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Simultaneous catalytic hydrolysis of low concentration of carbonyl sulfide and carbon disulfide by impregnated microwave activated carbon at low temperatures

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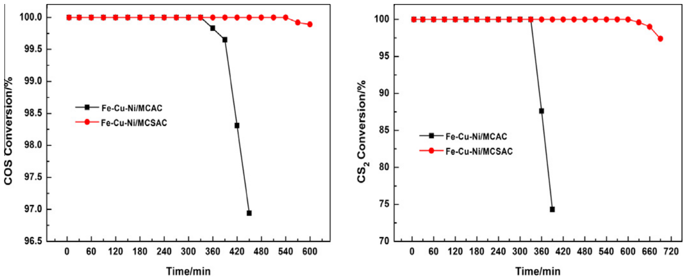
HIGHLIGHTS

- Simultaneous catalytic hydrolysis activity of COS and CS_2 over Fe–Cu–Ni/MCSAC was notable.
- Low generation of $K_3Na(SO_4)_2$ was in the Fe–Cu–Ni/MCSAC catalyst.
- High specific surface areas and more micropores enhanced catalytic hydrolysis activity.
- XPS results showed that most of COS and CS_2 hydrolysis products were S/SO_4^{2-}.

GRAPHICAL ABSTRACT

For sample Fe–Cu–Ni/MCAC, 100% COS conversion and 100% CS_2 conversion are observed for about 330 min and 360 min respectively, and for sample Fe–Cu–Ni/MCSAC, 100% COS conversion and 100% CS_2 conversion are observed for about 540 min and 600 min respectively.



(a) (b)

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ABSTRACT

The blank microwave coal-based activated carbons (MCAC) and blank microwave coconut shell activated carbons (MCSAC) were tested for simultaneous catalytic hydrolysis of carbonyl sulfide (COS) and carbon disulfide (CS_2) at relatively low temperature (at 50 °C). MCAC and MCSAC loaded by Fe–Cu–Ni metal mixed oxides were prepared by sol–gel method, and also tested for the simultaneous catalytic hydrolysis process. The results showed that Fe–Cu–Ni/MCSAC catalyst had the superior activity for the simultaneous catalytic hydrolysis of COS and CS_2. These modified catalysts were characterized by XRD, BET, EDS and XPS, the results of which can help us to understand the reasons of the superior catalytic activity and the reasons of catalyst deactivation. Lower generation of sulfate ($K_3Na(SO_4)_2$), high specific surface areas and more pore sizes of 0.3–1.2 nm and 3.5–4.0 nm may be the important role in COS and CS_2 catalytic hydrolysis reaction. The XPS results showed that most of products on the exhausted catalysts were S/SO_4^{2-} species which accumulated on the active carbon's surface and had a negative effect on the hydrolysis activity, and the contents of S/SO_4^{2-} species of exhausted Fe–Cu–Ni/MCAC were higher than which of exhausted Fe–Cu–Ni/MCSAC catalysts.

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1. Introduction

Phosphorus chemical industry is one of the important economy pillar industries. Recently, the output of yellow phosphorus can achieve to 80 million tons every years in China. The off-gas of yellow phosphorus contains plenty of CO, and the CO content is high to 85–95%. In recent years, with the development of one carbon (C1) chemical industry, it is possible to synthesize many organic compounds with economic value. However, organic sulfurs (COS, CS_2, etc.) in the yellow phosphorus off-gas are the harmful gases which can pollute the environment and result in the deactivation of catalysts [1–4]. Thus, if yellow phosphorus off-gas is as the virgin gas of one carbon chemical industry, the COS and CS_2 must be removed [5]. The conventional desulphurization methods are adsorption, oxidation conversion, hydrogenation conversion, etc. [6,7], but COS and CS_2 are difficult to be removed efficiently by these methods, especially, CS_2 is much more difficult to convert than COS [8,9]. As a kind of alternative technology, catalytic hydrolysis of COS and CS_2 have been used because of the mild reaction conditions, cheapness, and higher conversion efficiency [8–10]. The main reaction equations of hydrolysis of COS and CS_2 are:

$$COS + H_2O \rightarrow CO_2 + H_2S \tag{1}$$

$$CS_2 + H_2O \rightarrow COS + H_2S \tag{2}$$

$$CS_2 + 2H_2O \rightarrow 2H_2S + CO_2 \tag{3}$$

In recent years, the separate removal of COS and CS_2 have been reported over new catalysts, particularly supported metal oxides [11–13], but the reaction temperature was relatively high and the industrial application prospect is not optimistic. The application of activated carbons for air purification is so popular due to their large surface area and porous structure [14,15]. Coal-based carbon and coconut shell activated carbons are attractive alternative for its porous structure and low cost. The source and application of coal-based carbon are extensive, yet it has many impurities and it does not show so good performance in the deodorization process, because their surface reaction and chemisorptions surface chemistry is not potent enough to enhance the specific adsorption and catalytic processes. Whereas, the coconut shell activated carbons are purer than coal-based carbon, its high surface area and abundant micropore structures can enhance the adsorption and catalysis performance. Presently, more researchers pay attention to the preparation and application of microwave activated carbons. Because energy is readily transformed into heat inside the particles by dipole rotation and ionic conduction in the process of microwave treatment, the tremendous temperature gradient from the interior of the char particle to its cool surface, resulting in energy saving and shorter reaction time [16–18]. On this basis, the catalytic properties of AC surfaces can be enhanced by additional modification (noble metal oxides, transition metal oxides, etc.), for instance, the way of impregnation.

