



# The catalytic hydrolysis of carbon disulfide on Fe–Cu–Ni/AC catalyst at low temperature

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## ABSTRACT

It was investigated in this work that a series of coal-based active carbon catalysts (Fe–Cu/AC) loaded by metal oxides were prepared by sol–gel method for carbon disulfide (CS<sub>2</sub>) hydrolysis. The results showed that the kind of metal oxide and its content had obvious effects on hydrolysis removal of CS<sub>2</sub>. And the optimum conditions of the catalyst was with the addition of Ni and Fe: Ni (mole ratio) 10:1. The influences of operation conditions such as: temperature, O<sub>2</sub> concentration and relative humidity (RH) were also discussed respectively. The X-ray diffractometry (XRD) results revealed that additive doping level is an important factor which could control the generation of iron oxides as well as the incorporation crystalline phases of Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> can enhance the reaction activity of the catalysts. The surface area and pore size distribution results showed that the larger the surface area and pore volume of the samples were, the higher the hydrolysis activities were. Surface sulfate groups were observed by Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS) on exhausted catalysts and indicated that the products of CS<sub>2</sub> hydrolysis were SO<sub>4</sub><sup>2-</sup> species and the formation of SO<sub>4</sub><sup>2-</sup> had a negative effect on the hydrolysis activity.

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## 1. Introduction

CS<sub>2</sub> is a type of the sulfur-containing compounds existing in natural gas, petroleum and synthesis gas and various raw gases from coal [1]. Since CS<sub>2</sub> possesses high toxicity with a maximum permissible concentration in air of 0.5 mg/m<sup>3</sup>, its emission into atmosphere even in small amounts is inadmissible [2] and the presence of feedstock CS<sub>2</sub> can also lead to increased corrosion of the reactors used in refinery processes [3], which triggers an increasing interest in finding reliable, cost effective technologies for its control [4]. There are several approaches to remove CS<sub>2</sub> from the off-gas [5], including reduction, hydrolysis, adsorption, photolysis, oxidation, etc. [6], in which the hydrolysis of CS<sub>2</sub> was recognized as the most promising process due to the mild reaction condition, cheapness, and higher conversion efficiency [7], and the final hydrolysis products, carbon oxidation (CO<sub>2</sub>) and hydrogen sulfide (H<sub>2</sub>S), are much easier to be removal than CS<sub>2</sub> [6]. Catalytic hydrolysis of CS<sub>2</sub> follows the reactions:



Active carbon (AC) is widely used for various application field, such as catalyst support, adsorbent, and conductive material because of their stable structure, large specific surface area, well-developed porous structure and potential biocompatibility [8]. The pore is classified into micropore (<2 nm), mesopore (2–50 nm), and macropore (50 nm–) [9]. Many people have attempted to modify the surface properties of AC to improve their functions in order to meet the growing demand for clear air [10]. In this study, a part of Fe–Cu/AC catalysts were modified by different metal oxides to meet the changes of the samples.

## 2. Experimental

### 2.1. Catalyst preparation

The ash content of fresh AC (LJ-40 commercial) was 12% and S<sub>BET</sub> was 749 m<sup>2</sup>/g. The AC crushed and sieved to 40–60 mesh size was used a matrix. The AC was washed four times by distilled water. The catalyst was prepared with sol–gel method. Firstly, the commercial AC was dipped in a solution of 1 M caustic potash (KOH) and boiled for 1.5 h, then washed by distilled water till no further change in pH, followed filtered and dried for 3–4 h at 120 °C in the drying oven. Secondly, we made colloid solution with loaded 5% iron oxides and Fe:Cu (mole ratio) 5:1 with a certain amount of metal nitrate solution for additives. Then the sample was added into the hydrosol. Thirdly, the catalyst was dipped under the ultrasonic for 30 min,

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dried at 120 °C in the drying oven and calcined for 3 h at 400 °C in a tubular furnace in air atmosphere with 82.4 kPa of atmospheric pressure. At last the catalyst calcined was dipped in 5 wt% KOH and kept under the ultrasonic for 30 min, then dried for 3 h at 120 °C in the drying oven to get the catalyst needed for the experiments.

## 2.2. Characterization

### 2.2.1. X-ray diffraction (XRD)

X-ray diffraction (D/MAX-2200) pattern were obtained with a Rigaku diffractometer operated at 36 kV and 30 mA by using Ni-filtered Cu K $\alpha$  radiation ( $\lambda = 0.15406$  nm) at a rate of 5°/min from  $2\theta = 20^\circ$  to  $80^\circ$ . The powdered samples were analyzed without previous treatment after deposition on an agate mortar. The identification of crystalline phases was made by matching the JCPDS files.

### 2.2.2. Surface area and pore size distribution

Surface area and pore size distribution for the samples were measured using a NOVA2000e (Quantachrome instruments) surface area analyzer that uses a nitrogen adsorption–desorption method. The samples were initially outgassed at 393 K for 24 h before adsorption isotherms were generated by dosing nitrogen (at 77 K) on the carbons. The density functional theory (DFT) model was used to analyze the result.

### 2.2.3. X-ray photoelectron spectroscopy (XPS)

XPS (PHI 5500) analysis used Al K $\alpha$  radiation with energy of Al rake and power 200 W. Kinetic energies of the photoelectrons were measured with a two-stage spectrometer. The analyzer resolution was 1 eV. An Ar<sup>+</sup> ion gun was used to sputter clean specimen surfaces. The ion energy was set to 1 keV and the sputtering time was 10 min. The photoelectron spectra were calibrated using the C 1s signal detected at a binding energy of 284.8 eV from adventitious carbon. Atomic compositions were calculated with the corrected Scofield coefficients of the transmission function of the analyzer and/or with experimental coefficients determined for a reference compound. The continuum spectrum was fitted according to the Gaussian–Lorentzian files.

