NO removal by nonthermal plasma with modified sepiolite catalyst

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Abstract. Non-Thermal Plasma (NTP) combined with a catalyst is one of the effective ways to remove NO from auto exhaust gas. Sepiolite Ore Powder (SOP), which was modified by acid washing, copper nitrate soaking, drying and calcinations, served as the Modified Sepiolite Catalyst (MSC) for NO removal in a rod-cylinder Dielectric Barrier Discharge (DBD) reactor. The characteristic of the MSC was characterized by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). The experiment showed that the acid concentration, washing time, the packed site of MSC and input voltage of the NTP impacted the NO removal rate effectively. The NO removal rate increased and then decreased with an increase in the acid concentration and the washing time, and the NO removal rate increased monotonously with the increased input voltage. The NO removal rate was higher at the beginning, decreased gradually then maintained stability after 10 min. Thus, the result indicated that MSC has a good ability for adsorption and storage of NO.

1. Introduction
Non-Thermal Plasma (NTP) is an effective way to produce a large amount of free electrons, ions, active free radicals and various excited free particles, which have high active energy to improve the speed of chemical reaction. Dielectric Barrier Discharge (DBD) is one of the methods to generate NTP. The structures of DBD reactor are usually line-tube, line-plate, and plate-plate [1-3]. It has been researched that the DBD combined with catalyst can remove NOx from the exhaust gas [4, 5], but the step of oxidizing reaction from NO to NO2 is very difficult and slow [6]. The concentration of NOx in auto exhaust is common (200-300)×10^-6. In order to remove NOx effectively, the catalyst not only has a good adsorption and storage capability, but also has a good activity and high selectivity [7, 8]. The catalyst of γ-Al2O3, TiO2 and molecular sieve as a carrier have been widely researched, however, these kinds of

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catalyst are not only expensive but also easy to lose its activity when at higher temperature [9, 10].

Sepiolite Ore Powder (SOP) is a one kind of natural clay which contains the element of magnesium and silicate. Its micro structure is a large number of fiber-like gathered together to form irregular network, so it has a large of specific surface area and good capability of adsorption [11-13]. The SOP has a good thermal stability and low price [14-16]. The SOP had been modified by acid washing, copper nitrate soaking, drying and calcination to prepare Modified Sepiolite Catalyst (MSC) to instead of traditional catalyst in this paper. The characteristic of the MSC was detected by XRD and SEM. The plasma-catalysis process for NO removal took place in rod-cylinder DBD reactor in this study [17].

2. Experiment

2.1. Catalyst preparation

2.1.1 Reagents and experimental equipments

Reagents: SOP (Henan LeiBao Sepiolite Ore Company, 280 mesh, industrial grade); Nitric acid (the AR), Copper Nitrate, Air Cylinder, NO/N2 Cylinder (the content of NO 2011×10^{-6}, the balance is N2).

Main equipments: Automobile exhaust analyzer (Guangdong Fushan analysis instrument factory, FGA-4100; NO measurement range:0~4000×10^{-6}; Constant Temperature Oven (Model DHG-9240); Scanning Electron Microscope (SEM, SHIMADZU, KYKY-EM3200), X-ray Diffraction (XRD, XD-3 type crystal X-ray powder diffraction was produced by Beijing General Company); Muffle Furnace, Gas Mass Flow-meter, Transformer; Power Meter; High Voltage Power Supply (JNB-208B); High-voltage Probe; Digital Oscilloscope.

Rod-cylinder DBD reactor: The reactor is made of Borosilicate Pyrex Glass Tube of inner diameter 27 mm, wall thickness 2 mm and length 120 mm. The tube outer wall was pasted aluminum film of 60 mm length and 0.6 mm thick, served as cathode; the aluminum rod with diameter of 8 mm arranged in the center of the tube as anode. The MSC was loaded inside the tube; both end of the reactor was sealed by silicone rubber plug [18]

2.1.2. Catalyst preparation

Purification of SOP: 200 g SOP was mixed with 120 mL distilled water and stirred for 10 min. After a stillness moment, the SOP was deposited from the suspension and washed for four times with distilled water in the same way. The suspension was filtrated by vacuum filter, and then, the filter cake was dried in the oven at 105 °C and grinded and washed by nitric acid for 24 h, 48 h, and 72 h, respectively. The ratio of the SOP quality to the nitric acid volume is 1:10 (g mL^{-1}). The acidified SOP was washed for four times with de-ionized water and filtered. The filter cake was dried in Muffle Furnace at temperature of 120 °C for 4 h, then, grinded after natural cooling.