In our previous works, the transition metal oxide and alkali oxides impregnated AC catalysts were used to separate hydrolysis COS or CS_2 and adsorption H_2S [19,20]. The modified MCAC catalysts were tested to simultaneous catalytic hydrolysis of COS and CS_2 at the low temperature [5], but the hydrolysis activities of modified MCAC was not very good. As a matter of fact, still little research focuses on simultaneous catalytic hydrolysis of COS and CS_2 with other microwave activated carbons at the low temperatures (<100 °C). Therefore, in this study, the efficiencies of blank MCAC, blank MCSAC, Fe–Cu–Ni/MCAC and Fe–Cu–Ni/MCSAC for COS and CS_2 simultaneous removal at 50 °C were investigated. The reasons of activities difference among the four catalysts were studied by XRD, EDS, BET methods. The deactivation reasons of catalysts were researched by XPS measure.

2. Materials and methods

2.1. Materials preparation

The MCAC and MCSAC were from the faculty of materials and metallurgical engineering Kunming University of Science and Technology, the main preparation parameters: activation temperatures were 850–900 °C, microwave processing time was 40 min and water vapour activation flow was 5 g/min. First, the MCAC and MCSAC were crushed and sieved to 40–60 mesh size and used in this study. The catalysts were prepared by sol–gel method as similar to that used by Ning et al. [5]. The fresh activated carbons were first washed 3–4 times with tap water and 3–4 times with distilled water, then boiled in 1 mol/L KOH for 1.5 h and washed with distilled water to a constant pH, and finally dried at 120 °C for 3–4 h. Then, the iron oxides colloid solution (the Fe_2O_3 content was 5%) mixed with a certain amount of the copper nitrate ($Cu(NO_3)_2{\cdot}3H_2O$), nickel nitrate ($Ni(NO_3)_2{\cdot}6H_2O$) solution and Na_2CO_3 solution (the mole ratio of Fe:Cu:Ni was 10:2:0.5). The activated carbon catalysts were supported by desired proportion. The sample was dipped under the ultrasonic for 30 min, dried at 120 °C in the drying oven and calcined at 300 °C for 3 h under atmospheric condition (82.4 kPa). At last, the catalysts were impregnated by 13% (mass fraction) KOH, and kept under the ultrasonic for 30 min, then dried for 3–4 h at 120 °C. These materials are designated as Fe–Cu–Ni/MCAC and Fe–Cu–Ni/MCSAC respectively.

2.2. Catalysts characterization

X-ray diffraction (XRD, D/MAX-2200) patterns were recorded with a Rigaku diffractometer operated at 36 kV and 30 mA by using Ni-filtered Cu Kα radiation (λ = 0.15406 nm) at a rate of 5°/min from 2θ = 20–80°. Surface area and pore size distribution for the samples were measured using a Quantachrome surface area analyzer which used the nitrogen adsorption–desorption method. The samples were initially out gassed at 393 K for 24 h before adsorption isotherms were generated by dosing nitrogen (at 77.35 K). XPS (ESCALAB 250) analysis used Al Kα radiation with energy of Al target and power 200 W. QUANTA200 scanning electron microscope (SEM) coupled with energy-dispersive X-ray spectrometry (EDS) was used for microstructure observation of the interface and element distribution.

2.3. Experimental apparatus

Desulfurization tests were performed in a fixed-bed quartz reactor (3 mm inside diameter × 100 mm length) under atmospheric pressure. COS and CS_2 from gas cylinder (1% COS in N_2; 0.3% CS_2 in N_2) were diluted with N_2 (99.99%) to the required concentration (COS: 400 ppm; CS_2: 10 ppm). The overall flow rate was controlled using calibrated mass flow controllers and the overall gas hourly space velocity (GHSV) of the reaction mixture was standardized at 10,000 h^{-1}. The water comes from a saturator system, and the relative humidity (RH) was used to express the H_2O content. The water content was controlled by the temperature of saturator system. In the experiment, the temperature of water humidifier was 5.0 °C, and the corresponding RH was 49%. The reaction temperature of this reactor was controlled to 50 °C by water-bath with circulating pump, with accuracy of ±0.1 °C. The total COS and CS_2 concentration of gaseous feed and effluent from the reactor were analyzed by an online HC-6 sulfur phosphorus microscale analyzer with a FPD detector. “Chromatographic column 1” was used to analyze CS_2, and the “chromatographic column 2” was used to analyze COS and H_2S. The conversion of COS or CS_2 is determined by analyzing the inlet and outlet concentration of CS_2: