



Study on the adsorption behavior and mechanism of dimethyl sulfide on silver modified bentonite by in situ FTIR and temperature-programmed desorption



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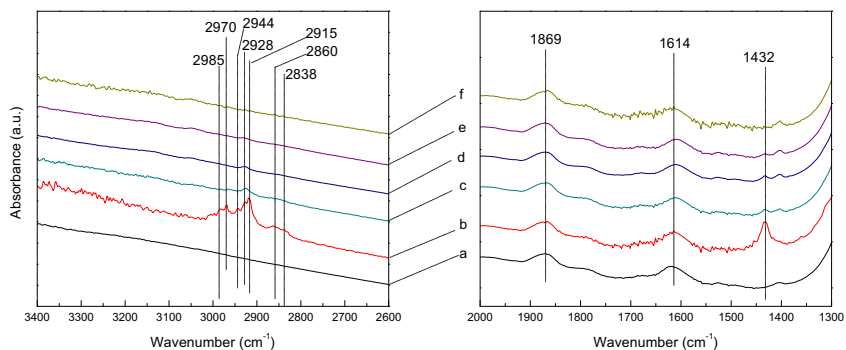
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HIGHLIGHTS

- Study on the adsorption of dimethyl sulfide (DMS) from liquid hydrocarbon streams.
- It demonstrated a high saturated sulfur capacity of 80 mg S/g adsorbent.
- Combined techniques of in situ FTIR and DMS-TPD were used.
- Adsorption mechanism of DMS on adsorbents was investigated.

GRAPHICAL ABSTRACT

In situ FTIR spectra recorded from the adsorption and thermal desorption of DMS on adsorbents with 8 wt% Ag⁺ loading (a) after pretreatment, (b) adsorption of DMS at ambient temperature, (c) desorption at 100 °C, (d) desorption at 200 °C and (e) desorption at 300 °C (f) desorption at 400 °C



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ABSTRACT

A high-performance adsorbent was developed by loading silver on bentonite for the adsorption of dimethyl sulfide (DMS) from liquid hydrocarbon streams under ambient conditions. It demonstrated a high saturated sulfur capacity of 80 mg S/g adsorbent when the bentonite was loaded with 8 wt% Ag⁺ and calcined at 150 °C. The prepared adsorbents were characterized by adsorption of nitrogen (BET), Transmission Electron Microscopy (TEM), X-ray diffraction (XRD), pyridine Fourier transform infrared spectroscopy (pyridine-FTIR) and Thermogravimetric Analysis (TG). The results showed that the silver species dispersed on the surface of bentonite had an important role in determining the DMS removal performance while the surface acid sites of adsorbent had little correlation with the DMS removal performance. Combined techniques of temperature programmed desorption of DMS (DMS-TPD) and in situ Fourier transform infrared spectroscopy (in situ FTIR) were used to investigate the adsorption mechanism of DMS on raw bentonite and Ag⁺ modified bentonite, respectively. The results revealed that three interaction patterns were existed between the adsorbed DMS and raw bentonite while two interaction patterns were observed between adsorbed DMS and Ag⁺ modified bentonite. The DMS molecules hardly entered into the interlayer of Ag⁺ modified bentonite due to the strong interactions between DMS molecules and silver cations.

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1. Introduction

Sulfur was the main contaminant present in crude oil. Dimethyl sulfide (DMS) is a non-polar, stable, organic, reduced sulfur compound [1] and is regarded as one of the most difficult sulfur compounds to remove from low carbon hydrocarbons [2]. Since the crude oil is getting much worse and heavier in recent years, the content of DMS present in the liquid hydrocarbon streams especially in low carbon hydrocarbons is also getting much higher [3]. Since the DMS present in the liquid hydrocarbon streams will reduce the purity of petrochemical products, deteriorate the process performance, and severely poison the noble metal catalyst used in subsequent processing [4,5], it should be removed in a pre-treatment process.

Due to the advantages that it does not require hydrogen addition and can be operated at ambient conditions [6], the adsorptive desulfurization method has attracted more and more attentions in removing sulfur compounds from pipeline natural gas or transportation fuels. Many efforts have been attempted to remove sulfur compounds from liquid hydrocarbon streams by adsorptive method on various adsorbents such as activated carbons [7,8], zeolites [9,10], and modified composite oxides [11,12]. However, the vast majority of them are aiming at thiophene and thiophene derivatives. Several studies have been reported about the removal of DMS from pipeline natural gas on zeolite or activated carbon. Wakita et al. [13] have studied the removal of DMS and *t*-butylmercaptan (TBM) from city gas by use of several zeolites and concluded that the main adsorption site on Na-Y was presumably Na⁺. Satokawa et al. [14] have investigated the adsorptive removal of DMS and TBM from pipeline natural gas by using silver exchanged Y zeolites (AgNa-Y) under ambient conditions. They concluded that the adsorption capacity for DMS and TBM on AgNa-Y were improved with increasing silver content of AgNa-Y and silver sulfide species were formed on AgNa-Y during the period of adsorption according to the clear color change of adsorbents. Cui and Turn [1] used iron chloride impregnated activated carbon to remove DMS from pipeline natural gas. They confirmed that the addition of FeCl₃ created some new active sites and these new active sites likely had stronger affinity with DMS molecule. However, few investigations of the removal of DMS from liquid hydrocarbon streams are to be found in the open literatures.

