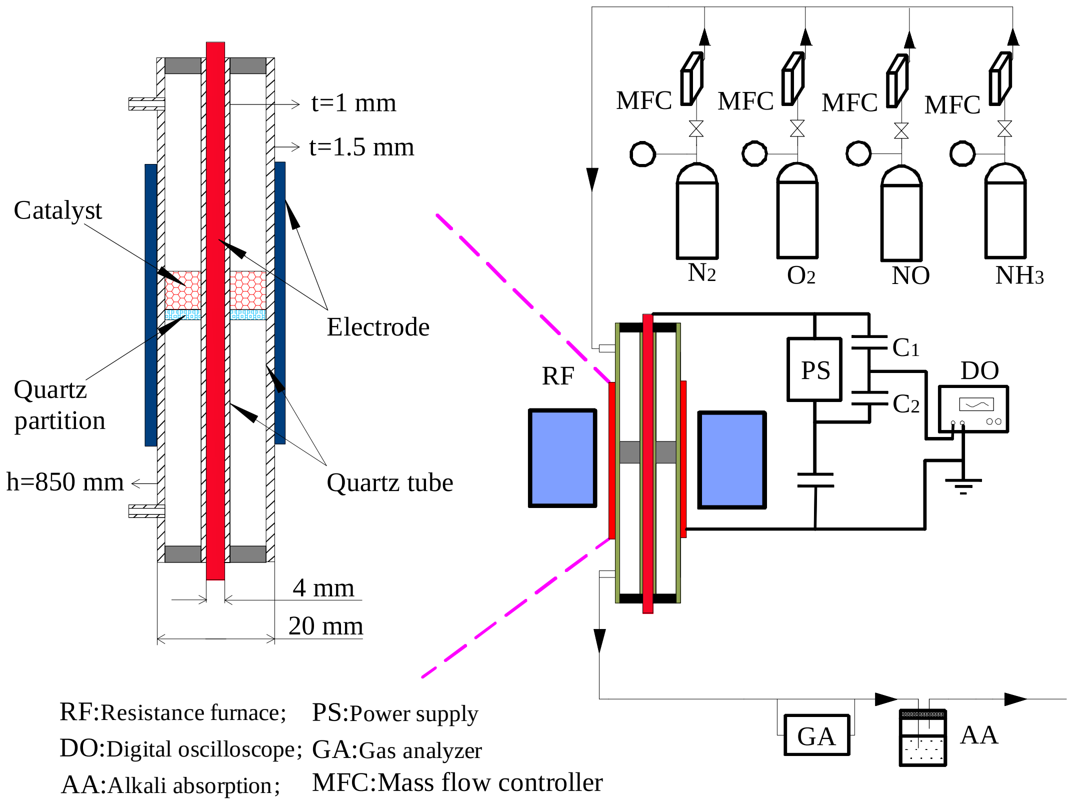

Fig. 1 Schematic of the DBD plasma experiment.

Result and Discussion

NO removal by DBD combined with catalyst

To examine the effects of temperature on NO removal, we adjusting the calcination temperature of catalyst at 350°C, 450°C, 550°C which is shown in Fig.2. For plasma without catalyst, a maximum NO conversion of approximately 50% was achieved at 18W. Whereas NO removal efficiency reached 95% with the manganese-copper bimetal oxide catalyst of 550°C at 18W, the result shows that the increased temperature has a evidently positive effect on NO removal efficiency.

Moreover, the augment of plasma discharge power also promotes the NO removal efficiency. However, it exhibited little change in NO removal activities when the discharge is over 10W. In the dielectric barrier discharge reactor, The major pathway for NO removal are: [4,5]:

$$O_3 + NO \rightarrow NO_2 + O_2 \quad (1)$$

$$O + NO \rightarrow NO_2 \quad (2)$$

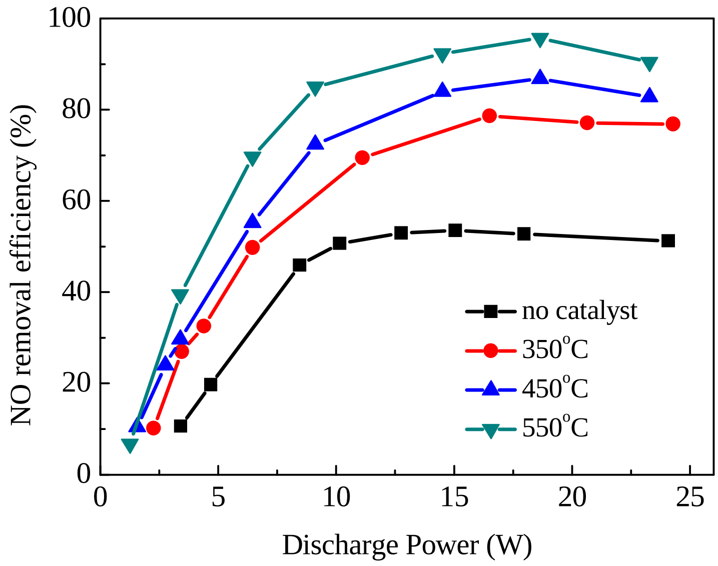

Fig.2 Effect of temperature and discharge power on NO removal efficiency

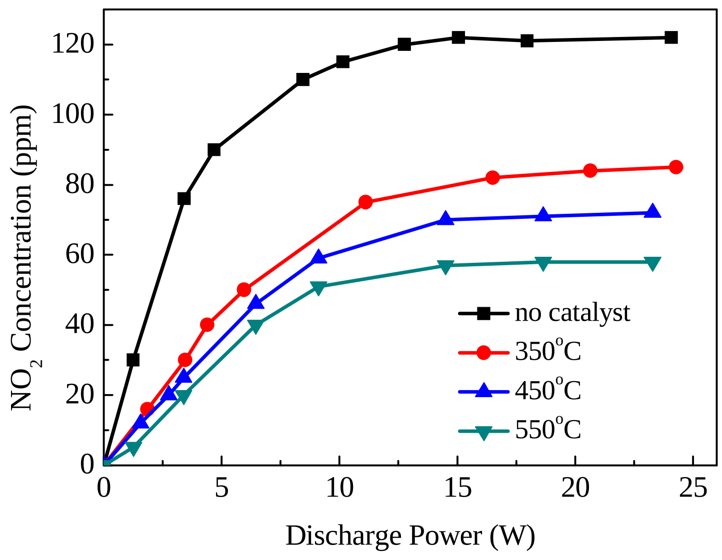

Fig.3 Effects of temperature on NO_2 concentration

The Fig. 3 has shown that the concentration of NO_2 is around 120 ppm with plasma alone but decreases to 58 ppm with Mn-Cu/ZSM5 and temperature of 550°C. Thus, Mn-Cu/ZSM5 evidently has a vital role in improving NO reduction. NO_2 conversion efficiency was dramatic enhanced with the increasing temperature of catalyst. In this system, the catalytic reaction of NO removal with catalyst is [6,7]:

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \quad (3)$$

$$4NH_3 + 2NO + 2NO_2 \rightarrow 4N_2 + 6H_2O \quad (4)$$

When the temperature is under 200°C, the fast SCR reaction (4) owns the leading role. With the existence of catalyst, NO_2 is the key factors which reacts with NH_3 and NO through (4) and can be decomposed through reactions (5) and (6) [8,9]:

$$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O \quad (5)$$

$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O \quad (6)$$

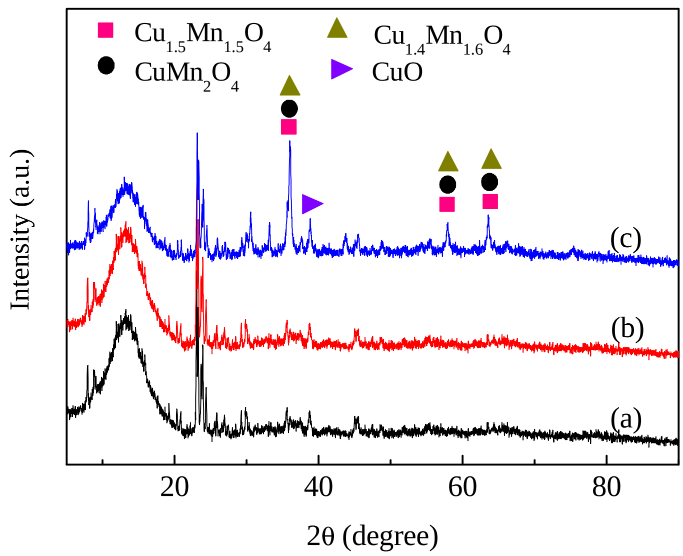

Fig.4 The XRD patterns of Mn-Cu/ZSM5 catalyst samples: (a) catalyst at 350°C; (b) catalyst at 450°C; (c) catalyst at 550°C

The effect of NO removal will be influenced by calcination temperature, XRD patterns for Mn-Cu/ZSM5 catalyst samples calcined at 350°C, 450°C and 550°C are shown in Fig.4. The peak located at 38.8º is the diffraction peak of CuO. Mn-Cu/ZSM5 catalyst exhibited the typical peaks corresponding to ZSM-5. The peak located at 36.0 º, 57.9º and 63.6º is the diffraction peak of $Cu_{1.5}Mn_{1.5}O_4$, The peak located at 36.0 º, 57.8º and 63.5º is the diffraction peak of $CuMn_2O_4$, The peak located at 36.0 º, 57.7º and 63.4º is the diffraction peak of $Cu_{1.4}Mn_{1.6}O_4$. Those manganese-copper bimetal oxides appeared when the calcination temperature increases to 550°C, which can obviously strengthen the activity of catalyst. Thus, the activity of Mn-Cu/ZSM5 catalyst is significantly enhanced with the temperature increase from 350°C to 550°C.

Table. 1 Surface properties of catalyst

Sample	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
350 °C	228.8	0.125	2.2
450 °C	227.1	0.122	2.1
550 °C	209.1	0.108	2.1

Table.1 shown that there is no significant change in the pore volume and pore diameter of Mn-Cu/ZSM5 catalyst samples with the temperature from 350°C to 550°C. Meanwhile, the BET surface area is reducing with the increasing temperature of catalyst samples. However, BET surface area is not the mainly factor in NO removal [10].

Conclusion

Manganese-copper oxide catalysts supported on ZSM5 combined with dielectric barrier discharge (DBD) reactor for NO removal is calcined at 350°C, 450°C and 550°C. The result of this experiment exhibited that Cu-Mn/ZSM5 catalysts calcined at 550°C owned best catalytic activity, the increased temperature of catalysts has an evidently positive effect on NO removal efficiency.

The dielectric barrier discharge technique combined with Mn-Cu catalysts was used to enhance the catalytic activity in SCR reaction, which can promote a new method in SCR study work. On this basis, the paper mainly investigated the influence of different calcined temperature on catalysts activity, which can improve the efficiency of SCR reaction.

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