Plasma Assisted NO_x Removal Using Modified Attapulgite Clay Catalyst

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Abstract: A Modified Attapulgite Clay (MAC) catalyst for plasma assisted NO_x removal is presented in this paper. The effect of plasma discharge voltage and the MAC calcination temperature on NO_x removal ratio was investigated. The micro-structure of the Clay at different calcination temperatures was analyzed by SEM. The experimental results show that NO_x removal ratio increases with input voltage and the calcination temperature has a significant influence on MAC catalyst performance. When the calcination was in the range of 400℃ to 600℃ the MAC has a good adsorbance and storage for NO_x even at room temperature. In oxidation process NO was oxidized to NO_2 and furthermore to NO_3^-. When the input voltage >30kV the highest NO_x removal ratio can reach 89.6%.

1. Introduction

One of most effective methods to remove NO_x from diesel exhaust gas is the use of plasma combined catalyst [1-3]. The plasma can generate electrons, ions, reactive radicals and many kinds of excited particles to improve the chemical reaction rate. When the catalyst can adsorb and store NO_x significantly, the starting reaction energy decreases. In this paper a Modified Attapulgite Clay (MAC) was used as catalyst, and the effect of plasma discharge voltage and Attapulgite Clay(APC) calcination temperature on NO_x removal was investigated.

The APC, also called palygorskite $[Mg_5Si_8O_{20}(OH)_2(OH_2)_4 \cdot 4H_2O]$, is a chain-layer configuration of magnesium-aluminum silicate clay mineral. The microstructure of the ATP with bound water has special fibrous crystals. Due to numerous micro-pores, the surface area is large, usually in the range of 125 ～ 210m^2/g [4]. Therefore, the APC has good adsorbance and storage capacity and can support other metal elements such as rare earth bind on its surface. In our experiment Ce was added to APC. By calcination, MAC loses some of the bound water enhancing its activity and selectivity.

Dielectric Barrier Discharge (DBD) is an efficient way to generate non-thermal plasma [5, 6]. In our experiment MAC was packed into the DBD reactor and used both catalyst and dielectric. A plasma assisted catalyst system can have synergetic effects on NOx removal [7-12].

2. Experimental materials and methods

2.1 Catalyst preparation

The APC powder (300 meshs, industrial grade, Anhui Mingguang Xiqi Mine Company, China,) was dried at 105℃ for 24h. 50g of the resulting powder was dissolved in 100ml de-ionized water inside a beaker bathed at 80℃ and continuously homogenized. 50ml of $Ce(NO_3)_3$ (AR grade) solution, concentration 0.2mol·L^{-1} , and aqueous ammonia, concentration 0.2mol·L^{-1} , were simultaneously fed into the APC solution. The mixture was stirred for 1h with ultrasonic waves. The pH value was maintained in the range of 6~7 [13]. The solution was placed for 24h to completely deposit and age. To separate the solid a filter was used. The filter cake was washed with de-ionized water four times until the pH value of filtrate was 7.

Subsequently, the filter cake was dried, passed through a 300 mesh sieve and blended with adhesives. Pellets were molded at ambient temperature and heated at 200℃ for 24h to fast the shape. Calcination was performed in order to activate the pellet in a Muffle Furnace

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(TOH-SHOKUNIN 0-1300℃) for 3h. Six pellet samples were prepared at different calcination temperature: 300, 400, 500, 600, 700, and 800 ℃, respectively.

2.2 Experimental Method

The rod-to-cylinder type of DBD reactor packed with catalyst was made of Pyrex tube (24mm inner diameter, 2mm wall thickness and 120mm length). An aluminum foil (0.6mm thickness and 50mm length) was wrapped on the outside surface of the tube and was used as ground electrode. A centered stainless steel rod (9mm outside diameter) was used as high voltage electrode. 25g of catalyst pellets (average diameter 3mm) was packed in the annular space between the two electrodes. The ends of the reactor were tucked with silicon rubber. The reactor structure is shown in Fig.1.