In comparison with well-known adsorbents such as carbon or zeolite, bentonite is relatively inexpensive and comparatively economical. In addition, because of its physical and chemical properties (i.e., large specific surface area and adsorptive affinity for organic and inorganic ions), bentonite has attracted more and more attention as a new type of microporous solid that can serve as separating agents or sorbents, etc. [15], Mikhail et al. [16] used several inexpensive solid materials (acid-activated kaolinite, acid-activated bentonite, charcoal, petroleum coke and cement kiln dust) to remove DMDS from its solution and confirmed that the acid-activated bentonite was the most suitable adsorbent at the reaction temperature of 30 °C. Tang et al. [15] have investigated the adsorption behavior of propylmercaptan (PM) from model gasoline on modified bentonite and the modified bentonites showed much better desulfurization performance than the raw bentonite. Tang et al. [17] studied the efficiency of bentonite and silver modified bentonite for removing alkyl dibenzothiophenes from liquid hydrocarbon fuel, and the results showed that the bentonite loaded with Ag⁺ had a significant enhancement of adsorption capacity for alkyl dibenzothiophenes. Zhang et al. [18] also confirmed that bentonite can be used to remove sulfur-containing compounds from diesel.

In the present study, bentonite was used as the support of adsorbents for the removal of DMS from liquid hydrocarbon

streams. In order to improve the desulfurization capacity, several transition metals were introduced to modify the bentonite. The DMS removal performance of the prepared adsorbents was evaluated in a fixed-bed flow adsorption system at ambient conditions. The silver modified bentonites were mainly studied and characterized by X-ray diffraction (XRD), pyridine-FTIR (Fourier transform infrared spectroscopy) and Thermogravimetric Analysis (TG), and the results were correlated with their DMS removal performance. The adsorption mechanism was also discussed on the basis of the combined analysis of in situ FTIR spectroscopy and temperature-programmed desorption of DMS (DMS-TPD).

2. Experimental section

2.1. Feedstocks and adsorbents

In this study, model liquid hydrocarbon stream was prepared by adding DMS (analytical grade from Aldrich) to sulfur-free n-hexane (analytical grade from Sinopharm Chemical Reagent Co., Ltd.) with the sulfur concentration of 2000 ppmw.

The raw activated bentonite used in this study was purchased from Hangzhou Yongsheng Catalyst Co., Ltd. The composition of bentonite is shown in Table 1. The adsorbents used in this study were prepared via a kneading method [19]. Raw bentonite powder was separately mixed sufficiently with corresponding concentration of AgNO₃, CuCl, Cu(NO₃)₂·2H₂O, Fe(NO₃)₃·9H₂O, Ni(NO₃)₂·6H₂O solutions and Nb₂O₅ powder (analytical grade from Sinopharm Chemical Reagent Co., Ltd.) for 0.5 h. Next, a liquid binder, dilute nitric acid, was added to the mixture to make the slurry. An extruder was used to formulate pellets to an outer diameter of 1 mm from the slurry. All of the adsorbents were dried overnight to remove moisture at 120 °C in an oven and then calcined in air at different calcination temperatures for 2 h in a muffle furnace. Finally, each sample was crushed and sieved to obtain its particle size between 20 and 40 mesh.

2.2. Characterization of adsorbents

2.2.1. Characterization of pore structure of adsorbents

The pore structure of adsorbents was characterized by using an ASAP 2020 (Micromeritics) instrument by adsorption of nitrogen at –196 °C on 200 mg of sample previously degassed at 200 °C for 2 h under high vacuum atmosphere. The nitrogen isotherms could be used to calculate the BET surface area (*S*_{BET}), total pore volume (*V*_t), micropore volume (*V*_{mic}) and average pore size (*L*).

2.2.2. X-ray diffraction

Crystal structure of powder adsorbents were characterized by means of X-ray diffraction (XRD) analyses, performed using a Siemens D-500 X-ray diffractometer equipped with Ni-filtrated Cu Kα radiation (40 kV, 40 mA). The 2θ scanning angle range was 10–80° with a step of 5 deg/min.

Table 1
The content of Yongsheng activated bentonite.

Components	wt%
SiO ₂	67.8
Al ₂ O ₃	16.3
Fe ₂ O ₃	4.0
TiO ₂	0.4
CaO	1.1
MgO	1.7
K ₂ O	1.6
Na ₂ O	0.9
Others	6.2

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