



Adsorptive separation of dimethyl disulfide from liquefied petroleum gas by different zeolites and selectivity study via FT-IR



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ABSTRACT

The removal of dimethyl disulfide from model liquefied petroleum gas using metal salt impregnated zeolite as the adsorbent was studied in a fixed-bed adsorption equipment. Effects of different carrier, metal iron species and content of active component, mass space velocity, temperature, as well as adsorption selectivity and regeneration performance were all investigated by performing the breakthrough experiment. Among all these adsorbents, 5 wt.%Ag₂O/NaY showed the highest breakthrough sulfur capacity. The adsorption selectivity of Ag₂O/NaY was studied by the infrared spectra. It was found that the direct S–Ag(I) interaction was the essential reason for the evidently improved adsorption ability and selectivity of Ag₂O/NaY for removing disulfide from solutions containing olefin. Regeneration study indicated that the saturated adsorbent was regenerated under the temperature of 550 °C for 8 h in the air atmosphere. After five times regeneration, the adsorbent Ag₂O/NaY still shows high breakthrough sulfur capacity.

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1. Introduction

In the refinery, further processing of crude oil will produce plenty of liquefied petroleum gas (LPG). LPG contains large amounts of C3 and C4 components which can be used as fuel and petrochemical feedstock. However, LPG also contains sulfur compounds such as H₂S and mercaptans, which are not only being well-known as catalyst poisons, but also their byproducts upon combustion (i.e., SO₂ and SO₃) are environmental pollutants. For all these reasons, desulfurization needs to be carried out when the LPG is for sale or as the petrochemical feedstock.

For the removal of mercaptans in LPG, the most extensively used technology is Merox process [1], which was developed by Universal Oil Products Company (UOP). The Merox process converts mercaptans to disulfides in alkaline solution using air as the oxidant in the presence of Merox catalyst. However, the major problem for ultradeep desulfurization of LPG by Merox process is that, being oxidation products, the disulfides such as dimethyl disulfide (DMDS) are difficult to be separated at the lye extraction step of Merox process [2]. This often leads to excessive sulfur content in LPG. If this kind of LPG is used as the petrochemical feedstock for the production of methyl tert-butyl ether (MTBE) and alkylates, which are commonly added to gasoline to boost the

octane number of gasoline [3], it will eventually lead to the high sulfur content in gasoline. This kind of gasoline cannot meet the increasingly stringent standards (sulfur content less than 10 ppmw, European V Emission Standard). Thus, the deep desulfurization of DMDS in LPG is important [4].

Up to present, the sulfide removal methods for hydrocarbon fuels mainly have the following several kinds, such as hydrodesulfurization (HDS) [5–7], selective catalytic oxidation (SCO) followed by adsorption [8] and adsorptive desulfurization [9–15]. HDS is a typical and very effective desulfurization process. However, HDS is operated at high temperature and pressure and requires addition of hydrogen [16]. Furthermore, during the desulfurization process, olefin may be lost significantly because of the conversion of olefin to alkane. Lampert [8] reported the desulfurization of natural gas and LPG by the SCO process. The sulfur compounds are oxidized to SO_x under air atmosphere firstly, and then the adsorption of converted SO_x is carried out at high temperature. While SCO has the advantage that it does not consume hydrogen, it has the disadvantage that the unconverted oxygen and nitrogen from the C4 hydrocarbon should be removed in an additional separation unit.

Comparing with the above methods, the adsorptive desulfurization has the advantages that it does not only can be operated at relative low temperature and pressure, but also requires no hydrogen. Thus, the adsorptive desulfurization is regarded as one of the most appropriate and promising methods.