Modification and Activation of SOP: Every sample of acidic and original SOP 50 g was immersed in Cu (NO3)2 solution for 24 h at room temperature (ensuring the CuO content of 8%), evaporated and dried at 60 °C in water bath and grinded to 240 mesh, and then the SOP was dried at the room temperature for 24 h and calcined in the Muffle Furnace at 500 °C for 5 h, respectively.

2.2. Experimental methods

The 30 g MSC was loaded into the same fixed bed reactor with NTP. The reactor was installed in a thermo-tank at the 180 °C. The simulation gas of the NO concentration 297×10^{-6} (297 ppm) went into the reactor from the bottom side. The gas flow was kept at 7.0 L min^{-1}, the input voltage (V_{p-p} peak-peak) and the frequency were fixed at 35 kV and 50 Hz, respectively. The NO removal rate =100×(inlet NO concentration-outlet NO concentration) /inlet NO concentration. The schematic experimental process
was shown in figure 1.

Figure 1. Schematic experimental process
1 Power, 2 Transformer, 3 Power meter, 4 High voltage power generator, 5 High-voltage probe, 6 Digital oscilloscope, 7 Non-thermal plasma catalytic reactor, 8 NO concentration online detector, 9 Air cylinder, 10 NO gas cylinders, 11 Gas quality controller, 12 thermo-tank, 13 capacity

Figure 2. XRD of the SOP and the MSC.

a. the original Ore; b. without acid washing, only soaking copper nitrate for 24 h and calcination for 5 h at 500 °C; c. with HNO₃ of concentration 1.0 mol L⁻¹ washing for 2 d and soaking copper nitrate for 24 h, calcination for 5 h at 500 °C; d. with HNO₃ of concentration 1.5 mol L⁻¹ washing for 2 d and soaking copper nitrate for 24 h, calcination for 5 h at 500 °C; e. with HNO₃ of concentration 3.0 mol L⁻¹ washing for 3 d and soaking copper nitrate for 24 h, calcination for 5 h at 500 °C

3. Results and discussions

3.1. Catalyst characterization

3.1.1 XRD analysis

Results of X-ray diffractometry for the SOP and the MSC are shown in figure 2. Diffraction conditions are target of Cu, tube voltage of 36 kV, tube current of 40 mA.

Figure 2 shows that the SOP contains a large amount of Si, Mg, Al and other elements, which exist in the different compounds. The peak values of 35.7° (2θ) and 39.1° (2θ) are corresponding of CuO, after soaking and calcination, a new material of CuO is formed on the surface of MSC, the Sepiolite keeps its basic structure. Compared with c, d, e, it shows that 2 day is the optimization acid washing time.
3.1.2. SEM analysis

The microstructure of the MSC is more improved than the SOP from the figure 3. The cross section and the number of micro-pore have been enlarged in the MSC surface, so the MSC has a good ability of adsorption and is benefit to carry the active component of CuO. Meanwhile, the acid washing can remove impurities from the SOP surface effectively. With the electronic probe, the active component of CuO has been detected in many bright points and distributed evenly in the SOP surface from the SEM in figure 3.

