Zn-Modified Hβ Zeolites Used in the Adsorptive Removal of Organic Chloride from Model Naphtha

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ABSTRACT: Different metal ions were used to modify Hβ zeolite adsorbents by an impregnation method to remove organic chlorides from the model naphtha. The dechlorination performance of different ion-modified adsorbents was evaluated using a microcoulometer. The effects of calcination time and temperature, metal loading, adsorption time and temperature, and dosage of adsorbent were investigated by batch adsorption experiments. The modified adsorbents were characterized by X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), NH3-temperature-programmed desorption (TPD), scanning electron microscopy (SEM), infrared spectroscopy of pyridine adsorption (Py-IR), and X-ray photoelectron spectroscopy (XPS). After modification, the modified Zn/Hβ zeolite exhibited the best dechlorination performance among the other metal-loaded zeolites. The removal percentage of organic chloride of the Zn/Hβ adsorbent prepared at optimum preparation and adsorption conditions can reach 72.54%, compared with 34.07% of Hβ zeolite. The Zn/Hβ adsorbent also maintained good dechlorination performance after regeneration by calcination for five times. The characterization results revealed that the concentration of the B acid sites in the zeolite decreased with the introduction of the metals, whereas that of the L acid sites increased. Zn/Hβ zeolite had the lowest B/L ratio but the best dechlorination performance, which meant that the type and amount of acidic sites present in zeolites played a significant role in dechlorination performance and L acid was beneficial for chloride compound removal.

1. INTRODUCTION

The organic chloride compounds in crude oil exhibit properties of polarity and electrophilicity, which would easily hydrolyze and convert into hydrochloric acid. The different kinds of organic chloride compounds, such as carbon trichloride, carbon tetrachloride, dichloroethane, and tetrachloroethane, generally distribute in all of the distillation of crude oil. Therefore, during the petroleum refining processes, these organic chlorides not only cause corrosion of the atmospheric and vacuum distillation units but also do great harm to the downstream equipment, affecting the stability of the reforming prehydrogenation, the catalytic cracking, and Naphtha hydrogenizing units.

According to previous reports, chlorine corrosion mainly includes hydrochloric acid corrosion, erosion-corrosion, and stress corrosion cracking of austenitic steel. It was known that during the distillation process, the organic chloride would hydrolyze and convert into HCl spontaneously. The generated HCl would react with H2S, leading to the “HCl–H2S–H2O” corrosion system at the low-temperature part of the overhead of the atmospheric and vacuum distillation unit. During the secondary refining processes of crude oil, both HCl from the organic chlorine and NH3 from organic nitride would react with hydrogen at a low temperature to form ammonium chloride, which could cause serious blockage to the prehydrogenation system and underdeposit corrosion. At the same time, chloride ions tend to react with metal ions of the catalysts, causing irreversible poisoning of catalysts. In recent years, organic chlorides in crude oil and its distillates have caused many safety and quality accidents in petrochemical operations, such as the intense corrosion of equipment, pipeline blockage, catalyst poisoning, and inactivity. Therefore, the removal of chloride from crude oil is essential for the stable operation of refineries.

At present, the methods for removing organic chloride in crude oil mainly include catalytic hydrodechlorination, dechlorination using a chlorine transfer agent, and dechlorination by adsorption methods. Catalytic hydrodechlorination is a widespread technology for dechlorination, which can efficiently remove organic chlorine by converting organic chloride, which could cause serious blockage to the prehydrogenation system and underdeposit corrosion. At the same time, chloride ions tend to react with metal ions of the catalysts, causing irreversible poisoning of catalysts. In recent years, organic chlorides in crude oil and its distillates have caused many safety and quality accidents in petrochemical operations, such as the intense corrosion of equipment, pipeline blockage, catalyst poisoning, and inactivity. Therefore, the removal of chloride from crude oil is essential for the stable operation of refineries.

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chlorine into hydrogen chloride in a hydrogen atmosphere in the presence of catalysts. McWilliams et al.15 provided a method for removing trace amounts of organic chlorides from feedstocks by the use of a novel guard bed catalyst comprising shaped particles formed by a mixture of magnesium oxide and a binder inert. The process has particular importance in removing organic chlorides from toluene feedstocks, and the average chloride removal can reach 98% in the temperature range of 200°C to 440°C. Murena et al.16 used a sulfided Ni-Mo catalyst for catalytic hydrodechlorination of PCBs in a commercial dielectric oil. The hydrodechlorination degree can also reach 90% at lower temperatures but longer reaction times. The main shortcomings of this method could be the severe dechlorination conditions, poor target selectivity, and the corrosion of generated HCl, which would be a challenge for its further industrial application.

