



The enhanced adsorption of dibenzothiophene onto cerium/nickel-exchanged zeolite Y

Juan Wang^a, Fang Xu^b, Wei-jie Xie^c, Zhi-jian Mei^b, Qiu-zhuo Zhang^a, Jun Cai^b, Wei-min Cai^{a,b,*}

^a School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, PR China

^b School of Environmental Science and Engineering, Shanghai Jiao Tong University, Dongchuan Road 800#, Shanghai 200240, PR China

^c Navy Submarine Academy, Qingdao 266071, PR China

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ABSTRACT

The investigations for selective adsorption of dibenzothiophene (DBT) over Ce/Ni-loaded Y zeolites with the emphasis on the effect of Ce as a cocation in the Ni-loaded Y zeolite are carried out in an attempt to produce more effective adsorbents for the desulfurization from transportation fuels. The promotional effects of Ce and coexisting toluene in the model fuel as well as contact time and adsorbent dose on the adsorptive performance were examined. The sulfur uptake strongly depends on the amount of Ce in the zeolite structure. The sorption data is varied according to both Langmuir and Freundlich isotherm models. The maximum sorption capacity by theoretical calculation is 22.2 mg/g at 25 °C. The Langmuir constants $b = 5.82$ mL/mg and the Freundlich constants $K = 1.042$ L/mg and $1/n = 0.4$ are evaluated. Ni/Ce-loaded Y zeolites (NiCeY) and NiY, CeY, NaY zeolites were used as adsorbents for the removal of DBT from model fuel containing 500 mg/L sulfur with 5 vol% of toluene by a batch method under ambient conditions. NiCeY exhibits higher adsorptive selectivity for DBT than NiY and CeY, indicating that NiCeY is a more effective adsorbent to remove sulfur compounds from transportation fuels.

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1. Introduction

Recently, more stringent regulations have been mandated [1,2] to further reduce the sulfur level in transportation fuels for the purposes of environmental protection around the world. Besides detrimental environmental effects, sulfur compounds in transportation fuels can poison both catalytic conversion automobile catalysts and fuel cell reformer catalysts. Thus, processes for their removal have been widely explored. Hydrodesulfurization (HDS), the conventional process to desulfurization of transportation fuels, is efficient in removing thiols and sulfides but less effective for the refractory sulfur compounds (e.g. dibenzothiophene) present in the fuels. To meet the new specifications in sulfur content in transportation fuels, the increase of the operating temperature and pressure are required, which would cause significant reduction of octane number and consume more hydrogen due to hydrogenation

of olefinic and aromatic molecules. Therefore, alternative technologies [3–22] have been developed to meet the urgent needs of clean fuels in recent years.

One of the promising new approaches is selective adsorption which can be performed at ambient temperatures and pressures. The key challenge of this approach is the development of adsorbents with high adsorption capacities and selectivities for sulfur compounds over other aromatic and olefinic compounds. Among the various types of porous materials reported in refs. [3–9], zeolites are important alternatives as adsorbents due to their high ion-exchange and size-selective adsorption capacities as well as thermal and mechanical stabilities. Zeolites such as 13X [10], ZSM-5 [11–13], HY [14,15] have been studied in desulfurization of transportation fuels. During the last decade, Yang and co-workers [16–19] reported that cation-exchanged Y zeolites, Cu(I)Y, AgY and NiY, are selective for the removal of sulfur compounds in fuels by π -complexation of sulfur compounds with the transition metal cations in the zeolites. Song and co-workers [20–22] reported that cation-exchanged Y zeolites (Cu, Ni, Zn, Pd and Ce) are effective for the adsorption of sulfur.

Among previous experimental works of zeolite-based desulfurization of liquid fuels, no researchers have studied co-exchanged Ni and Ce on Y zeolite in the application of transportation fuels desulfurization. Ni²⁺, which has the valence electronic configura-

* Corresponding author at: School of Environmental Science and Engineering, Shanghai Jiao Tong University, Dongchuan Road 800#, Shanghai 200240, PR China.

E-mail addresses: wjuan2005@hotmail.com (J. Wang), xu.fang.zh@hotmail.com (F. Xu), wjxie64@hotmail.com (W.-j. Xie), meizhijian007@hotmail.com (Z.-j. Mei), zhangqiuzhuo@126.com (Q.-z. Zhang), juncail@sjtu.edu.cn (J. Cai), cai.wm@yahoo.cn (W.-m. Cai).

Nomenclature

b	the Langmuir adsorption equilibrium constant (L/mg)
C_0	the concentration of the initial solution (mg/L)
C_e	the equilibrium sulfur concentration in solution (mg/L)
K, n	the Freundlich adsorption equilibrium constant
m	the grams of the composite adsorbent (g)
q	sulfur adsorption capacity (mg/g)
q_m	the maximum adsorption capacity of sulfur (mg/g)
V	the volume of the liquid phase (mL)

Greek symbol

η	sulfur removal (%)
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tion $3d^8 4s^0$, is well known for its π -complexation ability [23]. Ce^{4+} , with the valence electronic configuration $4f^0 5d^0 6s^0$, has high positive charge and polarizability. Sulfur compounds are adsorbed over CeY by a direct S–adsorbent (S–M) interaction [19]. NiCeY, which can be bound with organic sulfur compounds through the following two adsorption modes: π -complexation and direct coordination via S atoms and Ce ion, will exhibit higher selectivities and adsorption capacities for sulfur compounds.

Therefore, the objective of this paper is to investigate adsorptive desulfurization over Ce/Ni-loaded Y zeolites with the emphasis on the effect of Ce as a cocation in the Ni-loaded Y zeolite on the removal of dibenzothiophene (DBT) from model transportation fuels. Adsorptive desulfurization of simulated fuels was conducted in a batch reactor to evaluate the performance of the Ni/Ce-based adsorbent and to understand the fundamental adsorption mechanism. Adsorptive selectivity for DBT and effects of the coexisting aromatics as well as adsorption conditions on the adsorptive performance were studied in detail.

2. Experiment

2.1. Sample preparation

NaY zeolite (Si/Al = 5, Shanghai Hengye Chemical Corporation) with an ion-exchange capacity of 2.62 mmol/g was used as the starting material for preparation of the adsorbent samples. NiY zeolites were prepared by liquid-phase ion-exchange of the NaY with 0.1 mol/L $Ni(NO_3)_2$ solution at 80 °C for 6 h. After ion exchange, the zeolite suspension was filtered, washed thoroughly using deionized water, dried at 90 °C for 24 h, and then calcined at 450 °C for 6 h in air atmosphere to dehydrate. This ion exchange procedure was carried out twice without intermediate calcination [20]. The NiCeY zeolites were prepared by ion exchanging the NiY zeolite with $Ce(NO_3)_3$ solution as described above. NiY (5 g) was treated with 500 mL $Ce(NO_3)_3$ solutions of 0.01, 0.05, 0.1, 0.2 and 0.5 mol/L at 80 °C for 6 h, respectively. The Ce loading values of these samples were 0.665, 0.671, 0.748 and 0.762 mmol/g, respectively.

2.2. Reagents and standards

The simulated solutions of hydrodesulfurized fuel were prepared by dissolving a certain amount of dibenzothiophene (DBT) in *n*-octane. Because the main aromatics species presenting in commercial gasoline are alkyl benzenes, toluene is selected to be the model aromatic compound in this study. DBT used for preparing the model fuels was purchased from Sigma–Aldrich and used without further purification. Toluene and *n*-octane are all analytical reagent

grades. According to the actual sulfur content in transportation fuels of China, two sets of model solutions containing DBT with an initial concentration of 500 mg/L (ca. 87 mg/L S), without and with toluene, were prepared in *n*-octane and used as a model solution of transportation fuel.

2.3. Adsorption experiment

Adsorption experiments were carried out at room temperature in a stirred batch system. Before these experiments, kinetic studies were performed to determine the equilibration time. The model solution (20 mL) and the ion-exchanged zeolite (0.1 or 0.2 g) were mixed in a flask (50 mL) and the covered flasks were placed in a shaking bath and allowed to shake for a desired time at 25 °C. The treated liquid was then separated from the adsorbent and the DBT concentration in the solution was analyzed by a Shimadzu GC2010 sulfur analyzer equipped with a DB-5MS capillary column (30 m \times 0.32 mm \times 0.25 μ m) and a flame photometric detector (FPD).

The sulfur adsorption capacity (q) and sulfur removal (η , %) were calculated by using the following expressions [24,25]:

$$q = \frac{V \times (C_0 - C_e)}{m} \quad (1)$$

$$\eta = \left[\frac{C_0 - C_e}{C_0} \right] \times 100 \quad (2)$$

wherein V is the volume of the liquid phase, C_0 is the concentration of the initial solution, C_e is the concentration of the solution in equilibration, and m is the grams of the composite adsorbent.

