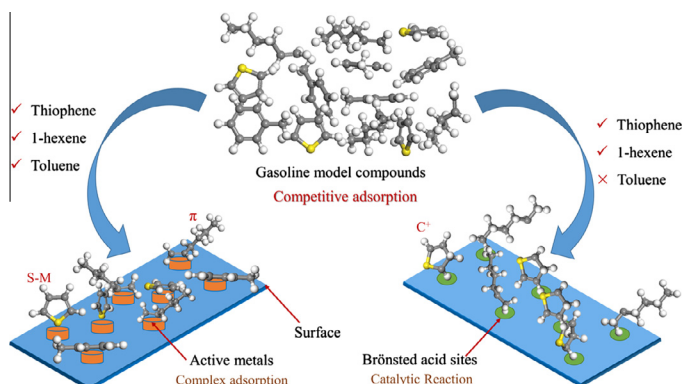Regular Article

Competitive adsorption desulfurization performance over K – Doped NiY zeolite

Haizheng Li, Xiaona Han, Haokai Huang, Yuxian Wang, Liang Zhao *, Liyuan Cao, Baojian Shen, Jinsen Gao, Chunming Xu

State Key Laboratory of Heavy Oil Processing, China University of Petroleum (Beijing), 18 Fuxue Road, Beijing 102249, PR China

GRAPHICAL ABSTRACT

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ABSTRACT

NiY and KNiY were successfully prepared by impregnation method and characterized by X-ray diffraction (XRD), N_2 sorption (BET), scanning electron microscope (SEM), infrared spectrum (IR) and X-ray Photoelectron Spectroscopy (XPS). The competitive adsorption mechanisms of adsorbents were studied by *in situ* FTIR to explain different desulfurization performance which was evaluated in a miniature fixed-bed flow by gasoline model compounds with 1-hexene or toluene. NiY and KNiY adsorbents showed better desulfurization performance than HY zeolite due to the high selectivity of loaded active metals. Especially, KNiY adsorbent showed its advantages in desulfurization performance with 5 vol% olefins or 5 vol% aromatics involvement. It could be assigned that introduced K cation enhanced dispersion and content of active Ni species on the surface which made Ni species reduce easily. On the other hand, adsorption mechanisms showed that the protonation reactions of thiophene and 1-hexene occurred on the Brönsted acid sites of NiY, which resulted in pore blockage and the coverage of adsorption active centers. By doping K cation on NiY, the amount of the Brönsted acid sites of NiY was decreased and protonation reactions were weaken. Therefore, the negative effects of Brönsted acid sites were reduced.

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1. Introduction

Increasing attention has been focused on improving the quality of fuels due to environmental awareness and stringent environmental regulations. An important aspect is to reduce the sulfur

* Corresponding author.
   E-mail address: liangzhao@cup.edu.cn (L. Zhao).

content of gasoline [1]. Conventional hydrodesulfurization can reduce the sulfur content effectively. However, saturation of olefins and loss of RON (octane number) will occur. To avoid these problems, new technologies have been proposed, such as biological desulfurization, oxidative desulfurization, extractive desulfurization and adsorption desulfurization. Among them, adsorption desulfurization is regarded as a promising technology with good desulfurization performance, small investment and no loss of RON [2].

Selective adsorption (SARS) is one of the representative desulfurization technologies, which can remove thiophene-type sulfide under moderate conditions selectively [3]. Various types of adsorbents, including zeolites [4–8], activated alumina [9], boron nitride [10–12] and activated carbon (AC) [13–19] have been well studied. Because of high specific surface area and ordered porous structure, zeolites are considered as promising adsorbents being utilized for the desulfurization of fuels. Salem et al. [20] investigated removal of sulfur compounds from naphtha solutions and found that zeolites 13X showed higher capacity at low concentration ranges.

One of the main concerns of adsorption desulfurization is the competitive adsorption of olefins and aromatics, which can result in the decrease of selectivity and adsorption capacity for sulfur compounds. Recently, studies revealed that by doping active metals such as Ce, La and Ni on zeolites, both selectivity and adsorption capacity could be significantly enhanced. Wang et al. [21,22] studied the effect of olefins and aromatics on the desulfurization efficiency of CeY adsorbent. It was found that in model gasoline containing olefins and aromatics, the selectivity of CeY for thiophene was obviously increased due to a direct interaction between Ce and S. The formation of M—S bond is the best way to improve the selectivity of sulfur in mixture compound [23]. Shi et al. [24] reported the effect of olefin for LaY adsorption desulfurization efficiency and obtained a similar conclusion. Yang et al. [2] proposed another adsorption mode of sulfur content compound as π complexation. For example, Song et al. [25,26] prepared a series of CuCe or AgCe dual-metals modified adsorbents and found adsorbents had a higher selectivity for thiophene than single-metal modification, which was attributed strong interaction between Ag^+ or Cu^+ and thiophene by π complexation. Current research results proved that these two mechanisms of adsorption could effectively enhance the selectivity of desulfurization, however, different active metals could play different role during desulfurization. Researchers also found that NiY was the excellent adsorbent for the removal of sulfur compounds from the fuel [5,27,28]. Hernández-Maldonado et al. [29] used the nickel-exchanged zeolites for adsorption desulfurization of commercial diesel fuels and founded that the NiY zeolites were superior adsorbents for the removal of sulfur compounds. Nevertheless, the function of Ni and the corresponding adsorption mechanism in olefins/aromatics mixture compound over NiY were rarely reported.