In addition, the use of chlorine transfer agents such as alkali metal, alkali metal carbonates, poly(ethylene glycol), and dimethyl sulfoxide is also a relatively competitive dechlorination method by which the organic chlorine is converted into inorganic chlorine, and then the inorganic chlorine is removed by electric desalting and dehydration. Sabata17 successfully used glycols acting as a phase transfer agent for the destructive removal of the higher chlorinated Delor 106 from nonpolar hydrocarbon liquids. The aryl glycols produced in this process were immiscible with the nonpolar liquid, and the two-phase system ensured the efficient removal of the product. However, this method consumes a large amount of the organochlorine transfer agent and has a long reaction time, which would limit its further application.

The adsorption dechlorination method, which utilizes adsorbents with different adsorption capacities to remove organic chlorine in crude oil, has promising application prospects because of its low dechlorination cost and good dechlorination effect. Typical adsorbents are silica gel,18 activated carbon,19 activated alumina,20 molecular sieves,19 and some special adsorbents. Among these adsorbents, zeolite adsorbents are not only widely used for adsorption desulfitization,22–24 denitrification,25 and the removal of volatile organic compounds26–28 in the production of basic organic chemicals but also exhibit excellent performance in the removal of organic chlorine. For example, Maglio29 used zeolite 13X to remove vinyl chloride by contacting the streams. But the vinyl chloride capacity of 13X zeolite samples can only reach 7.7 wt %. Ma30 used low-silicon X-type molecular sieve adsorption to remove organic chlorine in model jet fuel by batch adsorption experiments, which can reach a removal percentage of organic chlorine of 95% at optimal operational conditions. Moreover, the adsorption process was found to be an endothermic, feasible, and a spontaneous process under specified conditions by further thermodynamic analysis.

However, zeolites are usually limited by adsorption capacity and selectivity. Therefore, increasing the adsorption capacity and selectivity is critical for broadening the application of zeolite adsorbents. One method is to change the pore structure and acid properties of the zeolite by alkali or metal modification. Sun et al.31 used NaOH solution to treat NaY zeolite for the adsorption of benzothiophene from fuels. The sulfur removal from the model diesel of modified NaY zeolite can reach 99.9% compared with 7.4% of NaY zeolites. Metal modification is a more common method to enhance the adsorption performance of molecular sieves. Li et al.32 used CuO and MgO to modify ZSM-5 molecular sieves by an impregnation method to remove the organic chlorides in naphtha. The removal percentage of metal-modified molecular sieve adsorbents increased to 33.97 and 39.68%, respectively, compared with that of ZSM-5 molecular sieves of 6.93%. This group subsequently used the SAPO-34 molecular sieves modified by metal ions,33 such as Ni2+, Cu2+, Mg2+, and Zn2+, to remove the dichloroethane in the model oil. It was found that Na/SAPO-34 zeolite achieved a removal percentage of organic chlorine of 97.69% at a lower temperature and had a good regeneration ability. Guthrie34 used Pd to modify MCM-41 zeolite. It can degrade 92% of the total organochlorides in water and showed its long-term stability in solution compared to MCM-41 zeolite. Ge et al.35 used Y zeolites modified by transition metal ions of Co2+, Ce4+, Cu2+, and Ni2+ to remove organic chlorides in reformate oil by performing dynamic tests. Ce-Y zeolite exhibited the best adsorption dechlorination effect, and a removal percentage of organic chlorides of ~70% could be maintained for 7 h with a reaction temperature of 150°C.

In this work, Hβ zeolite was used to remove organic chlorides from the model naphtha that is composed of four chlorides commonly found in crude oil (carbon trichloride, carbon tetrachloride, dichloroethane, and tetrachloroethane). To increase the dechlorination capacity and selectivity of the adsorbents, Hβ zeolites were modified by the impregnation of several metals. The chloride compound removal performance of the prepared adsorbents was evaluated using a microcoulometer. The adsorbents were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), NH3-temperature-programmed desorption (NH3-TPD), infrared spectroscopy of pyridine adsorption (Py-IR), Brunauer–Emmett–Teller (BET), and X-ray photoelectron spectroscopy (XPS).