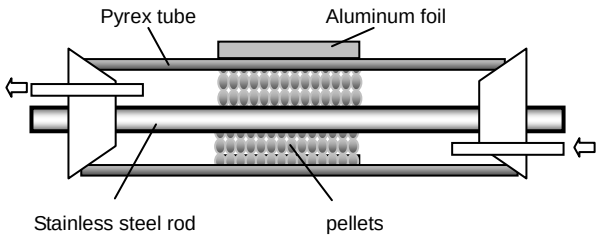


Fig.1 reactor structure

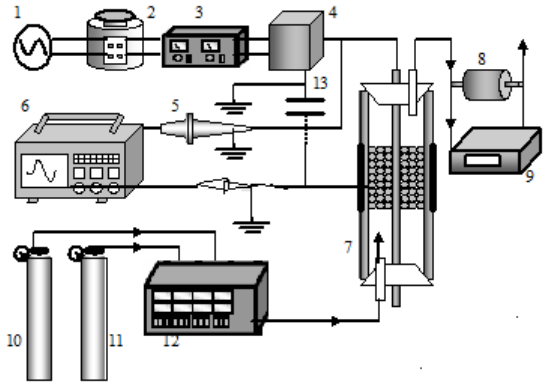


Fig.2 Sketch of Experimental setup

1. Power Supply; 2. Variable Auto-transformer; 3. Power Meter; 4. 100V:15kV, H. V. Power Amplifier; 5. 1000:1 H.V. Probe ; 6. Oscilloscope; 7. DBD packed catalyst reactor; 8. NO_x Sensor; 9. Horiba NOx meter, 10. Air Cylinder; 11. NO/N_2 Cylinder. 12. MFC; 13. Capacitor.

The experimental setup is presenced in Fig.2. The input power feeding to the setup was adjusted by an Variable Auto-Transformer (Type V-130-5, Volt-Slider. 61-18138. input 100V, output 0-130V, Max 5A, 0.5kVA, 50/60Hz) fed from AC power source (100V, 60Hz). The input power was measured with a digital power meter (HIOKI 3186, Hitester). An A.C. high voltage Power Amplify Transformer (LECIP 100V/60Hz, 15Kv/60Hz) was capable of delivering 0-60kV peak-to-peak voltage (V_{pp}) at 60Hz. The net output AC HV applied to the reactor was measured by a 1000:1 high-voltage probe (Tektronix P6015A 1000×3.0Pf, 100MΩ), and displayed on a four channel digital storage Oscilloscope (Tektronix TDS2014, 100MHz 1Gs/s). The Lissajous figures method was used to determine the plasma discharge power [14]. 10×10^5pF electric capacitor (IH104K R G) was used in the method. The plasma reactor was placed at ambient temperature.

A simulating gas was prepared from cylinder air and NO/N_2 (NO concentration 1990ppm and N_2 balance) using digital MFC (Model: 3660A, KOFLOC Co.). The NO_x concentration in the inlet gas was set at 200ppm and flow rate at $4.0l\cdot min^{-1}$. Corresponding space-velocity of $11000h^{-1}$ was used. The individual NO and NO_x concentrations in the outflow gas were on-line determined with Horiba (portable gas analyzer, PG-225) and a NGK NO_x Sensor (TCNS 6005-C3, NO_x1500ppm), respectively. The conversion of NO or NO_x was defined as follows:

$$NO_x \text{ conversion}(\%)=\frac{NO_{x,in}-NO_{x,out}}{NO_{x,in}}\times100 \quad (1)$$

$$\text{NO conversion }(\%)=\frac{NO_{,in}-NO_{,out}}{NO_{,in}}\times100 \quad (2)$$

Where $NO_{x,in}$, $NO_{,in}$, $NO_{x,out}$ and $NO_{,out}$ stands for NO_x and NO stable concentration in the inlet and outlet gas after 20min, respectively.

The microstructure of catalyst was analyzed by SEM (KYKY-EM3200).

3. Results and discussion

3.1 The effect of input voltage on NO and NO_x removal ratios

Fig.3 shows the co-relation between NO_x (and NO) removal ratio and voltage.

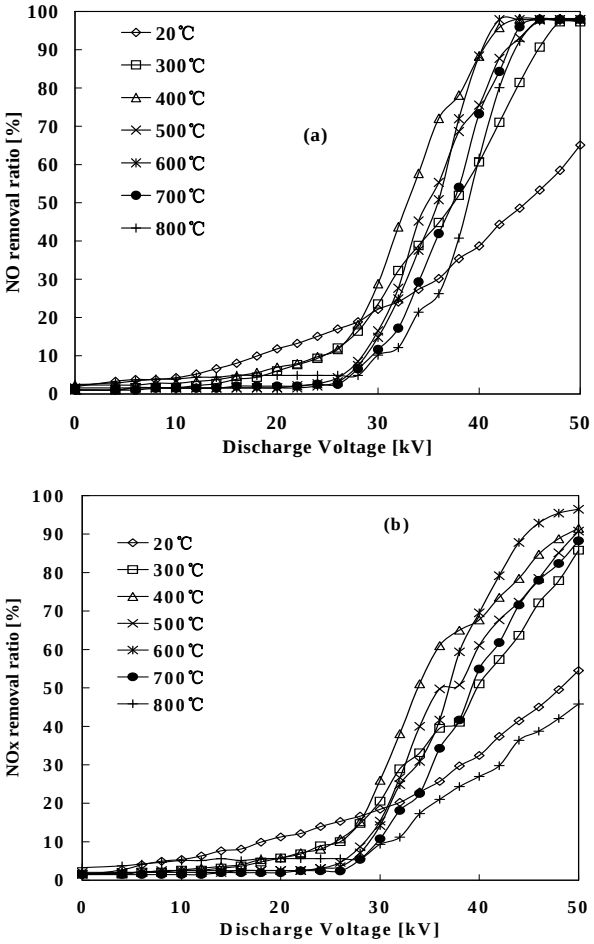


Fig.3 NO(a) and NO_x(b) removal ratio versus discharge voltage

Fig.3 indicates that NO(a) and NO_x (b) removal ratio increases with the increase of plasma discharge voltage. When the voltage is higher then 30kV the removal ratio is significantly increased. The increase of applied voltage leads to higher plasma discharge power density (defined as the electric discharge power divided by the inlet gas flow rate). With the increase of discharge energy density, this will in turn elevate oxygen atom (O) concentration. An elevated active oxygen atom concentration will improve the NOx removal ratio. When the voltage is 42kV the maximum NO removal ratio (98%) was obtained. The result demonstrates the MAC catalyst combined with plasma produce a good NO to NO_2 oxidation. The chemical reaction is following:

$$NO+O \rightarrow NO_2 \qquad (3)$$

In the same point the maximum NO_x removal ratio is 89.6%.

2g of used catalyst pellet, originally calcinated at 500℃ and used at 42kV input voltage for 40min, was immersed into 20ml de-ionized water for 24h. In the leaching solution the pH value was 6.2 (measured with pH sensor) and the concentration of NO_3^- ion s was 3.2mg·l^{-1} detected with Nitrate Ion Detector (761 Compact 1C Ω Metrohm). Therefore, the MAC has both the capability to adsorb and store NO_2, and to further oxidize it to NO_3^- . The chemical reaction is following:

$$NO_2+O \rightarrow NO_3^- \qquad (4)$$

3.2 Effect of MAC calcination temperature on NO and NO_x removal ratios

Fig.4 shows the calcination temperature of the ATC has significant effect on NO and NO_x removal ratios. If the temperature is smaller than 400℃, the effect on removal ratio is low. If the calcination temperature is in the range of 400℃to 600℃ the removal ratio is the highest. For calcinations temperatures higher than 600℃ the NOx removal ratio edges lower. Therefore the optimum calcination temperature range is 400℃ to 600℃.