In the previous studies, the most extensively studied adsorbent materials were activated carbon and zeolite. Cui and Turn [17]

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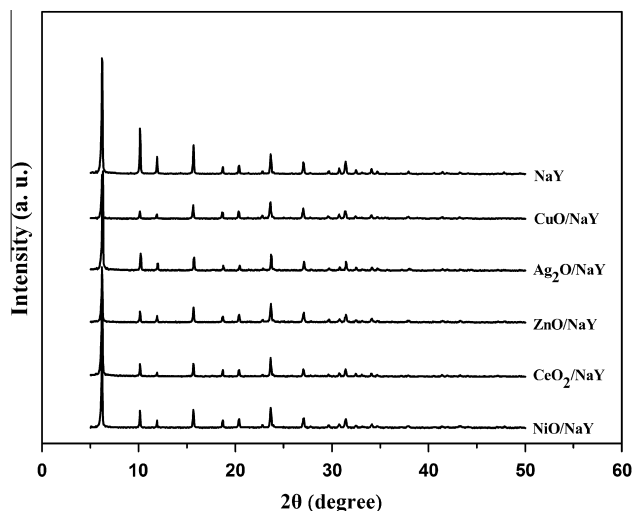


Fig. 1. XRD patterns of NaY and modified NaY.

modified activated carbon (AC) with FeCl_3 solution and reported that it has an improved adsorption capacity for dimethylsulfide (DMS) compared to the unmodified activated carbon. They inferred that the new active sites formed by the modification of FeCl_3 on the carbon surface likely had stronger affinity with DMS molecule, leading to the improvement of the DMS adsorption capacity. Xiao et al. [18] studied the adsorption of dibenzothiophene (DBT) on Ag/Cu/Fe-supported ACs prepared by impregnation method. The results indicated that adsorption capacity followed the order: Ag/AC > Cu/AC > AC > Fe/AC. Activated carbon impregnated with CuCl and PdCl_2 were used to remove methyl mercaptan (MM), DMDS and diethyl disulfide (DEDS) in Fluid Catalytic Cracking (FCC) C4 hydrocarbon mixture by Kim et al. [19]. The breakthrough experiments showed that the sulfur adsorption capacities of the adsorbents decreased in the following order: AC impregnated PdCl_2 , AC impregnated CuCl and non-impregnated AC.

Comparing with activated carbon, zeolites are more widely investigated as the adsorbents for its excellent thermal stability. Wakita et al. [20] have investigated the removal of DMS and t-butylmercaptan (TBM) in the city gas using Na-Y, Na-X, Ca-X, H-Y, USY, H- β and H-ZSM-5 zeolite. They concluded that the adsorption site of Na-Y was the Na^+ in the supercage. Adsorptive removal of DMS and TBM from pipeline natural gas was also efficiently carried out by Satokawa et al. [21] using silver exchanged Y zeolite in the presence of water. They reported that the sulfur removal capacity can be improved by an increase of the silver content. Lee et al. [22] studied the adsorptive removal of tetrahydrothiophene (THT) and TBM using AgNa-Y zeolites. The Ag-Na-Y were also obtained via Ag^+ -exchange, so as to form active adsorption sites (Ag^+ , Na^+ , Ag^0 , H^+ , and Ag_2O). According to the study, they found that the strongest adsorption site was Ag^+ and the adsorption strength of THT on these adsorption sites was higher than that of TBM. Song et al. [23] used transition metal nitrate impregnated β -zeolite (BEA) to remove THT and TBM from city gas. They found that AgNO_3 impregnated BEA showed the highest adsorption capacity among the metal nitrates used.

Gong et al. [24] have investigated the removal of thiophene and DBT in FCC gasoline using Cu(I) and Ag(I) metal exchanged β -zeolite. They reported that both adsorbents had similar sulfur removal capacity, when applied to the model gasoline. However, for the real FCC gasoline, the sulfur removal capacity was reduced greatly. They claimed that the reduction of sulfur removal capacity in real FCC gasoline was caused by the competitive adsorption between sulfur compounds and the olefin or aromatic component present in the real FCC gasoline.