2. EXPERIMENTAL SECTION

2.1. Materials. The Hβ zeolite with a SiO2/Al2O3 ratio of about 25 was used as the support of adsorbents for the removal of chloride compounds from the model naphtha; it was supplied by Zibo Qichuang Chemical Co., Ltd. Mg(NO3)2·6H2O, Zn(NO3)2·6H2O, Cu(NO3)2·3H2O, AgNO3·6H2O, and Ni(NO3)2·6H2O used for metal modification were supplied by Beijing Tongguang Fine Chemicals Co., Ltd. The feedstock n-heptane was supplied by Beijing Chemical Factory Co., Ltd. Carbon trichloride, carbon tetrachloride, dichloroethane, and tetrachloroethane as components of model oil were sourced from Aladdin Chemical Co., Ltd. All of the reagents were of analytical grade.

2.2. Adsorbent Preparation. The Hβ zeolite was first activated at 120, 240, 360, and 480°C for 2 h by stepped heating. Then, metal-modified Me/Hβ adsorbents (Me represents different metal ions) were prepared by impregnating different nitrates solutions on the activated Hβ zeolite powder thoroughly. The metals loaded on these samples were magnesium, zinc, copper, and silver, respectively, and the metal content in each metal-modified material was 5 wt % of Hβ parent zeolite, i.e., 0.05 g of Zn for 1 g of zeolite. After impregnation, the obtained zeolite adsorbents were allowed to stand for 4 h at room temperature, dried at 110°C for 2 h, and calcined at 550°C for 2 h. The obtained powder is labeled as Me/Hβ.

2.3. Adsorbent Characterization. The Me/Hβ adsorbents were characterized by various methods such as XRD, BET, SEM, Py-IR, XPS, and NH3-TPD analysis. XRD analysis
was calculated according to the following empirical equations:

$$Q_t = \frac{C_0 - C_f}{m} V$$

and

$$\Phi = \frac{C_0 - C_f}{C_0} \times 100\%$$

where $C_0$ and $C_f$ are the initial and equilibrium concentrations of organic chloride in the model naphtha (mg L$^{-1}$), respectively, $C_i$ is the concentration of organic chloride at a specified time $t$ (mg L$^{-1}$), $V$ is the volume of the model naphtha (mL), and $m$ is the mass of the adsorbent (g).

2.6. Regeneration Experiments. The spent Me/Hβ adsorbents were first filtered and washed with n-heptane solvent to remove the residue organic chloride and were then dried at 110 °C for 2 h and calcined at 550 °C for 2 h. Their regeneration properties for the removal of organochlorine from the model naphtha were also investigated.

3. RESULTS AND DISCUSSION

3.1. Characterization Results. 3.1.1. Structural Study of the Adsorbents. The XRD patterns of the Hβ and modified Hβ samples are depicted in Figure 1. The diffraction patterns for the Hβ and Hβ loaded with different metal ions (Mg$^{2+}$, Zn$^{2+}$, Cu$^{2+}$, Ag$^+$) had two broad peaks at 7.8 and 22.4° corresponding to (100) and (200) reflections of Hβ zeolite (ICSD 31136), respectively. No additional diffraction peaks can be observed in the XRD patterns of Me/Hβ, indicating that no big particles were formed both inside and outside the zeolite framework during the impregnation process and the metallic cations were probably successfully incorporated into the zeolite framework. However, a slight decrease in the diffraction peak intensity was observed after metal modification, showing that some loss of crystallinity occurred after introducing metal ions and calcinating at high temperatures. In addition, the diffraction peaks of both Cu/Hβ and Zn/Hβ were sharp and intense, indicating good crystalline nature. The relative crystallinity of Cu/Hβ and Zn/Hβ adsorbents decreased by 19 and 13% (Table 1), respectively, which was attributed to the slight destruction of the lattice during calcination.

3.1.2. N$_2$ Adsorption–Desorption Isotherms of the Adsorbents. The zeolite structure characteristics of metal-modified adsorbents were further revealed by N$_2$ adsorption
measurements. The adsorption isotherms and BJH pore size distributions are shown in Figure 2a. The N$_2$ physisorption isotherms of the five zeolite adsorbents are all of type IV. A hysteresis loop observed for all of the samples at a relative pressure range of 0.5 < $P/P_0$ < 0.7 indicated the presence of mesopores in the zeolite adsorbents. According to the BJH pore size distribution curve in Figure 2 b, a broad pore distribution existed in these adsorbents centering at around 4 nm, suggesting that there were considerable intracrystalline mesopores in the modified zeolite adsorbents. As summarized in Table 2, the presence of cations like Mg$^{2+}$, Zn$^{2+}$, Cu$^{2+}$, and Ag$^{+}$ slightly reduced the surface areas and the pore volume of the parent H$\beta$ zeolite. It was likely that the metal cations entered the H$\beta$ pores after modification and a part of them blocked the pores. However, compared with other metal-modified zeolite adsorbents, Zn/H$\beta$ possessed a better structural property with the highest BET surface area of 522 m$^2$ g$^{-1}$ and the largest pore volume of 0.36 cm$^3$ g$^{-1}$.

