



# Desulfurization activity of nickel supported on acid-treated activated carbons

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## ABSTRACT

Activated carbons from coal were treated with different acids and used as carriers. Ni catalysts supported on untreated and treated activated carbons were prepared by the excessive impregnation method and characterized using Brunauer–Emmett–Teller surface area characterization, X-ray diffraction, and X-ray photoelectron spectroscopy. The desulfurization activity of granular catalysts was evaluated at a fixed bed under a simulated gaseous mixture. The results showed the following: (1) the order of desulfurization activity is AC < Ni/AC < Ni/AC-H<sub>2</sub>SO<sub>4</sub> < Ni/AC-HNO<sub>3</sub>; (2) the specific surface area of the original activated carbons (723 m<sup>2</sup>/g) is less than that of the activated carbons treated with nitric (831 m<sup>2</sup>/g) and sulfuric acid (803 m<sup>2</sup>/g); (3) acid treatment can affect the surface functional groups of activated carbons, and activated carbons treated with nitric acid can significantly increase C=O or C–O— functional groups, which can enhance the desulfurization performance of the catalysts; and (4) Ni and NiO species coexist in the activated carbons before desulfurization, but after desulfurization, Ni and NiO species disappear and Ni<sub>2</sub>O<sub>3</sub> is observed, indicating that Ni species could be involved in the desulfurization reaction.

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## 1. Introduction

A more energy-efficient and environment-friendly removal of SO<sub>2</sub> from flue gas has been expected to be developed since SO<sub>2</sub> is the primary cause of acid rain. Because activated carbons possess large surface area, abundant microporous structure, and surface oxygen species, they have been extensively studied as suitable materials or adsorbents of many substances both in liquid and gaseous phases, as well as supports for catalysts [1–5]. Particularly, the use of the activated carbons in removing SO<sub>2</sub> from the industrial flue gas containing sulfur appears to be promising [6,7]. Although, carbon is considered an inert material compared with other catalyst supports, its surface is not as inert as expected due to the formation of active sites attributable to the presence of heteroatoms (O, H, and N) [8]. The nature of the functional groups, which can be modified by physical or chemical treatments [9], on the carbon surface can affect the characteristics of the catalyst [10]. Pretreatment of carriers or addition of promoters can improve the catalytic activity of activated carbon-supported catalysts, as well as the dispersion of the active species [9,11,12].

A large number of studies have shown that the sorption of large amounts of SO<sub>2</sub> is favorable when carbons with high surface area and with special acidic and basic surface chemical groups are used

[13–16]. Several studies have also reported that the addition of certain cations to the activated carbons can improve the sorption efficiency of SO<sub>2</sub> [17,18]. Transition metal oxides, such as nickel oxides, can easily change their valence state, promote the redox cycle, and show good oxidation performance because of their variable *d* electronic structure. Apart from the supported phase, carriers also strongly affect the surface morphology and electronic structure of the metal particle, which can directly affect the stability and catalytic activity of catalysts [19]. The aim of this study is to explore the possibility of obtaining activated carbons supported by a transition metal Ni with good desulfurization performance at low temperature. The product may be used as suitable material in industrial flue gas treatment at low production costs.

In this paper, the effects of acid treatment on the surface properties of activated carbons and the interaction between impregnated Ni and carriers during the preparation of Ni-supported catalysts are discussed. The catalytic activities during desulfurization under a simulated flue gas and the possible changes in the metal species on the surface of activated carbons during desulfurization are also investigated.

## 2. Experimental

### 2.1. Preparation activated carbons and catalysts

The original activated carbons from Henan coal were provided by the National Engineering Research Center for Flue Gas Desulfurization in China. Prior to pretreatment, these activated carbons

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were crushed using a mesh with a size between 12 and 16. The obtained activated carbons were completely immersed in 30% sulfuric acid solution and 30% nitric acid solution for approximately 1.5 h at 60 °C with vigorous agitation. After treatment, the samples were washed with distilled water until the pH of the washing fluid became neutral. The samples were then dried at 110 °C for 12 h. The carbon carriers treated with acid were denoted as AC-HNO<sub>3</sub> and AC-H<sub>2</sub>SO<sub>4</sub>. The untreated carbons with a mesh size between 12 and 16 were labeled as AC.

The catalysts were prepared by wet impregnation method. The precursor used was Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (AR grade). The carriers were impregnated with the desired precursor solution (0.1 g/ml) to achieve a Ni loading of 1%. The solutions were heated and continuously stirred until the liquid completely disappeared. All catalysts were dried at 110 °C overnight and calcined at 800 °C under a nitrogen atmosphere. The catalysts were denoted as Ni/AC, Ni/AC-HNO<sub>3</sub>, and Ni/AC-H<sub>2</sub>SO<sub>4</sub>, respectively. AC was used as comparative sample.

## 2.2. Activity evaluation

SO<sub>2</sub> removal was carried out at 90 °C in a fixed bed flow micro-reactor (18 mm I.D.). The micro-reactor contained 4 cm of the catalysts, and SO<sub>2</sub> removal was performed by passing a flue gas mixture. The gases were controlled by a rotor flow meter before they enter the blender. The flue gas mixture contained 0.23% SO<sub>2</sub>, 11% O<sub>2</sub>, 14% water vapor, and N<sub>2</sub> as the balance. The gas space velocity (SV) was 2000 h<sup>-1</sup>. A relation curve about SO<sub>2</sub> removal and reaction time was obtained. The flue gas before and after reaction was passed through a solution containing H<sub>2</sub>O<sub>2</sub> (3%), and the as-formed H<sub>2</sub>SO<sub>4</sub> was determined by titrating with NaOH (0.01 mol/L) solution. The amount of H<sub>2</sub>SO<sub>4</sub> was used to calculate the total sulfur amount on the catalysts.