2.4. Chemical and physical analyses

Chemical compositions of the ion-exchanged zeolites were determined by ICP elemental analysis using a high-resolution magnetic sector ICP-MS spectrometer (Iris Advantage 1000) after they were melted in HF acid. X-ray powder diffraction (XRD) patterns for the zeolites were collected in the 2θ range 5–50° using a D/max-2200/PC XRD instrument (Japan Rigaku Corporation) equipped with Cu K α radiation. The BET surface areas of the samples were measured by physical adsorption of N_2 at –196 °C using Micromeritics ASAP 2010 system. Pore size distribution and pore volume determinations were also analyzed by N_2 adsorption at –196 °C. Pore size distributions were calculated with the Horvath–Kawazoe equation.

3. Results and discussion

3.1. Characterization of ion-exchanged zeolites

Powder XRD patterns of metal-ion-exchanged zeolite samples after calcination have been collected in order to investigate whether the zeolite structure is retained after metal exchange (Fig. 1). The similarity in the XRD patterns and lattice parameter a_0 values of NiCeY, CeY, NiY to the original NaY indicates that the original zeolite structure is retained without any significance change upon cerium and nickel ion exchange followed by heat treatment. The Ni-exchanged zeolite has a greenish color at the end of ion exchange process and pinkish white after drying. In the case of Ce^{3+} -exchanged adsorbent, the color of CeY changed from white to light yellow after the calcination at 450 °C in air. On the basis of X-ray photoelectron spectroscopy, the color change corresponds to the oxidation of Ce^{3+} to Ce^{4+} [26,27]. The color behavior of the zeolites agrees with that reported in the literature [19,26,27].

The chemical compositions of original and ion-exchanged zeolites are summarized in Table 1. The molar ratio M^{n+}/Al^{3+} , where

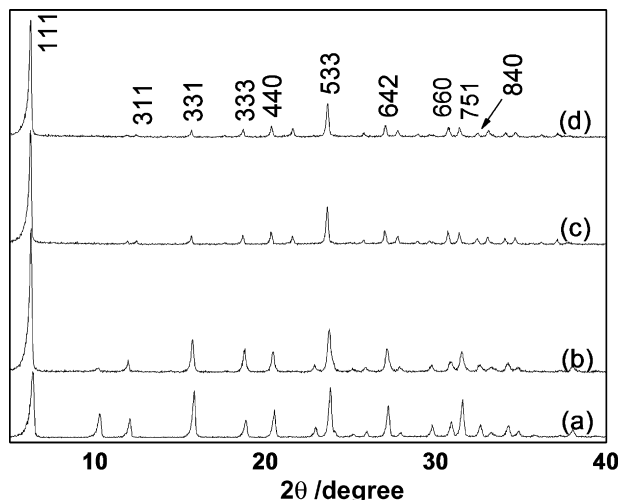


Fig. 1. XRD patterns of (a) original NaY-zeolite, (b) NiY-zeolite, (c) CeY-zeolite, (d) NiCeY-zeolite. All the samples were calcined at 450 °C for 6 h.

M^{n+} is the metal ion-exchanged, indicates the number of metal ions-exchanged per ion-exchangeable site. In case of Ni^{2+} exchange in NiY zeolite, if one Ni^{2+} compensates for two aluminum tetrahedral, then the ratio $2Ni^{2+}/Al^{3+} = 0.82$ indicates the cation-exchange capacities achieved in the exchange with Ni^{2+} are 82% in the present study. In the ion exchange with Ce^{3+} of CeY zeolite, for our case, the ion exchange resulted in 75% ($3Ce^{3+}/Al^{3+} = 0.75$) substitution of the original sodium ions for CeY assuming that each Ce^{3+} ion compensates three aluminum tetrahedrals. For NiCeY, Ni or Ce ion-exchange ratio were 22.8 or 68.7%, respectively. The ratio of $(Na + 2Ni + 3Ce)/Al$ is calculated as 1.28, which is close to the original Na/Al of 1.021, indicating that $Ni^{2+}-Ce^{3+}/Na^+$ exchange reaction progresses nearly stoichiometrically.