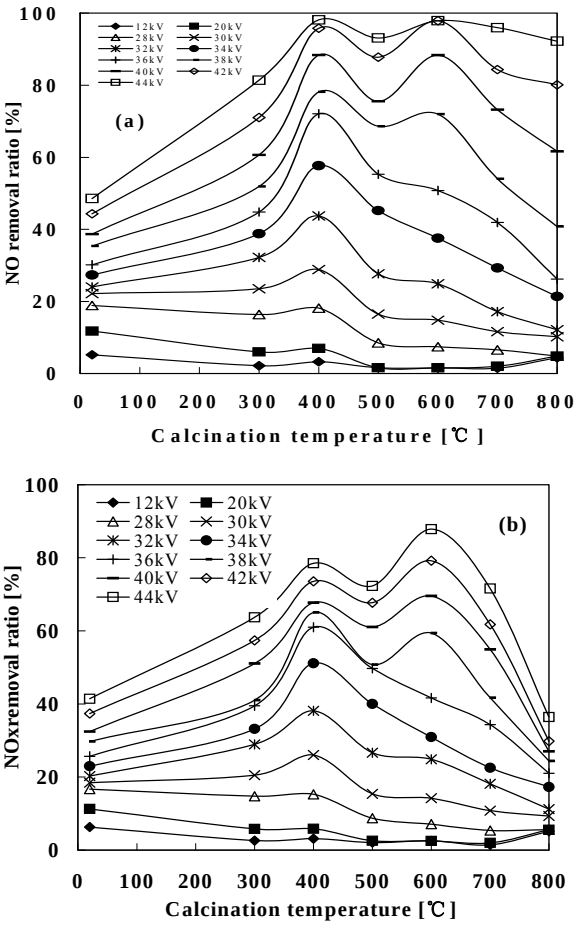
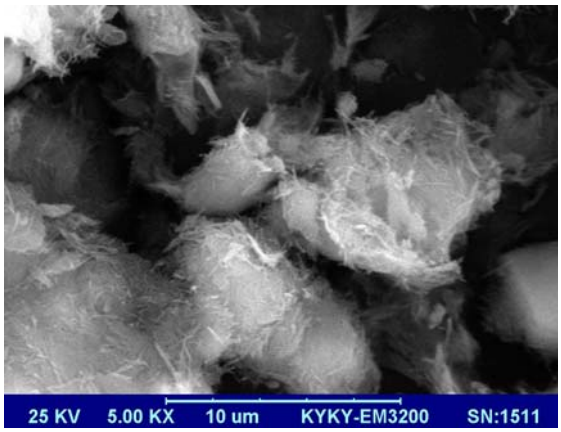
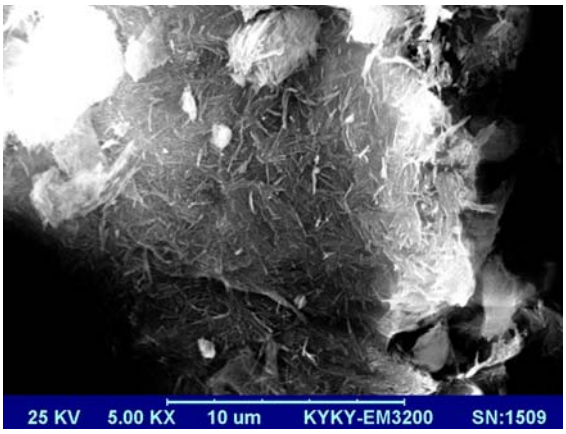


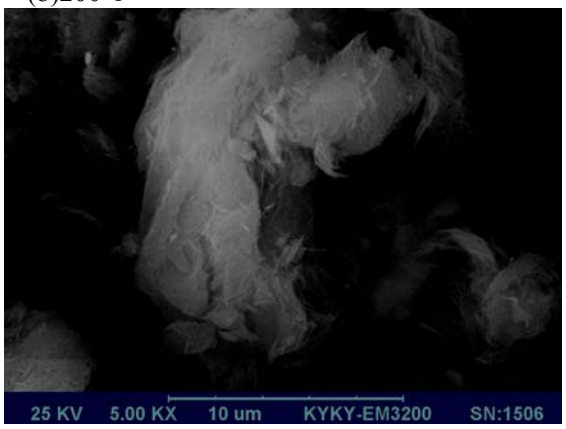
Fig. 4 The co-relation between MAC calcination temperature and （a）NO and (b)NO_x removal ratios for various discharge voltage