3.1.3. Morphology Study of the Adsorbents. The morphology and structure of the adsorbents are shown in Figure 3. Compared with H$\beta$ zeolite, Me/H$\beta$ zeolites prepared by metal modification were all typical spherical particles or aggregates but with a larger size and a more dispersed particle size distribution. The increase in particle size might be due to the agglomeration of original H$\beta$ zeolite after introducing metal oxides. Meanwhile, the highly dispersed metals on the zeolites were beneficial for the dispersion of the original H$\beta$ zeolite particles. Among them, the particle size of Mg/H$\beta$ zeolite increased most obviously because of the agglomeration. In general, an increase in the particle size decreases the number of particles in the case of a constant volume fraction. This, in turn, decreases the BET surface area of particles. Therefore, Mg/H$\beta$ zeolite had the lowest BET surface area. The Zn/H$\beta$ zeolites exhibited better morphology with almost uniformly dispersed spherical crystal grains, thus maintaining a high relative crystallinity and a large BET surface area. In a word, the average particle size of the modified zeolites increased in the following order: H$\beta$ < Zn/H$\beta$ < Ag/H$\beta$ < Cu/H$\beta$ ≈ Mg/H$\beta$, which was consistent with the order of the BET surface areas of these zeolites.

3.1.4. NH$_3$-TPD Spectra of the Adsorbents. The temperature-programmed desorption of ammonia (NH$_3$-TPD) profiles on parent H$\beta$ zeolite and Me/H$\beta$ zeolites are illustrated in Figure 4. As shown in Figure 4, all of the

Table 1. Relative Crystallinity of Different Adsorbents

| samples      | C/C$_0$ (%) |
|--------------|-------------|
| Mg/H$\beta$  | 61          |
| Zn/H$\beta$  | 81          |
| Cu/H$\beta$  | 87          |
| Ag/H$\beta$  | 65          |
| H$\beta$     | 100         |

Table 2. Specific Surface Area and Pore Structure of Different Adsorbents

| adsorbents | surface area (m$^2$ g$^{-1}$) | pore volume (cm$^3$ g$^{-1}$) | average pore size (nm) |
|------------|------------------------------|------------------------------|------------------------|
| Mg/H$\beta$ | 448                         | 0.33                         | 4.5                    |
| Zn/H$\beta$ | 522                         | 0.36                         | 4.0                    |
| Cu/H$\beta$ | 451                         | 0.32                         | 4.7                    |
| Ag/H$\beta$ | 467                         | 0.34                         | 4.2                    |
| H$\beta$   | 590                         | 0.40                         | 4.0                    |

Figure 1. XRD patterns of different metal-modified H$\beta$ zeolites (metal loading: 6 wt %; calcination conditions: 450 °C, 4 h).

Figure 2. (a) Nitrogen adsorption–desorption isotherms and (b) pore size distribution of different adsorbents.

Figure 3. Morphology of the adsorbents.

Figure 4. NH$_3$-TPD Spectra of the Adsorbents.

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adsorbents exhibited two NH$_3$ desorption peaks. The strong peaks in the range 220–370 °C were assigned to weak acid sites, and the peaks in the range 330–420 °C were assigned to strong acid sites. Compared with the parent Hβ zeolite, the introduction of zinc and copper led to the shift of the high-temperature peak toward lower temperatures, indicating that the acidity intensity of zeolites modified by metal zinc and copper decreased to some extent. However, compared to the spectra of Hβ zeolite, those of Me/Hβ zeolite indicated that the introduction of the metal led to the formation of strong acidic sites on the zeolite. Moreover, strong acidic sites were much greater in number than weak acidic sites by comparison of the peak areas of the spectra of the respective zeolites according to Table 3.