Both the BET surface and pore volume decreased when Na^+ was ion-exchanged by Ni^{2+} and Ce^{3+} , but not significant (Table 1). The mean pore radius is around 0.93 nm, regardless of the kind of metal and the amount of metal ion exchange.

3.2. Effect of contact time

The effects of stirring time on the sulfur adsorption over NiCeY at 25 °C in sulfur model solutions, without toluene and containing 5 vol% toluene, are shown in Fig. 2. It shows that the adsorption processes are fast and most of the sulfur compounds are adsorbed within 1 h. For the model solution without toluene, the DBT uptake reaches 54% after treatment for 30 min and the adsorption equilibrium is achieved after treatment for 2 h. Under this experimental condition, the sulfur adsorption capacity is above 9 mg/g, and increases to 11 mg/g when adsorption time reaches 2 h. However, the addition of 5 vol% toluene decreases the DBT uptake to 43% and the sulfur adsorption capacity to 6.8 mg/g.

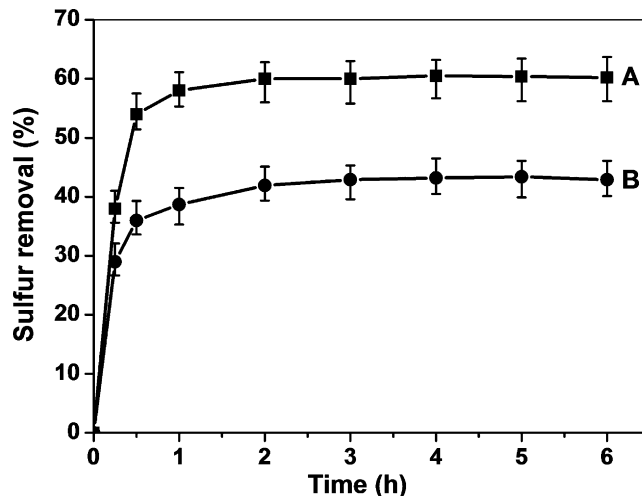


Fig. 2. Effect of contact time on uptake of DBT from DBT/n-octane (A) and DBT/toluene/n-octane (B) solutions. Temperature: 25 °C; adsorbent-to-solution ratio: 0.1 g/20 mL; concentration of DBT: 500 mg/L.

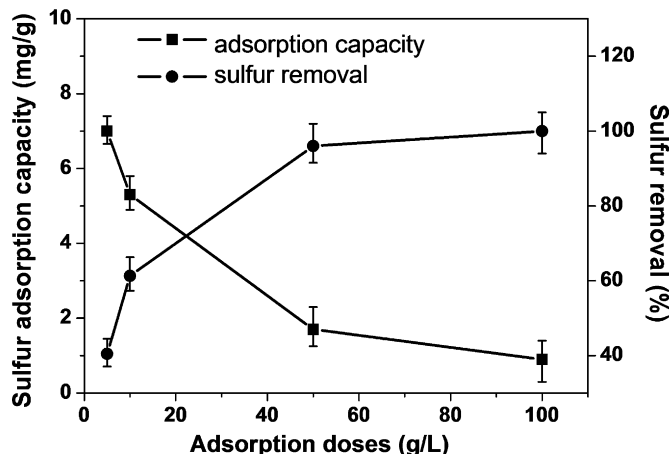


Fig. 3. Effect of adsorbent dose on uptake of DBT. Temperature: 80 °C; volume of model solution: 20 mL; concentration of DBT: 500 mg/L (without toluene); contact time: 3 h.

3.3. Effect of adsorbent dose

The influences of adsorbent dose on the uptake and removal of DBT are shown in Fig. 3. When the adsorbent dose increases from 5 to 100 g/L, the sulfur removal increases from 40 to 100% and the sulfur adsorption capacity decreases from 7.0 to 0.9 mg/g. Obviously, the equilibrium sorption capacity and removal percentage are sensitive to the adsorbent dose variation.

Table 1

Chemical and physical properties of metal-ion-exchanged Y-zeolites after calcination

Zeolite	Chemical composition (mmol/g)				Molar ratios			S_{BET} (m^2/g)	V_p (cm^3/g)	r_p (nm)
	Al	Na	Ni	Ce	Na/Al	Ni/Al	Ce/Al			
NaY	3.474	3.547	–	–	1.021	–	–	600	0.28	0.93
CeY	3.138	0.4	–	0.816	0.128	–	0.260	600	0.27	0.90
NiY	3.409	0.452	1.498	–	0.133	0.439	–	585	0.26	0.89
NiCeY	3.190	1.165	0.364	0.730	0.365	0.114	0.229	568	0.25	0.88

NiCeY: Obtained by ion-exchange with NiY and 0.1 mol/g $Ce(NO_3)_3$ solution.