LPG can be regarded as the mixed C3–C4 stream, which contains sulfur compounds and olefin compounds. The major sulfur compound found in LPG is DMDS, which accounts over 80% of total sulfur compounds in the LPG stream. Takatsu et al. [25] investigated the removal of DMDS in LPG by use of activated carbon, $\text{ZnO}/\text{Al}_2\text{O}_3$, Ag-exchanged β -zeolite and Ag/CeO_2 . Among the tested adsorbents, Ag-exchanged β -zeolite showed better adsorption capacity for sulfur compound DMDS. They deduced that the electrostatic attraction between Ag(I) and the sulfur atom of DMDS played a critical role in the adsorption. Nonetheless, the model gas they used contains 98% propane, and the impact of the olefin in LPG was not concerned. In fact, in most cases, the LPG stream is rich in olefin compounds. It is well known that the competitive adsorption between organic sulfur compounds and olefins is one of the crucial factors affecting adsorption selectivity for sulfur containing molecules from real fuels. However, few studies about the impact of olefins on the desulfurization of hydrocarbon fuels are found in the open literatures. Thus, it is necessary to consider the impact of olefin on the adsorption removal of DMDS in LPG.

For the adsorptive desulfurization of disulfide in olefin rich hydrocarbon fuels, Lee et al. [3] investigated the removal of DMDS in the olefin rich FCC C4 hydrocarbon mixture. They used the TPD method to investigate the adsorption strength of DMDS and 1-butene on Ag(I) exchanged β -zeolite. In addition, the Fourier transform infrared (FT-IR) spectroscopy was also applied in the competitive adsorption mechanism study by Tian et al. [11] to investigate the competitive adsorption of thiophene and aromatics, and the results show that it is also an effective means.

In this paper, the removal of DMDS from LPG was investigated by using metal oxide loaded zeolite. The metal elements used were Ag, Cu, Ni, Ce, and Zn. The breakthrough experiments with model solution (1468 ppmw DMDS, i.e. 1000 ppmw S, 50 wt.% petroleum ether and 50 wt.% 1-hexene) were performed to select the best active component of adsorbent for the removal of DMDS. Content of active component and regeneration ability of adsorbent were also investigated. Furthermore, Fourier transform infrared (FT-IR) spectroscopy was employed to study the adsorption behavior of DMDS and olefin on adsorbents.

2. Experimental section

2.1. Material

Analytical reagent grade DMDS (Development of Beijing Chemical Technology Co., Ltd., 99.5%) was selected as the target sulfide. The olefin rich model LPG was prepared with 1000 ppmw of S in 50 wt.% petroleum ether (Sinopharm Chemical Reagent Co., Ltd., boiling range: 30–60 °C) and 50 wt.% 1-hexene (Aladdin Chemistry Co., Ltd., analytical reagent). While the model LPG without olefin was prepared by dissolving a certain amount of DMDS in organic solution petroleum ether to make sulfur content of 1000 ppmw. The real LPG was obtained from PetroChina Co., Ltd., the component of the LPG is ethane (0.802 wt.%), propane (39.71 wt.%), propylene (0.008 wt.%), isobutene (24.848 wt.%), butane-1 (19.972 wt.%), butane-2 (3.332 wt.%), *n*-butane (11.328 wt.%). The sulfur compounds in the LPG were H_2S (5 ppmw), $\text{CH}_3\text{-SH}$ (12 ppmw), $\text{CH}_3\text{CH}_2\text{-SH}$ (15 ppmw), $\text{CH}_3\text{-S-S-CH}_3$ (187 ppmw), $\text{CH}_3\text{CH}_2\text{-S-S-CH}_2\text{CH}_3$ (10 ppmw).

2.2. Adsorbents

The starting material used in this study was sodium type Y zeolite (The Catalyst Plant of Nankai University, Si/Al molar ratio = 5.3) and 13X zeolite (The Catalyst Plant of Nankai University, Si/Al molar ratio = 2.0). Adsorbent $\text{Ag}_2\text{O}/\text{NaY}$ was prepared by

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