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# Physicochemical properties of pine-derived bio-chars modified by metal oxides and their performance in the removal of NO

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ABSTRACT

Pine-derived bio-chars have been prepared at different temperatures with and without KOH chemical activation. Three metal oxides ($V_2O_5$, MnO and CuO) were loaded on this chars by incipient-wetness impregnation method respectively. Pine wood pellets were characterized by thermogravimetric, and pine-chars samples were characterized by SEM-EDS, XRD, $N_2$ physisorption and FTIR. Activity test for the selective catalytic reduction of NO with $NH_3$ was also carried out in dry simulated flue gas at fixed temperature 160 °C. The results show that pretreatment with KOH and carbonization at 600 °C seems to be the best method for pine-chars preparation. Active metal oxides are well distributed on the surface of carbon support and are partly reduced by carbon during preparation. The mesopores disappear in V- and Mn-containing samples, and V-addition could decrease the amount of micropores as well. At the fixed temperature 160 °C, the active metal oxides have an order of CuO > $V_2O_5$ >> $MnO_x$ >> Non-modified sample on the NO reduction activity. Pine-chars modified by CuO seems to be the best option in this research.



## 1. Introduction

It is well known that nitrogen oxide ($NO_x$), most emitted from coal-fired power plants and steel plants, will cause a series of threats to the environment since it can cause acid rain, photochemical smog, ozone depletion and greenhouse effect [1,2]. Catalyst is the key part in SCR de-$NO_x$ units and it is usually operated at about 350–410 °C and worked before flue-gas purification equipment. So the catalyst is highly exposed to harsh environment, such as fly ash, $SO_x$, alkali (earth) metals and poisoning heavy metals, which ultimately results in serious catalytic deactivation and lifespan cutting [1–3]. Therefore, it is of great significance if the catalysts could be installed behind flue-gas purification system and worked at low-temperature environment. Under industrial settings, the gas temperature drops to below 200 °C after dust-cleaning apparatus and traditional commercial catalysts are unable to meet catalytic reaction temperatures. Therefore, low-temperature catalysts have received much concern in recent years.

Carbon-based catalysts were considered to be the optimal materials for flue gas purification because of its superior properties and price advantages [4,5]. Carbonaceous materials modified by metal oxides ($MnO_x$ [6–8], CuO [7,9,10], $V_2O_5$ [11,12]), that have mostly been studied, were proved to be excellent for $NO_x$ removal below 200 °C. Gao et al. [13] studied the physicochemical properties of seven metal-doped activated carbons and revealed that V, Ce and Cu showed better activity for NO removal. They found that Cu performed the optimal NO reduction efficiency at 200 °C while Mn showed negative NO reduction. However, almost all of these researches focused on active carbon or carbon nanomaterials as the carbon support and bio-chars rarely attracted researchers' interest. China is a big agricultural country, and it produces hundreds of million tons of biomass raw materials every year. Therefore, biomass materials will in the future have a vast application prospect in the NO removal field because of its ultralow cost and easy preparation.

The main objective of this work is to prepare bio-chars using pine wood pellets at different temperatures with and without KOH activation, impregnate metal oxides into pine-chars and characterize their physicochemical properties and NO reduction. $V_2O_5$, $MnO_x$ and CuO were selected due to their outstanding NO removal ability that have been proved on other carbon-based supporters. The authors expect to

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clarify whether these three metal oxides would perform the same or better properties over bio-chars. Results from this research might be helpful for the alternative enhancement for NO removal in flue gas purification processes in our country.

## 2. Experimental

### 2.1. Samples preparation and characterization

Pine wood pellets (diameter 1–3 mm) were selected as raw material to obtain the target samples. For studying the transformations of pine wood during thermal treatment, thermogravimetric analysis was conducted under $N_2$ atmosphere from 50 °C to 900 °C at 15 °C/min. According to the thermogravimetric analysis results (see Fig. 1), 400 °C is selected as a starting point of pine carbonization, with heating rate of 15 °C/min, and with no maintenance at that temperature. The sample was then cooled in the furnace in a flow of $N_2$. Pervious researches [14,15] have revealed that temperature performed serious influences on the properties of carbonaceous materials for the removal of NO and $SO_2$. So, other two target temperatures, 600 °C and 750 °C, are also selected in this study, aiming at exploring optimal carbonization temperature. KOH was employed as activating agent with concentration of 4 mol/L. In detail, pine was impregnated with KOH aqueous solution, stirred at 60 °C for 4 h, dried at 100 °C for 12 h and then carbonization. The modification reagents in this study are $V_2O_5$, $MnO_x$ and CuO with weight percentage of 7.0%. The modified samples were achieved by impregnating pine chars with metal nitrate and $NH_4VO_3$ precursor solution via incipient wetness impregnation, then dried at 80 °C for 6 h, calcined in $N_2$ at 450 °C for 4 h and finally in air at 250 °C for 2 h. The char samples obtained by thermal treatment, KOH addition and metal oxides modification are respectively denoted as AC-*x*, $AC_{KOH}$-*x* and Me-$AC_{KOH}$-*x*, where *x* are the carbonization temperatures and Me are the metal oxides species.