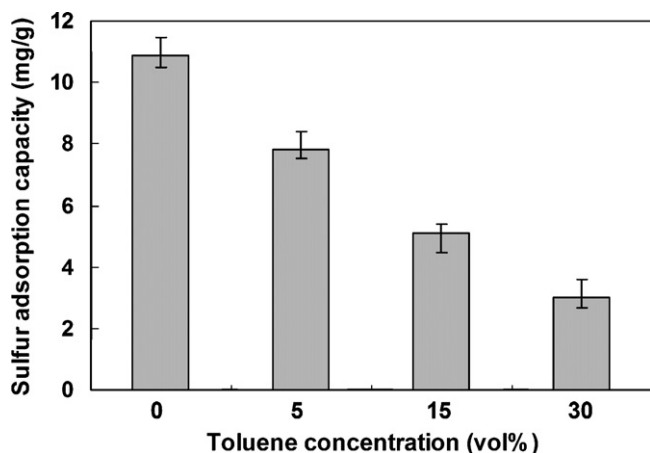


Fig. 4. Effect of aromatics on sulfur adsorption capacity. Temperature: 25 °C; adsorbent-to-solution ratio: 0.1 g/20 mL; concentration of DBT: 500 mg/L; contact time: 3 h.

3.4. Effect of aromatics

Apart from the organic sulfur compounds presented at the several-hundred-ppmw level, a certain amount of aromatics (less than 40 vol%) also exists in commercial fuels. It is necessary to investigate the effect of aromatics on sulfur removal efficiency. In this section, three different toluene concentrations (vol%) are employed, viz. 5, 15 and 30 vol% toluene in the model fuel (500 mg/L DBT). The effect of toluene and the reduction in sulfur adsorption capacity is presented in Fig. 4. The results show that there exists drastic reduction in sulfur adsorption capacity with increased aromatics concentration. In the case of 5 vol% toluene, the sulfur adsorption capacity decreases from 10.9 mg/g without toluene to 7.8 mg/g. When the concentration of toluene is 30 vol%, the adsorption capacity dropped to just 4.3 mg/g. This phenomenon is caused by the competitive adsorption between DBT and toluene, both of which have similar aromatic skeleton structure. The same result for the influence of aromatics on sulfur removal was also reported [28].

3.5. Effect of Ce

To study the effect of Ce content on the sulfur adsorption performance, five kinds of NiCeY with Ce loadings of 0.665, 0.671, 0.730, 0.748 and 0.762 mmol/g, were prepared, respectively, by liquid-phase ion-exchange treatment of NiY with Ce(NO₃)₃ solution, and their sulfur adsorption performances were evaluated at room temperature in a batch reactor. The Ce exchange was performed, respectively, in 0.01, 0.05, 0.1, 0.2 and 0.5 mol/L Ce(NO₃)₃ solution, as evidenced from the ICP analysis data. The chemical compositions of NiCeY zeolite are summarized in Table 2. It can be seen that, the contents of Ce in NiCeY increased with Ce(NO₃)₃ concentration increase, and the content of Ni decreased slightly, indicating that Ni can be leached in the Ce ion-exchange procedure but not significantly.

Table 2
Composition data for NiCeY zeolites obtained from ICP

Concentration of Ce(NO ₃) ₃ (mol/L)	Chemical composition (mmol/g)			
	Al	Na	Ni	Ce
0.01	3.160	1.225	0.426	0.665
0.05	3.004	0.833	0.372	0.671
0.1	3.190	1.165	0.364	0.730
0.2	3.120	1.005	0.357	0.748
0.5	3.222	0.891	0.354	0.762