![Figure 3. SEM photos.](image)

- a. the original Ore; b. without acid washing, only soaking copper nitrate for 24 h and calcination for 5 h at 500 °C; c. with HNO₃ of concentration 1.0 mol L⁻¹ washing for 2 d and soaking copper nitrate for 24 h, calcination for 5 h at 500 °C; d. with HNO₃ of concentration 1.5 mol L⁻¹ washing for 2 d and soaking copper nitrate for 24 h, calcination for 5 h at 500 °C; e. with HNO₃ of concentration 3.0 mol L⁻¹ washing for 3 d and soaking copper nitrate for 24 h, calcination for 5 h at 500 °C

3.2. Effect of nitric acid concentration on NO removal rate

The concentrations of nitric acid solution are 1.0, 1.5 and 2.0 mol L⁻¹, respectively, the SOP is soaked for 2 days, the weight ratio of acid to SOP is 1:10 and to prepare the MSC. The relationship between nitric acid concentration and NO removal rate is shown in figure 4.

When the HNO₃ concentration is above 1.5 mol L⁻¹, the NO removal rate reaches the maximum value stably. When the SOP has no processes of acid washing, only soaking and calcination, the NO removal rate is lower than others condition. Firstly, it is because that micro-pore (<1.5 nm) and part of medium-pore (1.5-5.0 nm) on the surface of SOP is developed and enlarged by acid washing. Next, magnesium is removed from the SOP surface by acid washing and leave behind many pores.

When the HNO₃ concentration is smaller than the optimum value (1.5 mol L⁻¹), some of magnesium are apart from the SOP and reproduced many new micro-pores which connected each other forms many pore-nets in the SOP surface. The new micro-pore and pore-net is benefit to improve the capability of adsorption and the activity of the MSC. With the acid concentration increasing, the surface area of SOP is been increased.
When the HNO<sub>3</sub> concentration is bigger than the optimum value (1.5 mol · L<sup>-1</sup>), the most of the micro-pore and the medium pore have been developed and become the big-pore with the diameter bigger than 10 nm. So the surface area of the MSC and the NO removal rate is decreased.

**Figure 4.** The relationship between HNO<sub>3</sub> concentration and NO removal rate. 

a: plasma+ SOP without acid washing, only soaked Cu(NO<sub>3</sub>)<sub>2</sub> for 24 h and calcination for 24 h at 500 °C; b: plasma+ SOP with HNO<sub>3</sub> of concentration 1.0 mol L<sup>-1</sup> washing for 2 d and soaked Cu(NO<sub>3</sub>)<sub>2</sub> for 24 h and calcination; c: plasma+ SOP with HNO<sub>3</sub> of concentration 1.5 mol L<sup>-1</sup> washing for 2 d and soaked Cu(NO<sub>3</sub>)<sub>2</sub> for 24 h and calcination; d: plasma+ SOP with HNO<sub>3</sub> of concentration 2.0 mol L<sup>-1</sup> washing for 2 d and soaked Cu(NO<sub>3</sub>)<sub>2</sub> for 24 h and calcination.

3.3. Effect of washing time on the NO removal rate

The concentrations of nitric acid solution 1.5 mol L<sup>-1</sup>, the SOP is soaked for 1 day, 2 days and 3 days, respectively. The weight ratio of acid to SOP was 1:10. The relationship between the acid washing time and NO removal rate is shown in figure 5.

**Figure 5.** The relationship between the washing time and NO removal rate. 

a: plasma+ SOP without acid washing, only soaking Cu(NO<sub>3</sub>)<sub>2</sub> for 24 h and calcination for 5 h at 500 °C; b: plasma+ SOP with HNO<sub>3</sub> of concentration 1.5 mol L<sup>-1</sup> washing for 1 d and soaking Cu(NO<sub>3</sub>)<sub>2</sub> for 24 h and calcination; c: plasma+ SOP with HNO<sub>3</sub> of concentration 1.5 mol L<sup>-1</sup> washing for 2 d and soaking Cu(NO<sub>3</sub>)<sub>2</sub> for 24 h and calcination; d: plasma+ SOP with HNO<sub>3</sub> of concentration 1.5 mol L<sup>-1</sup> washing for 3 d and soaking Cu(NO<sub>3</sub>)<sub>2</sub> for 24 h and calcinations.

