

REMOVAL OF BENZOTHIOPHENIC COMPOUNDS FROM HYDROCARBON FUELS USING BIMETAL MESOPOROUS Y ZEOLITES

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Abstract

Adsorptive desulfurization of sulfur compounds, such as benzothiophenes from jet fuel and dibenzothiophenes from diesel fuel can be challenging in the presence of aromatic hydrocarbons. The goal of this work is to demonstrate that adsorptive desulfurization using bimetal-exchanged mesoporous Y zeolites can overcome this challenge, by improving the mass transfer of sulfur adsorption and selectively targeting only sulfur-containing molecules. The introduction of mesoporosity allows sulfur to access the internal active sites, while the metals (Ce and Cu) strengthen the binding energy with sulfur compounds via various modes of adsorption. All materials were characterized using N₂ adsorption/desorption, X-ray diffraction (XRD), temperature program reduction (TPR) and high-resolution transmission electron microscopy (HRTEM). The adsorption experiments were performed in a fixed-bed adsorption column at ambient conditions. Here we will present how bimetallic mesoporous Y zeolite (CeCuSAY) exhibits the highest sulfur capacity in the presence of competing aromatics. The adsorption mechanisms were further studied using *in-situ* Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS).

Keywords

Adsorptive Desulfurization, Selective Adsorption, Zeolites

Introduction

Despite advancement in alternative energy, fossil fuel is still considered the dominant source of energy. Conventional hydrodesulfurization (HDS) has been widely used at the refinery to remove sulfides, mercaptans and thiophenes. The disadvantages of HDS include the use of expensive catalysts and excessive energy. Refractory sulfur compounds, such as 4,6-dimethyldibenzothiophene in diesel requires extremely high H₂ temperature and pressure. Adsorptive desulfurization using zeolites, has been widely studied as one alternative to HDS. In particular, the Y zeolite is an interesting adsorbent due to its highly acidic and microporous nature. Unfortunately, selective removal of refractory sulfur compounds may be challenging due to diffusion limitations and selectivity challenges. Thus, physical and chemical modifications

were performed on the Y zeolite to overcome the aforementioned challenges.

One approach to minimize diffusion limitations is by introducing mesopores via well-controlled modification using templates. Recently, our group, Valla et al. (2017), has successfully engineered metal-exchanged mesoporous Y zeolites, which combined hierarchical pores and metal cations. The goal of our work is to understand the effect of mesoporosity, metal cations and competing aromatic compounds on the overall desulfurization of fuels.

Methods and Materials

Mesoporous Y (SAY) has been prepared using a surfactant-assisted method. Metals, Cu and Ce, were incorporated using ion-exchange technique. Metal-

exchanged mesoporous Y was prepared ion-exchanging SAY with the metal cations. For bimetallic zeolites, Ce was first ion-exchanged, due to higher selectivity at the exchange sites, followed by Cu. The surface area and the micropore and mesopore volume of the zeolites were measured by N₂ adsorption/desorption. Metal phases and crystallinity were identified using X-ray diffraction. *In-situ* IR CO adsorption was also used to identify the topology and the state of each metal species on the support. All dynamic adsorption experiments were performed using fixed-bed column at room temperature and atmospheric pressure. Sulfur compounds in fuels were analyzed using Gas Chromatography equipped with Sulfur Chemiluminescence Detector (GC-SCD) for sulfur concentration. TPD analysis was conducted using *in-situ* DRIFTS to determine the mechanism of sulfur adsorption.

Removal of benzothiophene and dibenzothiophene in the presence of aromatics

Figure 1(a) shows the breakthrough curves of benzothiophene (BT) in a mixture of 80% *n*-octane and 20% benzene on parent and modified Y zeolites. BT breaks through very early on parent Y and reaches saturation within 5 mL/g of feed. When Ce cations were incorporated in the Y zeolite, the breakthrough point was extended to 8.5 mL/g indicating an increase in the adsorption of BT. CuY showed an even higher adsorption capacity of about 12 mL/g. When both Ce and Cu cations were in the Y zeolite, the ability to adsorb BT increase to 15 mL/g of sulfur-free fuel.