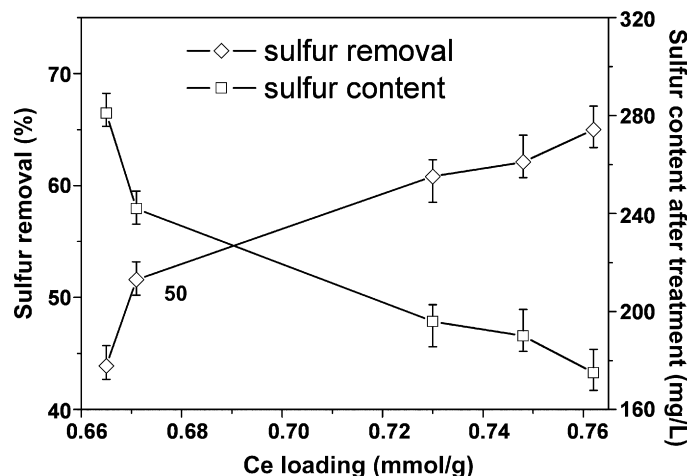


Fig. 5. The variation of DBT uptake on different Ce-loaded NiCeY zeolites. Temperature: 25 °C; adsorbent-to-solution ratio: 0.1 g/20 mL; concentration of DBT: 500 mg/L; contact time: 3 h.

The effect of Ce loading on the adsorptive properties for DBT is shown in Fig. 5. The DBT removal from the model solution increases from 44 to 65% and the sulfur content of model solution decreases from 281 to 175 mg/L with the increase of Ce loading from 0.665 to 0.762 mmol/g, which indicates that increasing Ce loading of NiCeY can further enhance its adsorptive capacity for organic sulfur compounds.

As can be seen, the sulfur adsorption capacity increases from 44% for NiCeY containing 0.665 mmol/g Ce to 65% for NiCeY containing 0.762 mmol/g Ce. Therefore, the increase of the Ce loading can enhance NiCeY sulfur adsorption efficiency. The improved sulfur adsorption performance of Ce-containing NiY indicates that the Ce as a cocation plays a promoting role in sulfur adsorption.

3.6. Adsorption isotherms

The Langmuir model is developed to represent chemisorption on a set of well-defined localized adsorption sites having the same sorption energies independent of surface coverage and no interaction between adsorbed molecules. The Langmuir equation is represented in the linear form [29]:

$$\frac{C_e}{q} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (3)$$

wherein q is the sulfur adsorption amount at equilibrium (mg/g), C_e is the equilibrium sulfur concentration in solution (mg/L), q_m is the maximum adsorption capacity (mg/g), and b is the Langmuir adsorption equilibrium constant (L/mg). Maximum sorption capacity (q_m) represents monolayer coverage of adsorbent with sorbate and b represents the affinity between the adsorbent and sorbate [30]. As shown in Fig. 6, the plot of C_e/q versus C_e yielded a straight line. From the slope and intercept, the values of q_m and b might be estimated to be 22.2 mg/g and 5.82 mL/mg, respectively, with a correlation coefficient of 0.9946. It demonstrates that the experimental data fit the Langmuir adsorptive isothermal equation very well.

The Freundlich sorption isotherm gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies. The linearized form of Freundlich sorption isotherm [31] is:

$$\log q = \log K + \frac{1}{n} \log C_e \quad (4)$$

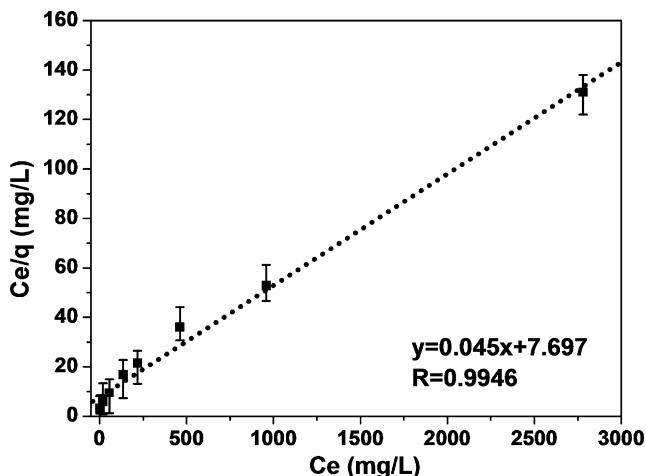


Fig. 6. Langmuir isotherm at 25 °C. Adsorbent-to-solution ratio: 0.2 g/20 mL; contact time: 3 h.

wherein q is the equilibrium sulfur adsorption amount (mg/g), C_e is the equilibrium sulfur concentration in simulated solution (mg/L) and K and n are the equilibrium constants indicative of adsorption capacity and adsorption intensity, respectively. From the fitting of experimental data by plotting $\log q$ against $\log C_e$, the values of K and n for the DBT adsorption are evaluated as 1.0421 L/mg and 2.47, respectively, with a correlation coefficient of 0.9917. The plot is displayed in Fig. 7. It shows that the adsorption of DBT onto NiCeY conforms to the Freundlich isothermal model as well. The numerical value of $1/n < 1$ ($1/n = 0.4$) indicates that sorption capacity is only slightly suppressed at lower equilibrium concentration. This isotherm does not predict any saturation of the adsorbent by the sorbate thus infinite surface coverage is predicted mathematically, indicating a multilayer sorption of the surface [19,32].

