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Modified and ion exchanged clinoptilolite for the adsorptive removal of sulfur compounds in a model fuel: New adsorbents for desulfurization

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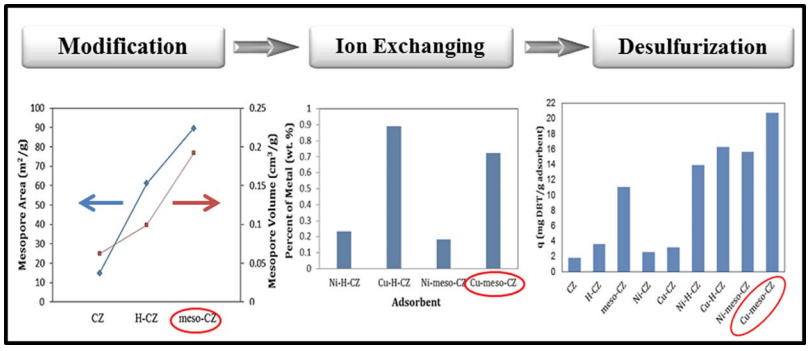
GRAPHICAL ABSTRACT



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ABSTRACT

In this research, modified and ion exchanged natural clinoptilolite (CZ) were prepared for adsorptive desulfurization of refractory dibenzothiophene (DBT) and 4,6-dimethyl dibenzothiophene (4,6-DMDBT) sulfur compounds in a model fuel. For this purpose, H-form (H-CZ) and mesopore (meso-CZ) clinoptilolite were prepared and then ion exchanged with Cu^{+} and Ni^{2+} cations. The raw and treated samples were characterized by X-ray diffraction (XRD), X-ray fluorescence (XRF), FTIR spectroscopy and N_2 adsorption-desorption (BET) analysis. The obtained surface areas of CZ, H-CZ and meso-CZ were 19.6, 249.71 and 194.65 m^2/g, and their obtained total pore volumes were 0.0644, 0.1869 and 0.2404 cm^3/g, respectively. In Ni^{2+}- and Cu^{+}-exchanged adsorbents due to presence of d-electrons, sulfur compounds interact with the cations through π-complexation which resulted in significant increase adsorption capacity of ion exchanged samples, compared to parent samples. The experimental data were analyzed using Langmuir, Freundlich, Langmuir-Freundlich (L-F) and Dubinin-Radushkevich (D-R) isotherms. For adsorption of DBT onto all adsorbents, L-F was the best-fitting isotherm to the experimental data. Due to high surface area and mesopore volume, large pore width, higher ion exchange compared to Ni-meso-CZ, and also formation of π-complexation between sulfur atom and Cu^{+} cation, Cu-meso-CZ gives the best results for removal of DBT (28.12 mg DBT/g adsorbent) based on L-F isotherm. In addition, the effect of solvent and sulfur compound on adsorption capacity of adsorbents and regeneration of them were investigated by thermal method.

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1. Introduction

High rates of the crude oil, including diesel oil and gasoline, are used widely in different transportation applications. In addition, both diesel and gasoline fuels are suitable for using in fuel cells due to several reasons, such as: high energy associated with them, their availability, simple storage, and safety issues that are easy to handle. But such fuels contain high contents of sulfur impurities, mainly in the form of organic sulfur compounds [1–3]. Accordingly, there are numerous problems in the environment; for instance, acid rain and higher contents of sulfuric oxides that are responsible for lowering the efficiency of the catalytic converters. Thus, some countries imposed a series of shared specifications or standards on using most of the fuels in order to reduce the level of fuel emissions. The Environmental Protection Agency (EPA) of USA was aimed at reducing sulfur level of highway diesel fuel to less than 15 ppmw by 2010. Moreover, the European Committee for Standardization developed standards to set the maximum sulfur content around 10 ppmw, in 2009. These standards faced refineries with major challenges in reaching the new specifications of allowed sulfur contents of diesel fuel [4,5].

Hydrodesulfurization (HDS) is a catalytic process that is commonly used for reducing sulfur compounds in hydrocarbons. However, this process is associated with using extremely high temperature (up to 400 °C) and pressure (up to 100 bars) conditions and extensive catalysts. [6,7]. Thus, due to high cost and different limitations that are associated with HDS process, alternative or supplement technologies are increasingly selected in the petroleum industry. These include adsorptive desulfurization, extractive desulfurization, biological sulfur removal, oxidative desulfurization and membrane desulfurization. The main goal of such technologies is to find an effective alternative for desulfurization of low reactive sterically hindered alkyl DBTs that hardly can be removed in HDS process [8].

The adsorptive desulfurization process is one of the best economically attractive and environmentally friendly techniques. This is due to their simple operating conditions, availability of economical and regenerable sorbent materials. Most of the used adsorbents can be regenerated easily either by thermal processes or washing with a solvent. [9,10]. So far, different adsorbents are used in the adsorptive desulfurization processes. Some of these adsorbents are as follows: metallic oxides such as TiO_2, alumina, silica, alumina-silica [11–13], zirconia-silica [14], metal organic framework (MOF) [15], activated carbon [16]; commercial adsorbents like CDX [17]; and different synthetic zeolites, such as Beta [18], Na-X, 13X [19], ZSM-5 [20], MCM-41, SAB-15 [21], and Na-Y [2,22–24] zeolites.