### Table 3. Semiquantitative Analyses of NH$_3$-TPD Profiles of the Different Metal-Modified Hβ Zeolites

| Adsorbents | Weak Acid | Strong Acid | Total |
|------------|-----------|-------------|-------|
|            | $T_m$ (°C) | peak area   | $T_m$ (°C) | peak area | total |
| Hβ         | 265       | 1.8 (76.3%) | 416     | 0.56 (23.7%) | 2.36  |
| Zn/Hβ      | 230       | 0.85 (34.1%) | 330     | 1.64 (65.9%) | 2.49  |
| Cu/Hβ      | 223       | 0.64 (31.1%) | 339     | 1.42 (68.9%) | 2.06  |

![NH$_3$-TPD spectra of different metal-modified Hβ zeolites.](image)

**Figure 3.** SEM images of zeolite samples: (a) Mg/Hβ, (b) Zn/Hβ, (c) Cu/Hβ, (d) Ag/Hβ, and (e) Hβ.

**Figure 4.** NH$_3$-TPD spectra of different metal-modified Hβ zeolites.
sites in the metal-modified adsorbents. As shown in Figure 5, several absorption peaks in the wavenumber range of 1400–1650 cm$^{-1}$ were observed, which was due to the interaction of pyridine molecules with Lewis and Brønsted acidic sites of the modified zeolites. The IR bands appearing at 1545, 1621, and 1636 cm$^{-1}$ were assigned to the vibrations of pyridine molecules bound at bridge-bonded Bronsted acidic sites. However, the last two peaks often overlap with each other, and it is difficult to determine the intensity and peak areas of the two characteristic vibration absorption peaks. Herein, the number of Bronsted acid sites was calculated according to the strength of the peaks at 1545 cm$^{-1}$. On the other hand, the IR spectra of zeolites revealed that all of these samples contained at least two distinct Lewis acid sites. We observe mainly a pair of bands at 1613 and 1452 cm$^{-1}$, arising due to $\delta\nu(C\cdotsC)$ and $19b\nu(C\cdotsC)$ vibrations of pyridine adsorbed at Lewis acid (designated as $L_1$) sites, and another pair of bands at 1595 and 1444 cm$^{-1}$ (referred to as $L_2$ sites) may be attributed to certain weak Lewis acid sites. Therefore, the number of Lewis acid sites was calculated according to the strength of peaks at 1595 and 1444 cm$^{-1}$ and 1613 and 1452 cm$^{-1}$. The acidity analysis results are shown in Table 4. In addition, the intense band at 1490 cm$^{-1}$ was attributed to the contributions of Lewis acidic and Bronsted acidic sites to pyridine adsorption. The IR spectrum of the parent Hβ zeolite showed obvious differences from those of the metal-modified zeolites, which confirmed that metal introduction to zeolites caused variation of the acidic properties on adsorbent surfaces, especially the content of Lewis acid sites. Compared with Hβ zeolite, the intensity of the peaks at 1444, 1595, or 1613 cm$^{-1}$ of Me/Hβ adsorbents increased, whereas the strength of the peak at 1545 cm$^{-1}$ decreased considerably, and the peak strength at 1444, 1595, or 1613 cm$^{-1}$ was much higher than that at 1545 cm$^{-1}$. These results confirmed that the amount of Lewis acid increased after metal modification, while the amount of Bronsted acid obviously decreased. Moreover, the amount of Lewis acid was much larger than that of Bronsted acid. It has been reported that some positively charged metal species in Hβ zeolite could neutralize the negative charge of AlO$_4^-$ tetrahedra and could decrease the concentration of Bronsted sites. On the other hand, it can also be deduced that some new Lewis acid sites were formed by the conversion of Bronsted acid sites with the introduction of these metal species. The introduction of a new species (MeOH$^+$) after modification may further increase the amount of Lewis acid sites.

In addition, the ratios of the number of Bronsted acid sites to Lewis acid sites (B/L) both in the total acid and the strong acid decreased after metal modification. The B/L ratio of both the total acid and the strong acid of modified zeolites decreased in the following order: Hβ > Mg/Hβ > Ag/Hβ > Cu/Hβ > Zn/Hβ.

3.1.6. X-ray Photoelectron Spectroscopy Analysis of the Zn/Hβ Zeolite. To further evaluate the influence of metal cations on the modified zeolites, XPS analysis on Zn/Hβ zeolite was carried out, as shown in Figure 6. The introduction of a new species (MeOH$^+$) after impregnation may increase the amount of Lewis acid, which can be confirmed by an XPS study. It was reported that the binding energy of the XPS peaks at 1045.3 eV is relative to Zn 2p$_{1/2}$ and another at 1022.1 eV can be attributed to Zn 2p$_{3/2}$, which may identify other zinc species present on the catalysts’ surface. The Gaussian–Lorentzian function was used to fit the peak of Zn 2p$_{3/2}$. Two peaks were obtained at 1022.2 and 1023.1 eV, corresponding to two different states of zinc on the modified zeolites. It is reported that the state of Zn species depends on the topology of the zeolite, as well as the methods and conditions of Zn introduction. The low-intensity peak at 1022.1 eV can be assigned to ZnO particles, which were highly dispersed on the surface of Zn/Hβ zeolite, and the 1023.1 eV BE peak can be reasonably assigned to (ZnOH)$^+$, which were formed by the combination of Zn (2p$_{3/2}$) and Si–O(H)–Al in the molecular sieve. (ZnOH)$^+$ species were usually in a