3.7. Selective adsorption of DBT

The liquid hydrocarbon fuels contains not only sulfur compounds but also a large number of aromatic compounds which have an aromatic skeleton structure similar to the coexisting sulfur compounds. This inherent problem is a great challenge for the development of an effective adsorbent with high adsorptive selectivity for the sulfur compounds.

To compare the sulfur selective adsorption capacity of different adsorbents, desulfurization of model solution containing 500 mg/L

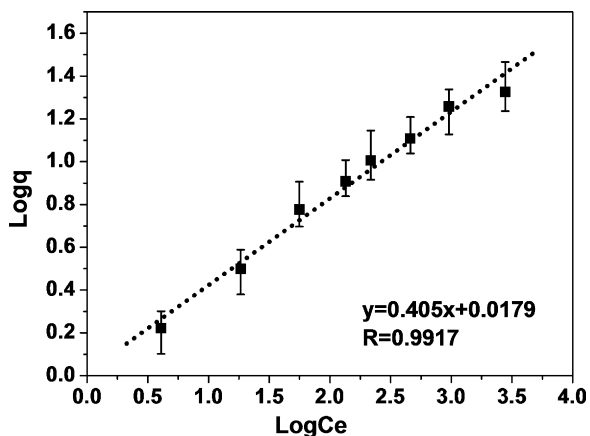


Fig. 7. Freundlich isotherm at 25 °C. Adsorbent-to-solution ratio: 0.2 g/20 mL; contact time: 3 h.

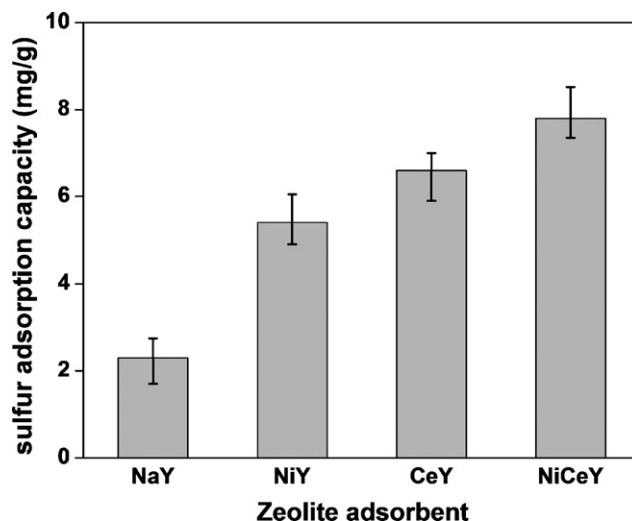


Fig. 8. DBT uptakes by metal-ion-exchanged zeolites 25 °C; adsorbent-to-solution ratio: 0.1 g/20 mL; concentration of DBT: 500 mg/L.

DBT with 5 vol% toluene using various metal ion-exchanged zeolites was studied, and the results are listed in Fig. 8.

When toluene exists, the removal of sulfur increases according to the following order: NaY < NiY < CeY < NiCeY, with the adsorption capacity of 2.3, 5.4, 6.6 and 7.8 mg/g, respectively. It can be seen that the adsorption capacity of NaY is the lowest. On the other hand, NiCeY exhibits the highest adsorption capacity (7.8 mg/g), which is 31% higher than NiY and 16% higher than CeY. This result implies that the NiCeY, prepared by exchanging both Ni and Ce ions with NaY, shows a higher selectivity for DBT compounds than single ion-exchanged NiY and CeY.

3.8. Adsorption mechanism

For NaY, desulfurization relies on the physical adsorption of zeolite pore channels. Besides DBT compounds, NaY also adsorbs toluene existing in the fuel, which would cause competitive adsorption with DBT. So the sulfur removal over NaY zeolite is very low.