Figure 1(b) displays the effect of naphthalene on the desulfurization of DBT. Both SAY and CeSAY displays slightly higher DBT capacity compared to parent Y. The presence of Ce did not improve the desulfurization performance, which can be attributed to the limited accessibility of the metal. CuSAY, on the other hand, drives the adsorption capacity to 20 mL/g; twice the amount of CeSAY and SAY. The best sorbent is still, by far, CuCeSAY with a DBT adsorption capacity of about 45 mL/g. This suggest that the synergistic interaction between Ce and Cu metals plays an important role in the selective adsorption of refractory sulfur compounds, while the mesoporosity yields higher bulk mass transfer to the internal active sites.

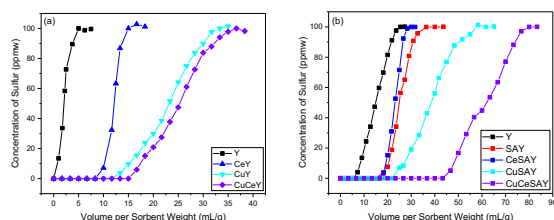


Figure 1. Breakthrough curves of (a) BT in the presence of 20% benzene and (b) DBT in the presence of 1% naphthalene

To better understand the adsorption behavior of the studied sulfur compounds, *in-situ* DRIFTS experiments were performed in a temperature and atmosphere controlled reaction chamber. Figure 2 shows the DRIFT spectra of BT on the tested materials recorded from TPD under vacuum. The spectra in Fig.2(i) suggest a π -complexation interaction between the aromatic character of BT and Cu, while Fig.2(ii) suggests π -complexation in addition to σ -bond between S and Ce. Fig.2(iii) shows the synergy between Ce and Cu. The band at 1425 cm⁻¹ has been shifted lower from 1460 cm⁻¹ ($\nu(\text{C}=\text{C})_{\text{sym}}$ of free BT) due to a decrease in electron density from π -complexation interaction. The band at 1490 cm⁻¹ is a positive shift resulting from an increase in electron density from the σ -bond interaction. The TPD profiles also suggest that higher temperature conditions are required to completely desorb BT, underscoring a stronger binding energy between BT and CuCeY.

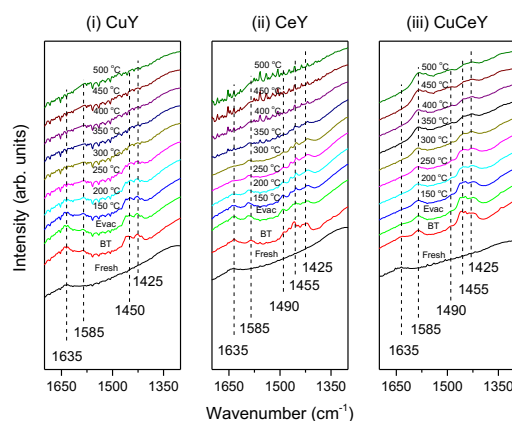


Figure 2. FTIR spectra during BT adsorption and TPD on metal-exchanged zeolites of the sulfuric C=C region

Conclusions

Adsorptive desulfurization using bimetal mesoporous zeolites is a promising sulfur removal process. The experimental results showed that CuCeSAY zeolite produced 45 mL/g of DBT-free solution in the presence of naphthalene, at least two times more than unmodified Y and SAY. While the importance of synergy effects between metals has been demonstrated, the coexistence of both mesoporosity and metal cations must not be overlooked, as the mesopores provide access for bulky sulfur compounds to the sulfur-selective metal cations. This presentation will focus on the roles of mesoporosity and metal cations on sulfur removal in the presence of aromatics.

References

Lee, K., Valla, J.A., 2017. Investigation of metal-exchanged mesoporous Y zeolites for the adsorptive desulfurization

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