![Image](https://dx.doi.org/10.1021/acsomega.9b04417)

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Table 4. Surface Acidity Analysis of Hβ Modified by Different Ions

| Samples  | Acid amount (total acid) at 200 °C/mmol g$^{-1}$ | Acid amount (strong acid) at 350 °C/mmol g$^{-1}$ | B acid | L acid | B/L | B acid | L acid | B/L |
|----------|-----------------------------------------------|-------------------------------------------------|--------|--------|-----|--------|--------|-----|
| Mg/Hβ   | 0.089                                         | 0.471                                           | 0.188  | 0.067  | 0.364 | 0.184  |        |      |
| Zn/Hβ   | 0.004                                         | 0.743                                           | 0.005  | 0.002  | 0.657 | 0.003  |        |      |
| Cu/Hβ   | 0.002                                         | 0.276                                           | 0.007  | 0.002  | 0.271 | 0.006  |        |      |
| Ag/Hβ   | 0.018                                         | 0.763                                           | 0.024  | 0.006  | 0.653 | 0.010  |        |      |
| Hβ      | 0.240                                         | 0.370                                           | 0.649  | 0.131  | 0.379 | 0.347  |        |      |

Figure 5. Pyridine-IR patterns of different metal-modified Hβ zeolites. Pyridine desorption at (a) 200 °C and (b) 350 °C.
thermodynamically unstable state and easily decomposed by dehydration at high temperatures, interacting with acidic hydroxyl groups, Si(OH)Al, to form water and a bridging Zn$^{2+}$ cation ($\text{Zn}^{2+}(\text{O}^2\text{−})_2$), at low Zn$^{2+}$ loading, or undergoing dehydration by the coupling of two (ZnOH)$^+$ species to form water and two Zn$^{2+}$ cations bridged by oxygen ((Si(O$^−$)Al)$\text{−Zn}^{2+}$)$_2\text{O}$ at high Zn$^{2+}$ loading. This result was also verified by the report for Zn/HZSM-5, in which Zn$^{2+}$ interacted with Si(OH)Al to form strong Lewis acid sites and partially eliminated Brønsted acid sites. In addition, (ZnOH)$^+$ may also interact with acidic sites corresponding to the (AlO)$^+$ extra framework aluminum to generate strong Lewis acid sites and simultaneously develop bridging hydroxyl groups, Si(OH)Al. The possible mechanism for the interaction of Zn$^{2+}$ with Hβ zeolites is shown in Figure 7.

Therefore, whether the (ZnOH)$^+$ species undergone dehydration at high temperatures or interacted with the (AlO)$^+$ extra framework aluminum, it would increase the acidic centers for Lewis acid sites and change the acidic character of the samples. The XPS analysis of Zn/Hβ zeolite was in good agreement with the Py-IR results.

3.2. Batch Experimental Adsorptions. 3.2.1. Effect of Metal Ions. The above absorbents were used to investigate the effect of metals ions on dechlorination. From Figure 8, it could be observed that the removal percentage of organic chloride of modified adsorbents varied in quality but were all better than that of the parent Hβ zeolite. Among them, the modified Zn/Hβ exhibited a significantly enhanced removal percentage of organic chloride. The removal percentage of organic chloride decreased in the following order: Zn/Hβ > Cu/Hβ > Ag/Hβ ≈ Mg/Hβ > Hβ. According to the above characterization results, the modified Zn/Hβ maintained high crystallinity, exhibited a better morphology, and a more dispersed particle size distribution. Furthermore, the Zn/Hβ clearly exposed more active surface sites relative to the other modified samples.

![Figure 6. XPS spectra for Zn of Zn/Hβ.](Image)

![Figure 7. Possible mechanism for the interaction of Zn$^{2+}$ with Hβ zeolites (adapted from refs 45, 47).](Image)

![Figure 8. Evaluation of dechlorination performance of different metal-modified Hβ zeolites.](Image)
because of its higher specific surface area and pore volume. Besides, NH$_3$-TPD showed that the number of strong acidic sites increased most significantly after modification by zinc. Py-IR further confirmed that the increase in the amount of Lewis acid after metal modification contributed most to the increase of strong acidic sites. The dechlorination performance of modified adsorbents was consistent with the B/L order, in which the B/L ratio of the Zn/Hβ was the lowest, suggesting that Lewis acid was beneficial for removal of the chloride compound. Therefore, it can be deduced that one of the significant factors affecting the adsorption dechlorination capacity was the proportion of Lewis acid, especially strong Lewis acid.