For NiY, the high adsorption capacity for DBT is obtained due to a π -complexation between the Ni^{2+} ions ($[Ne]3s^23p^63d^84s^0$) and the DBT aromatic rings [20]. As seen in Fig. 9, through the π -complexation mechanism the Ni^{2+} ions can form the usual σ bonds with their empty s-orbitals and, in addition, their d-orbitals

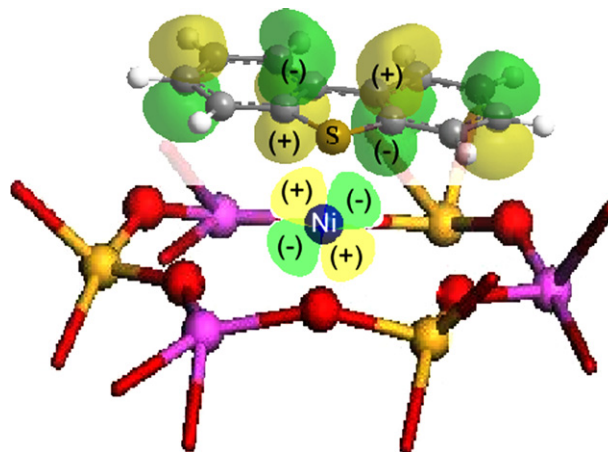


Fig. 9. Means of interaction for a DBT molecule with NiY, corresponding to π -complexation.

can back-donate electron density to the antibonding π -orbitals (π^*) of the sulfur rings [33]. This has been proven by Yang and his co-workers both at the theoretical and experimental level.

Ce^{4+} has the valence electronic configuration $4f^05d^06s^0$. Unlike Ni^{2+} cation, the cerium ions, being an f block element with high positive charge, have a low tendency to form π -complexes with π -bonding ligands [31]. Sulfur compounds are adsorbed over CeY zeolite by a direct S-adsorbent (S-M) interaction. The better performance of Ce-exchanged zeolite as compared to divalent metal Ni-exchanged zeolite in the adsorption of DBT could be due to the high polarizability of Ce^{4+} cation [9].

The highest DBT selective adsorption performance of NiCeY indicates that the presence of Ce as a cocation plays a promoting role in sulfur adsorption. NiCeY zeolite bind the organic sulfur compounds through two types of adsorption modes: π -complexation between Ni^{2+} ions and sulfur ring, and direct coordination via S atoms and Ce ion. In Velu et al.'s [9] study on the adsorptive desulfurization of a model gasoline over zeolite-based adsorbents, a higher adsorption capacity has been observed over the Y zeolite co-exchanged with both Cu^{2+} and Ce^{3+} (HCuCeY) as compared to the HCeY zeolite without Cu^{2+} and HCeY without Ce^{3+} . They thought the higher adsorption capacity of HCuCeY is probably due to the synergistic interaction between Cu and Ce. In our research, the better performance of NiCeY maybe due to the synergistic interaction between Ni and Ce, which is hardly influenced by toluene coadsorption. Therefore, the two types of adsorption modes are in favor of preventing the competitive adsorption of aromatics. Our conclusion is in full agreement with those obtained by Velu.

4. Conclusions

NiCeY, exchanging both Ni and Ce ions with NaY zeolite by aqueous ion exchange, exhibits higher adsorption selectivity to organic sulfur compounds in solution containing aromatics than NiY and CeY. The adsorption capacity of NiCeY is 7.8 mg/g, which is 31% higher than NiY and 16% higher than CeY under the same conditions. The synergistic interaction between Ni and Ce of NiCeY makes DBT adsorption relatively less affected by the presence of aromatic compounds such as toluene. Therefore, NiCeY is a more effective adsorbent to remove sulfur compounds from transportation fuels.

The coexisting toluene in the model fuel is disadvantageous to DBT adsorption. Ce as a cocation in NiCeY plays a promoting role in sulfur adsorption. The adsorption of DBT onto NiCeY conforms to the Langmuir and Freundlich isothermal model.

Appendix A

$$q = \frac{V \times (C_o - C_e)}{m} \quad (A1)$$

$$\eta = \left[\frac{C_o - C_e}{C_o} \right] \times 100 \quad (A2)$$

$$\frac{C_e}{q} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (A3)$$

$$\log q = \log K + \frac{1}{n} \log C_e \quad (A4)$$

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