Meanwhile, Brönsted acid sites of adsorbents had a negative effect on the adsorption desulfurization for metal modified adsorbent [30], since catalytic reactions of olefins and sulfur contain compounds may occur on the Brönsted acid sites, which resulted in pore blockage and the coverage of adsorption active centers [31–34]. Doping alkali or alkaline-earth metals into the zeolite structures has been proved effective to reduce the amount of Brönsted acid [35]. Mao et al. [36] utilized the MgO-modified HZSM-5 for the direct synthesis of dimethyl ether from syngas. The results showed that modification of HZSM-5 with Mg cation significantly decreased the number of strong Brönsted acid sites and the selectivities for undesired by-products. TynjäLä et al. [37] used Ba cation to adjust the acidic properties of ZSM-5 and also found that introducing Ba cation reduced the amount of Brönsted acid sites. However, adsorbents modified by alkali or alkaline-earth metals and utilized for adsorption desulfurization were

rarely reported. Furthermore, the corresponding adsorption mechanism and function of alkali metals were never been concerned.

In this paper, NiY adsorbents were prepared by incipient wetness impregnation. To reduce the amount Brönsted acid sites and improve the desulfurization performance of NiY, K cation was doped within the as-synthesized NiY structure. The as-prepared adsorbents were characterized by XRD, BET, SEM, IR and XPS. Effects of 1-hexene or toluene on adsorption desulfurization capacity of NiY and KNiY are investigated and the adsorption mechanisms are studied by *in situ* FT-IR spectroscopy.

2. Experiment

2.1. Synthesis of adsorbents

The HY zeolite was purchased from the Catalyst Plant of Nankai University (SiO_2/Al_2O_3 = 5.2). $Ni(NO_3)_2·6H_2O$ and KNO_3 were loaded on HY by incipient wetness impregnation using HY zeolites. In a typical synthesis of NiY adsorbent, 5.96 g $Ni(NO_3)_2·6H_2O$ was dissolved in a 7 mL, 0.4 M citric acid solution. Then the solution was added to the HY zeolite dropwisely under constant stirring. After stirring for 4 h, the sample was kept in an oven at 120 °C for 6 h followed by calcining in the air at 450 °C for 6 h. The NiY adsorbents were obtained by screening the calcined samples to 40–60 mesh. In the process of KNiY adsorbent synthesis, the weight of $Ni(NO_3)_2·6H_2O$ and KNO_3 was 5.96 g and 0.43 g, respectively.

2.2. Model compounds

The performance of the adsorbents was evaluated by gasoline model compounds. The detailed compositions of the gasoline model compounds (denoted as MG-1, MG-2, and MG-3, respectively) were listed in Table 1.

2.3. Characterization of adsorbent

X-ray diffraction (XRD) was used to characterize the crystal structure and metal dispersion on a Bruker D8 advance-X-ray diffractometer using Cu Kα radiation under the setting conditions of 40 kV, 30 mA. The morphology of the samples was observed by Cambridge S-360 scanning electron microscope (SEM). The N_2 adsorption-desorption isotherms of the adsorbents were measured at −196.15 °C using a Micromeritics ASAP 2020. Prior to testing, the samples were degassed at 120 °C. The specific surface areas of the adsorbents were obtained by BET (Brunauer Emmett Teller) method and the micropore specific surface areas and micropore volumes were measured by t-plot method. Framework vibrations of the samples were recorded on a Fourier transform infrared (FT-IR) spectrometer by scans of 32 with a resolution of 4 cm^{-1} at room temperature. To identify the chemical state and surface compositions of NiY and KNiY adsorbents, X-ray Photoelectron Spectroscopy (XPS) spectra of the adsorbents were obtained by using a Thermo Fisher K-Alpha analyzer. Acid amount and acid type of adsorbents were obtained by Py-FTIR adsorption on the

Table 1
Composition of the model gasolines.

No.	Component	1-hexene or toluene content (vol%)	Sulfur content (mg/L)
MG-1	Thiophene + cyclohexane		52.3
MG-2	Thiophene + 1-hexene/cyclohexane	5.0	45.6
MG-3	Thiophene + toluene/cyclohexane	5.0	48.5