### 2.2.4. Fourier transform infrared spectroscopy (FT-IR) analysis

Fourier transform infrared spectroscopy (FT-IR) made in American Varian Company was used to determine sulfur-containing species formed on catalyst surface. Before the analysis, the samples were ground, mixed, and palletized with potassium bromide.

## 2.3. Experimental procedure

Catalytic activity tests were carried out under atmospheric pressure in a fixed-bed quartz reactor system (4 mm inside diameter  $\times$  100 mm length). The catalyst was loaded into the fixed bed and a wad of cotton wool was inserted into the reactor so that the catalyst could not escape from the vessel during the operation. CS<sub>2</sub> from gas cylinder (0.3% CS<sub>2</sub> in N<sub>2</sub>) was diluted with nitrogen (99.99%) and oxygen (99.999%). Water was introduced using a saturator system. The temperature of this reactor was controlled by water-bath with circulating pump, with accuracy of  $\pm 0.1$  °C. The total CS<sub>2</sub> concentration of gaseous feed and effluent from the reactor were analyzed by an online HC-6 sulfur phosphorus microscale analyzer with a FPD detector while the different S-components (COS and H<sub>2</sub>S) in outlet gas were determined by switching chromatographic column.

In this paper, a method simultaneously removing CS<sub>2</sub> and its hydrolysis products COS and H<sub>2</sub>S at lower temperature (50 °C) was introduced, with other conditions of gas hourly space velocity

(GHSV) of 7000 h<sup>-1</sup>, 255 mg/m<sup>3</sup> CS<sub>2</sub> and atmospheric pressure. The conversion of CS<sub>2</sub> is determined by analyzing the inlet and outlet concentration of CS<sub>2</sub>:

$$\text{CS}_2 \text{ conversion (\%)} = \frac{\text{CS}_{2\text{inlet}} - \text{CS}_{2\text{outlet}}}{\text{CS}_{2\text{inlet}}} \times 100$$

Sulfur capacity is defined as the sulfur deposition in the unit mass of desulfurizer agent in CS<sub>2</sub> (in the quality of agent sulfur) quality, by conversion of the time points. The conversion rate of 90% of the sulfur content is defined as the penetration of sulfur content.

## 3. Results and discussion

### 3.1. Effect of different metal oxides for additive on Fe–Cu/AC catalyst and Ni loading amount on catalytic hydrolysis of CS<sub>2</sub>

The experiments in this part were aimed to find the optimal additive and component of Fe–Cu/AC catalyst for CS<sub>2</sub> hydrolysis. Additives can change the properties of catalyst, which are chemical structure and composition, the pore and crystal structure, pH, etc. To investigate the effect of different additives on catalytic hydrolysis of CS<sub>2</sub>, nickel nitrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), aluminum nitrate (Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) and zinc nitrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) were respectively added with the concentration of 5% Fe<sub>2</sub>O<sub>3</sub> and mole ratio Fe:Cu:A=10:2:1 (A is Ni, Al or Zn). The data were plotted in Fig. 1(a). The results showed that the addition of Ni or Zn to Fe–Cu/AC, especially of Ni, showed obvious advantage in catalytic hydrolysis of CS<sub>2</sub>. Fe–Cu–Ni/AC catalyst exhibited significantly better performance compared with other catalyst. Moreover, the catalytic activity of Fe–Cu–Al/AC was significantly lower than that of Fe–Cu/AC. This may be because: the addition of Al makes the promote interaction between the active component disappearing and the reactivity of active sites on the catalyst surface is not formed with S atoms in the initial reaction. In addition, Al is a kind of amphoteric metal while alkaline is beneficial to CS<sub>2</sub> hydrolysis. While the addition of Ni or Zn may increase active sites on the surface of the catalyst and stable activity of Fe atoms with crystal face. These results also suggested that NiO–CuO–Fe<sub>2</sub>O<sub>3</sub> interaction was favorable and the interaction between Fe–Cu and the supporter was also greatly enhanced with the addition of Ni.

As discussed previously, Ni provided active sites and improves the catalytic activities. To get the optimal catalyst, in this study, with Fe/Cu molar ratio fixed at 5, three Fe/Ni mole rates were used to prepare Fe–Cu–Ni/AC catalysts: 5, 10, 20. As described in Fig. 1(b), the addition of different Ni loading had increasing the activity to different extents regardless of the Ni composition, and Fe–Cu–Ni/AC catalyst with Fe/Ni = 10 showed the highest activity. However, sequentially increasing the Ni content had a negative effect on CS<sub>2</sub> hydrolysis, while the activities were not significantly changed when the Fe/Ni ratio fell from 20 to 5. Maybe too high loading amount of Ni formed nickel particles reunion so that the contact between CS<sub>2</sub> and aggregate grains or particles of Ni was restricted, then the hydrolysis activity decreased.

The structural characterizations of different samples were performed by XRD analysis in order to explain the influence of the different metal oxides for additives. The phase and crystalline orientation of samples were exhibited in Fig. 2. The peak intensity of five samples changed with doping different precursors, but these changes were comparatively weak. This is due to the poor crystallinity and the amounts of metal oxides (CuO, NiO, ZnO, Al<sub>2</sub>O<sub>3</sub>) are far less than AC. In the XRD peak patterns, peaks with strong intensity appear at  $2\theta = 30.175^\circ$ ,  $35.439^\circ$ ,  $57.193^\circ$  and  $62.895^\circ$ , and

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