The thermogravimetric and proximate analysis of pine was conducted in a STA449 F3 unit (NETZSCH Instruments). The powder X-ray diffraction (XRD) patterns were determined by Rigaku D/max-2500/PC diffractometer, operating at 40 kV and 40 mA using CuKα radiation. The specific surface areas and porosity of the samples were measured by $N_2$ physisorption at −196 °C using MICROPORE Analyzer ASAP2020M. Before the measurements, all samples (40–60 mesh) were degassed at 250 °C for 2 h prior to the measurement. SEM-EDS measurements were conducted using TESCAN VEGA 3 LMH SEM at a voltage of 20 kV. FT-IR spectra were recorded at room temperature with Nicolet 5DXC Fourier Transform Infrared spectrometer in the 4000–400 $cm^{-1}$ range, with a resolution of 4 $cm^{-1}$. The sample (1 mg) was mixed with 100 mg of KBr and pressed into a disk.

### 2.2. Activity tests of samples

The NO removal activity tests of all samples were tested in a fixed-bed quartz reactor, containing 200 mg sample of 40–60 mesh (volume of 2.5 $cm^3$). The total gas flow rate was 500 ml/min with GHSV of 12,000 $h^{-1}$, containing 500 ppm NO, 500 ppm $NH_3$ and 11% $O_2$. The outlet NO concentration was detected by flue gas analyzer (MRU, Germany OPTIMA7), and the catalytic activity was evaluated by NO conversion (%) according to the following formula:

$$No\ conversion\ (\%) = \frac{NO_{in} - NO_{out}}{NO_{in}} \times 100\% \quad (1)$$

The measurement was performed at fixed temperature 160 °C and kept for at least 20 min to reach a stable test condition.

The turnover frequencies (TOF), defined as the number of moles NO converted per mole of metal atom per minute, can be calculated as Eq. (2) [16].

$$TOF = -\frac{F0}{M}\ln(1 - X), \quad (2)$$

where $F_0$ is the molar NO feed rate (mol/min), M is the moles of metals, and X is the conversion.

## 3. Results and discussion

### 3.1. Carbonization of pine

Pine wood is a nature polymer with major components of hemicellulose, cellulose and lignin. The proximate analysis results revealed a composition of 3.9, 0.4, 81.6 and 14.1 *wt.%* corresponding, respectively, to moisture, ash, volatile and fixed carbon. The thermogravimetric analysis result in $N_2$ is presented in Fig. 1. The first mass loss, corresponding to 8.5 *wt.%*, occurred in the temperature range of 30–120 °C, can be attributed to the evaporation of water. The second mass loss occurred in the temperature range of 200–500 °C. During this period, it is decomposition of hemicellulose and cellulose, respectively, ranging from 225 to 350 °C and 350 to 500 °C. It is the major degradation stage with a weight-loss of 64.3%. At the third stage (>500 °C), mass loss could be attributed to the lignin decomposition. A certain amount of volatiles are generated and the weight loss is about 7.3%. Throughout the carbonization process, the productivity of pine chars is only 20%.

In order to explore the effect of KOH and carbonization temperature, NO removal efficiency of pine chars obtained at different treatment temperatures, with and without KOH addition, was tested at 160 °C. The results are showed in Fig. 2. NO removal efficiency of KOH-free samples decrease with the increasing treatment temperatures. While KOH is doped, the efficiency is improved especially for the sample that treated at 600 °C. Sample $AC_{KOH}$-600 shows the highest NO removal efficiency among them all. It means too high carbonization temperature is not good at enhancing the sample's performance further and KOH shows positive promotion to the properties of pine chars, which are coincident with previous studies on other materials [17,18]. Based on these results, the authors choose $AC_{KOH}$-600 as the original sample to be modified by metal oxides, and their physicochemical characteristics were also tested.

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