Among various adsorbents that have been investigated so far, metal ion exchanged zeolites have excellent results for sulfur removal. V.M. Bhandari et al. studied adsorptive desulfurization of refractory sulfur compound using model diesel and they found that level of sulfur removal with Ni-Y and Cu-Y obtained 42 mg/g and 31 mg/g, respectively [25]. D.C.S. Azevedo et al. showed that maximum adsorption capacity of thiophene on Na-Y, Zn-Y, Ni-Y and Ag-Y zeolites (adjusted by L-F equation) are 3.32, 4.61, 4.70 and 5.43 mmol S/g, respectively [24]. In addition, W.-m Cai and et al. investigated the adsorption of DBT on Ce-Ni-Y zeolite. The maximum adsorption capacity of DBT for this adsorbent was 22 mg S/g [26]. Ralph T. Yang et al. examined maximum capacity of sulfur compound by three adsorbent. According to Langmuir-Freundlich isotherm, maximum adsorption capacity of DBT with activated carbon, $AgNO_3$/MCM-41, and Cu(I)Y obtained 0.51, 0.87 and 1.3 mmol S/g, respectively [27]. JU Shengui et al. studied the modified 13-X for removal of different sulfur compound. To do so, 13-X zeolite was loaded by Cu and La-Cu metals. Maximum adsorption capacity of benzothiophene on Cu-13-X and La-Cu-13-X were 179.8 and 197.3 mg/g, respectively [19]. The study of isothermal adsorption of benzothiophene on Cu-Ce-Y zeolite was conducted by Hua Song et al. and the maximum adsorption capacity at 30 °C was 1.189 mmol S/g [28]. Hua Song et al. also investigated the adsorption of thiophene (TP) and bezothiophene (BT) on Ag-Ce-Y zeolite and the maximum adsorption capacity of TP and BT at 30 °C was 0.392 and 0.660 mmol S/g [29].

In addition to aforementioned adsorbents, there are also a few reports that studied the use of natural adsorbents for adsorptive desulfurization process, including natural adsorbents studied so far: Bentonite [30,31], Montmorillonite [32], Kaolinite [33], Vermiculite [34], Charcoal [33] and Natural Zeolites [35,36]. Among them, due to features such as ion-exchange properties, high chemical and thermal resistance, porous structure and also very cheap price and access to its abundant sources in Iran and elsewhere in the world, Natural Zeolites can be used as an efficient adsorbent in adsorptive desulfurization process. Natural zeolites generally have greater thermal stability and better resistance to acid environments than many common commercial synthetic adsorbents [37–40]. Some of the application areas of natural zeolites are: 1) as a cation exchanger and adsorbent for removing heavy metals, ammonia-nitrogen [40,41], dyes [42] and other pollutants from water and wastewater [40], 2) as a catalyst in refinery and petrochemical processes such as catalytic cracking, hydrocracking and isomerization of hydrocarbons [43–45], 3) in dehydration and rehydration, 4) in biological reactivity, 5) anaerobic digestion processes, 6) purification and separation of gases and etc. [46–49]. In previous studies, it has been proved that clinoptilolite is an effective adsorbent for removal of hydrogen sulfide and sulfur dioxide [49]. However, very few studies have been carried on natural zeolites in the process of removing sulfur from liquid fuels. In 2010 Al-Ghouti et al. investigated the effect of particle size of chabazite natural zeolite on adsorption capacity of sulfur compounds from diesel fuel. They showed that smaller particles have better results in sulfur removal. Based on the Langmuir adsorption isotherm, the maximum sulfur adsorption capacity for chabazite with mesh size between 100 and 200 was 7.15 mg S/g [35]. In addition, in 2016, Falamaki and Mahmoudi assessed the adsorptive desulfurization using clinoptilolite. In this study, the influence of the ratio of Si/Al on the adsorption of thiophene (TP), benzothiophene (BT) and dibenzothiophene (DBT) was investigated. The results indicated 10.4 as an optimal ratio. Moreover, for optimum adsorbent, maximum adsorption capacities of TP, BT and DBT, using Langmuir isotherm, were 6.33, 3.6 and 2.7 mg S/g, respectively. The maximum adsorption capacity of DBT for optimum adsorbent was approximately 2 times more than not-dealuminated Ni^{2+}-ion-exchanged or raw clinoptilolite [36].

One crucial factor in the adsorption of thiophenic compounds with large molecular size (like DBT and its derivatives) is the surface area, porosity, and pore size of the adsorbent. Unfortunately, clinoptilolite naturally has a low porosity and surface area. Thus, a series of pretreatments are necessary to solve these defects. There are several ways to improve physical and chemical properties, particularly porosity of natural zeolite:

- Modification of natural zeolite with a solution of inorganic salts like NaCl, $FeCl_2$, NH_4Cl, surfactants and etc. [39,50–52].
- Treatment with acidic or basic solutions such as HCl, HNO_3, oxalic acid, phosphoric acid, NaOH, KOH and etc. [38,39,53].
- Preparation of H-forms natural zeolite (H-CLN) by using one of the following methods: acid leaching or ammonium exchange-calcination [38,54,55].
- Synthesis of mesopore natural zeolite by sequential acid-base treatment [56,57]

Among these methods, preparation of H-forms and mesopore natural zeolite is very effective method to improve porosity, surface area and other physical characteristics of this adsorbent. The use of ammonium exchange-calcination method for preparation of H-forms zeolite compared to acid leaching brings about less damage to structure of zeolite and results in more preserved zeolite crystallinity [36,38]. Also, existence of mesopores in zeolite structure dramatically increases access of larger molecules (like DBT and its derivatives) to active sites of adsorbent [58].