However, according to the nominal metal loading in Table 5, we can see that Zn/Hβ and Cu/Hβ had a similar metal loading of about 0.9 mmol g^{-1}, but Zn/Hβ had the highest removal percentage of organic chloride of 52.49%, indicating that Zn/Hβ was better than Cu/Hβ. Ag/Hβ, Cu/Hβ, and Mg/Hβ had a similar removal percentage of organic chloride, but Ag/Hβ had the lowest metal loading and Mg/Hβ the highest, suggesting that their modification effects on the Hβ zeolite decreased in the following order: Ag/Hβ > Cu/Hβ > Mg/Hβ. However, the comparison between Ag/Hβ and Zn/Hβ needs further investigation.

### 3.2.2. Effect of the Amount of Metal Loading

The effect of loading amount of Zn on the removal percentage of organic chloride was investigated in the range of 2.5–15 wt %.

**Table 5. Nominal Metal Loading of Different Metal-Modified Hβ Zeolites**

|        | Mg/Hβ | Zn/Hβ | Ag/Hβ | Cu/Hβ |
|--------|-------|-------|-------|-------|
| wt %   | 6     | 6     | 6     | 6     |
| mmol g^{-1} | 2.5  | 0.92  | 0.56  | 0.94  |
| ϕ (%)  | 38.75 | 52.49 | 39.4  | 40.54 |

*This is the metal concentration in the material as calculated from the nominal metal loading.*

As shown in Figure 9, the removal percentage of organic chloride of the model oil initially increased from 29.85 to 60.4% with an increase in the loading amount from 2.5 to 7.5 wt % and then decreased to 54.88% with further increase of the loading amount to 15 wt %, which showed that the most optimal loading amount was around 7.5 wt %. The zeolite absorbent obtained at the most optimal loading amount was denoted as Zn/Hβ-0.075. The reason was that the active sites of adsorbents would increase with the increase of the loading amount, leading to an increase in the adsorption efficiency. Nevertheless, when the loading amount further increased, the adsorption efficiency would reduce due to the partial aggregation of zeolites, as shown in the SEM images of Figure 3b, or the loss of acid sites by dehydration with more (ZnOH)$^+$ species, which reduced the specific surface area (BET) and the number of active centers, thereby weakening the adsorption dechlorination effect. Besides, from Figure 9, we can see that Zn/Hβ with a metal loading of 5 wt % (=0.77 mmol g^{-1}) had a removal percentage of organic chloride of 40.33%, which was similar to that of Ag/Hβ with a metal loading of 0.56 mmol g^{-1}, suggesting that Ag/Hβ was a little better than Zn/Hβ. As a result, we can conclude that when the amount of metal on these absorbents was the same, the dechlorination performance of these adsorbents may decrease in the following order: Ag/Hβ > Zn/Hβ > Cu/Hβ > Mg/Hβ. However, considering that Zn(NO$_3$)$_2$·6H$_2$O is much cheaper than AgNO$_3$·6H$_2$O, Zn/Hβ-0.075 was selected as an adsorbent to explore the effects of other adsorption conditions on its dechlorination performance.

#### 3.2.3. Effect of Calcination

Calcination is another important factor that affects organic chloride adsorption. The effect of variation in calcination temperatures (250, 350, 450, 550, 650 °C with a constant calcination time of 4 h) and durations (2, 3, 4, 5, 6 h with a constant calcination temperature of 350 °C) on organic chloride uptake was investigated over Zn/Hβ-0.075. As shown in Figure 10, the organic chloride removal rate increased first and then dropped with the increase of the calcination temperature and reached a maximum of 60.4% at 350 °C for 4 h. The same trend can also be seen in the condition of calcination durations, which peaked at 3 h with the organic chloride removal of 72.54% at 350 °C. The reason may be that different calcination temperatures and durations mainly affect the state of Zn species on the surface of zeolites and the removal rate of impurities in the zeolite channels, thereby affecting the acidity and pore properties of molecular sieves. The poor dechlorination performance at lower temperatures or shorter calcination durations may be due to its inadequate ability to remove polar molecules adsorbed in the pores of the adsorbents, which would impede the exposure of active centers. When calcinated at a higher temperature and longer duration, agglomerate particles would be formed by coagulation and sintering. What is worse, Zn species can also interact with some acidic sites corresponding to the (AlO)$^+$ extra framework aluminum to form ZnAl$_2$O$_4$ crystal phases, leading to the loss of the acid sites and the structural collapse of zeolite adsorbents. Hence, the suitable activation conditions can not only remove the impurities on the surface of adsorbents to expose more surface active sites but also introduce more active centers to enhance the adsorption performance of organic chlorine without changing the crystal structure of adsorbents.