When the SOP without acid washing used as catalyst, the NO removal rate is the lowest. When the MSC of washing is for 2 days, the NO removal rate reaches the highest value. The reason is that the acid washing of the SOP is a fast chemical reaction [19]; the magnesium ions are apart easily from the SOP to form the new micro-pore. As the washing time prolong, the ion of H<sup>+</sup> has diffused to the deep channels of micro-pore. When the time is smaller than 2 days, as the effect of diffusing resistance, the
acid concentration decreased gradually in the deep hole, so it is difficult to remove magnesium from the deep channel of the SOP. When the washing time is bigger than 2 days, the impurities which washed away may be adsorbed on the hole well again.

3.4. The relationship between NO removal rate and the MSC packed condition

At the same experimental condition: input voltage is 35 kV, NO initial concentration $297 \times 10^{-6}$, inlet gas volume flow 7 L min$^{-1}$ (space-velocity 10.2 s$^{-1}$). The MSC packed condition is: (a) only used plasma, without any stuff, (b) plasma combined with the SOP, (c) plasma combined with the MSC of without acid washing, only soaking Cu(NO$_3$)$_2$ and calcination, (d) plasma with MSC of washing by HNO$_3$ of concentration 1.5 mol L$^{-1}$ for 1 day and soaking Cu(NO$_3$)$_2$ for 24 h and calcination, (e) without plasma, only used MSC of washing by HNO$_3$ of concentration 1.5 mol L$^{-1}$ for 1 day and soaking Cu(NO$_3$)$_2$ for 24 h and calcination. The relationship is shown in figure 6.

![Figure 6](image_url)

Figure 6. The relationship between NO removal rate and time in different of stuff condition.

- a: only plasma, without any stuff; b: plasma+ packed SOP; c: plasma+ MSC made of without acid washing, only soaking Cu(NO$_3$)$_2$ for 24 h and calcination for 5 h at 500 °C; d: plasma+ MSC made of washing by HNO$_3$ of concentration 1.5 mol L$^{-1}$ for 1 d and soaking Cu(NO$_3$)$_2$ for 24 h and calcination for 5 h at 500 °C; e: MSC made of washing by HNO$_3$ of concentration 1.5 mol L$^{-1}$ for 1 d and soaking Cu(NO$_3$)$_2$ for 24 h and calcination for 5 h at 500 °C.

Figure 6 shows: (1) Either the SOP or the MSC is packed in the NTP reactor, NO removal rate is higher at the beginning and then reduce gradually with time going on, until a plateau is reached after 10 minutes. It attributes that the SOP and the MSC can adsorb and store the NO, when the quantity of adsorption and storage reaches its equilibrium value; the NO removal rate decreases and reaches stability state. (2) After 15 minutes, when the chemical reaction reaches stable situation, the NO removal rate order is: (d) > (e) > (c) > (b) > (a). The information shows that the NTP combined with MSC (washing by HNO$_3$ of 1.5 mol L$^{-1}$, soaking Cu(NO$_3$)$_2$ and calcination) has a good ability to remove NO. (3) The NO removal rate in the condition of the NTP combined with the MSC is bigger than only NTP. This informs that NTP with the MSC is an effect way to remove NO.

4. Conclusions

Relating with the XRD and SEM results, it is found that the Mg and other impurities have been removed effectively from the SOP and the number of the micro-pore and its cross-section area in the MSC surface has been increased by acid washing. The new active CuO has been formed stably and distributed evenly in the MSC surface and micro-pores by the process of acid washing, copper nitrate solution soaking, drying, calcination and activation. The MSC combined with NTP has a good ability to absorb, store and remove NO from exhaust gas. The NO removal rate increases with the increasing of input voltage. The NO removal rate order is: (plasma with MSC made of washing by HNO$_3$ of concentration 1.5 mol L$^{-1}$ and soaking Cu(NO$_3$)$_2$ and calcination) > (MSC made of washing by HNO$_3$ of concentration 1.5 mol L$^{-1}$ for 1 d and soaking Cu(NO$_3$)$_2$ and calcination) > (plasma with MSC made of
without acid washing, only soaking Cu (NO₃)₂ and calcination) > (plasma with SOP) > (only plasma, without any stuff).

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