## 2.3. Catalyst characterization

The N<sub>2</sub> adsorption isotherms of the samples at the temperature of liquid nitrogen were obtained on using a Micromeritics ASAPM2020 apparatus. Before each analysis, in order to remove physisorbed material from their narrowest pores, the samples were degassed at 200 °C for approximately 12 h to reduce the residual pressure to 30 mmHg and to remove the physisorbed material from the narrowest pores. The adsorption isotherm data were used to calculate the surface area (S<sub>BET</sub>) of each sample via the Brunauer–Emmett–Teller (BET) equation at relative pressures between 0.05 and 0.35.

The crystal structures of the selected samples were determined by an X-ray diffractometer (XRD) (DX-2000) using Cu-Kα radiation (λ = 0.15406 nm). The X-ray tube was operated at 40 kV and 25 mA. The samples were scanned within the 2θ range of 10–90° at a scanning rate of 0.03°. The crystalline phases were identified by comparing them with the reference data from the International Center for Diffraction Data (JCPDS).

X-ray photoelectron spectroscopy (XPS) experiments were conducted on a spectrometer (XSAM-800, KRATOS Co.) using Al-Kα radiation under ultra-high vacuum and operated at 12 kV and 12 mA. Energy calibration was conducted by recording the core level spectra of Au 4f<sub>7/2</sub> (84.0 eV) and Ag 3d<sub>5/2</sub> (368.3 eV). Peak

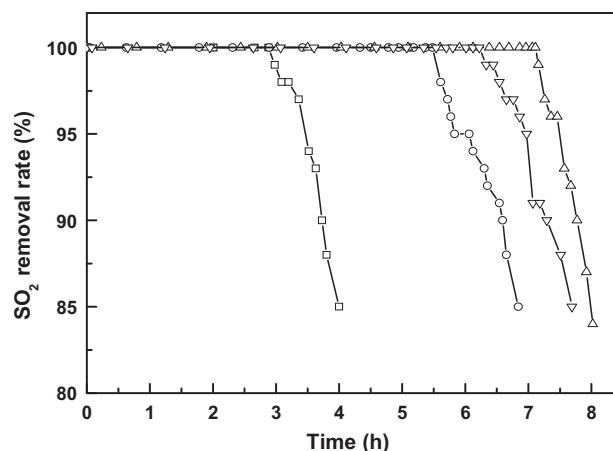


Fig. 1. The curves about the relation between SO<sub>2</sub> removal rate and time. □-, AC; ○-, Ni/AC; △-, Ni/AC-HNO<sub>3</sub> and ▽-, Ni/AC-H<sub>2</sub>SO<sub>4</sub>.

areas, including satellites, were computed by a program which assumed Gaussian-line shapes and flat background subtraction.

## 3. Results and discussion

### 3.1. Desulfurization performance of catalysts

The desulfurization performance of all catalysts, including the relationship among SO<sub>2</sub> removal, working time, and sulfur capacity (SO<sub>2</sub> removal rate decreases to 90% corresponding to the total amount of SO<sub>2</sub> removed), is presented in Fig. 1. The catalysts containing Ni exhibited good desulfurization activity and high sulfur capacity compared with AC, which shows that Ni on AC can significantly improve desulfurization performance. This result is probably related to the catalytic activity of Ni species (active site) during the SO<sub>2</sub> oxidation process. When Ni species are supported on the acid-treated activated carbons, the catalysts exhibit better catalytic activity, indicating that acid treatment can further improve the catalytic activity of activated carbon-supported catalysts because of the different functional groups. This result is in agreement with the literature [12]. Sulfur capacity also increases with prolonging the working time. When SO<sub>2</sub> removal rate decreases to 90% under the same experimental conditions, the working time of AC is 3.73 h and has a sulfur capacity of 127 mg/g. The working time and sulfur capacity of Ni/AC are 6.59 h and 206 mg/g, respectively. The working times of Ni/AC-HNO<sub>3</sub> and Ni/AC-H<sub>2</sub>SO<sub>4</sub> are 7.77 and 7.29 h, respectively, with sulfur capacities of 238 and 223 mg/g, respectively. According to the results, the order of desulfurization activity of catalysts from poor to excellent is as follows: AC < Ni/AC < Ni/AC-H<sub>2</sub>SO<sub>4</sub> < Ni/AC-HNO<sub>3</sub>. This result could be attributed to the Ni species and functional groups on the surface of activated carbons.

### 3.2. Surface area of samples

The specific surface areas of the untreated and treated activated carbon samples, as well as Ni-supported activated carbons, are listed in Table 1. AC has a high surface area (723 m<sup>2</sup>/g), whereas that of Ni/AC decreases to 697 m<sup>2</sup>/g, possibly because the loading of Ni species on activated carbons blocked some the microporous surface [9]. After acid treatment, the BET surface area of

Table 1  
The specific surface area of samples.

Samples	AC	Ni/AC	AC-HNO <sub>3</sub>	AC-H <sub>2</sub> SO <sub>4</sub>	Ni/AC-HNO <sub>3</sub>	Ni/AC-H <sub>2</sub> SO <sub>4</sub>
S <sub>BET</sub> (m <sup>2</sup> /g)	723	697	832	803	831	786

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