#### 3.2.4. Effect of Adsorption Time

Zeolite Zn/Hβ-0.075 was used to investigate the effect of adsorption time on the removal of organic chloride in the model naphtha (adsorption temperature was 20 °C and the dosage of adsorbent was 34.2 g L^{-1}). The amount of adsorption of chloride of the zeolite as a function of adsorption time is shown in Figure 11. It can be seen that the amount of adsorption of chloride...
increased rapidly during the first 7 h, which was attributed to the adequate exposure of the active sites after calcination. Therefore, the naphtha in contact with the adsorbent was rapidly consumed in the beginning, while the number of the adsorbed active sites would decrease at the same time because the organochlorine in the solution would occupy these active sites gradually. When the adsorption time was 10 h, the concentration of chlorine in the model naphtha was the lowest and kept constant as time increased, indicating that the adsorption had reached saturation.

3.2.5. Effect of Dosage of the Adsorbent. The dosage of the adsorbent is an important parameter that determines the capacity of adsorbent for a given concentration of chloride. As illustrated in Figure 12, increasing the dosage of Zn/Hβ-0.075 from 19.5 to 68.4 g L\(^{-1}\) in the model naphtha led to an increase in organic chloride removal, from 55.38 to 76.91%, but a decline of the adsorption capacity from 1.84 to 0.73 mg g\(^{-1}\). At this temperature, physisorption is a dominant process and adsorption capacity is directly proportional to the surface area of adsorbents.\(^{50}\) The enhancement of organic chloride removal with higher adsorbent dosage can be attributed to the increased surface area of adsorbent and availability of more active adsorption sites, but the adsorption capacity reduced due to the partial aggregation or overlapping of Zn/Hβ-0.075 zeolite particle. However, when the adsorbent dosage increased from 34.2 to 68.4 g L\(^{-1}\), the equilibrium adsorption capacity of Zn/Hβ-0.075 increased slightly, which indicated the achievement of equilibrium between organic chloride and adsorbent under the given operating conditions. Therefore, it can be concluded that the optimal absorbent dosage for the removal of chloride compounds on modified Zn/Hβ zeolites was 34.2 g L\(^{-1}\), with the adsorption removal of 72.54% and the equilibrium adsorption capacity of 1.38 mg g\(^{-1}\).

3.2.6. Regeneration Performance of the Adsorbent. Regeneration performance is an important factor for an industrial adsorbent. For the model naphtha, Zn/Hβ-0.075 zeolite possessed stable regeneration properties after five cycles; the percentage of organic chloride removal dropped from 72.54 to 67.38% (Figure 13). It was probably that the specific surface area and pore structures of the adsorbents...
decreased after regeneration. After several times of high-temperature activation, the collapse of the adsorbent structure would cause the blockage of zeolite pores, and the loss of active sites would occur during the roasting process, both of which had negative impacts on dechlorination ability.

4. CONCLUSIONS

Several metals were introduced to Hβ zeolites by impregnation to remove organic chlorides from the model naphtha, and Zn/Hβ zeolite had the best dechlorination performance. According to Py-IR results, Zn/Hβ zeolite had the lowest B/L ratio among all samples, which indicated that L acid was beneficial for the removal of chloride compound. To be specific, (ZnOH)⁺ species of Zn/Hβ zeolites contributed to increasing the dechlorination capacity, which eliminated Brensted acid sites and increased the strong acidic centers for Lewis acid sites by undergoing dehydration at high temperatures or interacting with extra framework aluminum. Compared with the conventional Hβ zeolite absorptions, the removal percentage of organic chloride of which is 34.07%, Zn/Hβ-0.075 zeolite with 7.5 wt % metal loading can reach 72.54% when prepared at the optimum conditions. The Zn/Hβ-0.075 zeolite adsorbent also had good regeneration ability, which recovered almost all of the original adsorption capacity after regeneration for five times.

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Notes

The authors declare no competing financial interest.

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