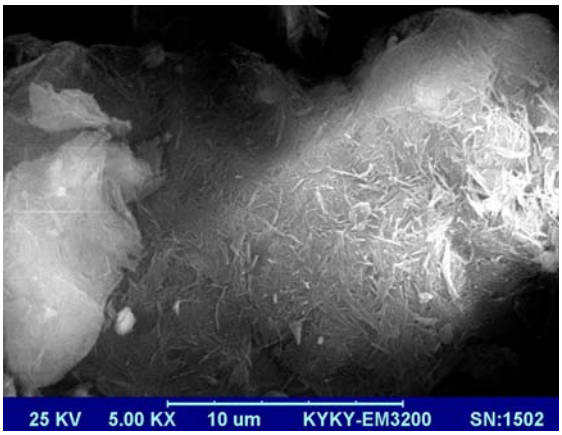
(a) ambient temperature



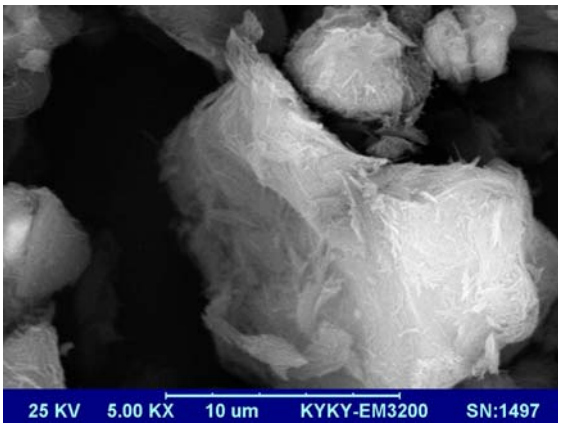
(b)200℃



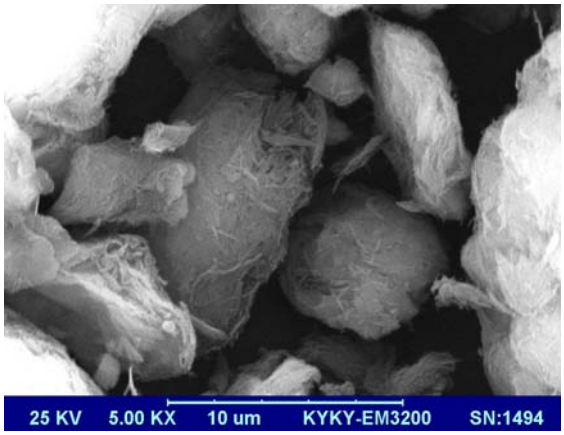
(c)300℃



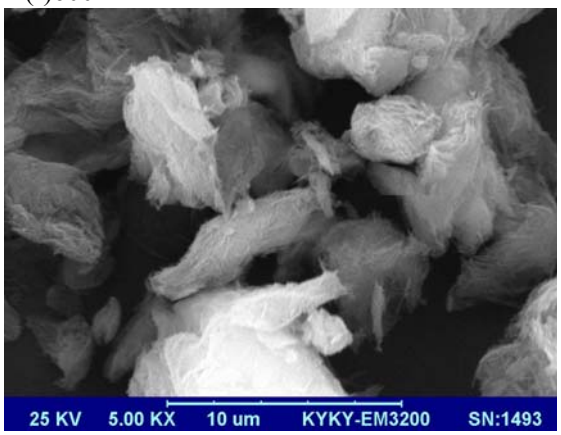
(d)400℃



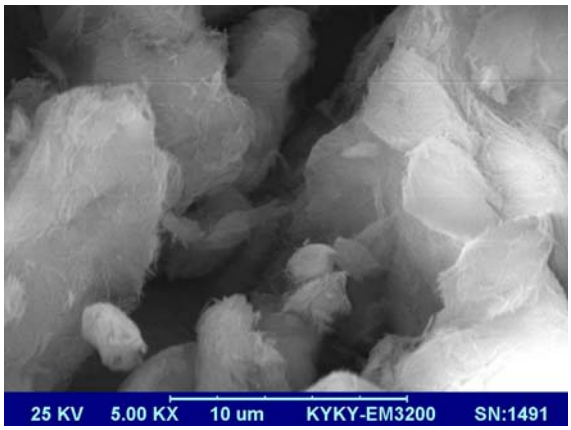
(e)500℃



(f)600℃



(g)700℃



(h)800℃

Fig.5 SEM capture of MAC structure for various calcination temperatures

The removal ratio is higher for NO compared with NOx since the chemical reaction rate of NO oxidation to NO_2 is controlled by the oxygen atom concentration produced by plasma, while the removal rate of NO_x is determined by NO_2oxidation to NO_3^- which is restricted by chemical reaction kinetics.

3.3 SEM analysis

Fig.5 shows the micro-structure of MAC at different calcination temperatures.

According to crystallography theory, there are three kinds of activated adsorption centers in the ATC crystal surface: the oxygen atom in the silicon-oxygen tetrahedron surface, the H_2O molecule on the ATC crystal edge, and the ion cluster of Si-OH. The great number of defects located on the ATC surface gives a high surface activity.

In the optimum calcination range, Fig.5 d, e and f (between 400℃ and 600℃), the shape of fibrous crystal presents cluster of fine rod-like fibers or a single fiber with the diameter of 25nm, and the length of 1μm. In this case some of the bound water in ATC is lost leaving more empty spaces. The defect density defined as the number per unit area of the ATC surface is increased. The performance of MAC activation is furthermore improved.

When the calcination temperature is over 600℃ (Fig.5 g and h), the micro-structure of the crystal shrinks is sintered and melts, thus reducing the density of activated points. Under 400℃ (Fig.5 a, b and c) the micro-structure of MAC is raw and loose fibers are not sufficiently activated.

4. Conclusions

A plasma assisted catalyst system using modified attapulgite clay can effectively remove NO_x even at room temperature. NO_x removal ratio increases with plasma discharge voltage. The calcination temperature has a significant influence on MAC performances. The modified attapulgite clay will have good NO_x absorbance and storage when the calcination is in the 400□ to 600℃ range. NO is oxidized to NO_2 and furthermore to NO_3^-. If the input voltage is higher then 30kV NO_x removal ratio can reach 89.6%.

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