

Article

Research on the Adsorption Performance of Zeolites for Dimethyl Ether

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Abstract: The purification and removal of polar impurities in olefin feedstocks is crucial for downstream deep processing, and adsorption is the main method for deep purification of such impurities. This article takes dimethyl ether, a typical oxygen-containing compound impurity in MTOs, as a polar impurity molecule, and LTA and FAU topological zeolites as research objects. The influence of zeolite topology, morphology, skeleton silicon–aluminum (Si/Al) ratio, and ion type on the adsorption and removal of trace dimethyl ether was investigated by XRD, SEM, XRF, and nitrogen adsorption–desorption methods. The FAU topological zeolites show a better adsorption performance for dimethyl ether owing to their larger specific surface area and unobstructed pores compared with LTA zeolites. Among FAU topological zeolites, the NaX zeolite with a lower framework silica–alumina ratio has the highest adsorption capacity for dimethyl ether. Magnesium ion exchange on NaX zeolites (MgNaX) reduce the specific surface area and adsorption capacity of the NaX zeolite. However, after forming with alumina as a binder, the adsorption capacity of the MgNaX–Al₂O₃ adsorbent is about 13% higher than that of the NaX–Al₂O₃ adsorbent without Mg ion exchange. This may be due to the decomposition of residual organic Mg salts in the Mg ion exchange samples during high-temperature calcination, resulting in a larger specific surface area for the formed adsorbent. Further characterization of NH₃–TPD and CO₂–TPD shows that Mg ion exchange weakens the acid–base active sites on the adsorbent surface. The reduction in acid–base sites reduces the occurrence of side reactions such as polymerization and isomerization caused by the exothermic adsorption of olefins on adsorbents. Repeated adsorption data show that the formed adsorbent has excellent regeneration–adsorption performance.

Keywords: olefins; ion exchange; formed zeolite adsorbents; dimethyl ether adsorption



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1. Introduction

Low-carbon olefins (ethylene, propylene, and butene) are very important chemical raw materials. Starting from low-carbon olefins, they can produce a variety of life and industrial products through hydrocarbon processing (polymerization, disproportionation, isomerization, etc.) [1–5]. At present, methanol-to-light olefin (MTO) technology, as one of the important routes of olefin production, is rising rapidly [6,7]. Different from traditional oil routes [8–11], affected by the source of raw materials, trace amounts of methanol, dimethyl ether, propionaldehyde, water, and other oxygen-containing organic compounds are widely present in low-carbon olefins produced by the MTO process [12–15]. The presence of these polar impurities poses a great challenge to the stable operation of downstream olefin processing units, such as polyolefins and olefin disproportionation, and even causes catalyst poisoning and plant shutdown, resulting in significant economic losses [16,17]. Therefore, it is of great significance to develop a method for efficiently removing oxygen-containing

compounds from MTOs to ensure the stable operation of olefin production and olefin processing in a coal chemical route.

In industry, extraction, distillation, and adsorption are generally used to remove polar compound impurities in hydrocarbon raw materials [18–20]. Compared with the extraction and distillation methods, the adsorption method has the characteristics of low energy consumption, high removal accuracy, low cost, no environmental pollution, and easy operation. Especially when the impurity content is very low, the purification depth of adsorption is much higher than that of other purification processes, which is very suitable for the fine removal of trace impurities in raw materials [21–23]. Compared with activated carbon, silica gel, activated alumina, and other porous materials, zeolites have been widely used in the adsorption and removal of trace oxygen-containing compound impurities in hydrocarbons due to their controllable pore structure and easy-to-adjust surface acid–base properties and good adsorption selectivity [24–26]. Pascual-Muñoz et al. investigated the effect of the sodium–potassium ratio on the adsorption of methanol and water on LTA molecular sieves and found that the sodium LTA zeolite (4A) can strongly adsorb water and methanol [27]; Zhou et al. modified 13X zeolite powder using liquid–phase ion exchange method and evaluated the adsorption performance of the modified adsorbent for organic oxygen-containing compounds in hydrocarbon streams [28]. They found that the modified zeolites had excellent adsorption performance; the optimal adsorption breakthrough time for dimethyl ether can reach 170 min. Zhou et al. prepared high-performance adsorbents by loading active components onto NaY carriers using the equal volume impregnation method and maintained stable adsorption performance for dimethyl ether, MTBE, and methanol in C₄ after regeneration [29]. The above studies investigated the adsorption properties of 4A, 13X, and NaY zeolites for oxygen-containing compounds, but there was no systematic comparison between different zeolites. Li et al. used the desiccator method to carry out the static adsorption experiments of formaldehyde molecules on 3A, 5A, 13X, and MCM-41 zeolites, but they did not investigate the dynamic adsorption behavior of zeolites in industrial applications [30].

In addition, the removal of impurities by adsorption usually occurs at low temperatures, so researchers often pay more attention to the structure–activity relationship between adsorption performance and specific surface area, pore structure, metal ions in the framework, etc., but they pay less attention to the surface acid–base sites that need to active at higher temperature and are closely related to the catalytic activity of zeolites. However, it cannot be ignored that in industrial applications, a large amount of adsorption heat will be generated when the material medium initially contacts the porous adsorption material, which may cause a catalytic reaction, such as the polymerization and isomerization reactions of olefins [31].

In this paper, the adsorption performance of commercially available LTA and FAU zeolites were systematically investigated by using dimethyl ether (a typical oxygen-containing compound in MTO products) as a probe molecule. On this basis, the preferred zeolite was modified by ion exchange, and then the formed zeolite adsorbent meeting the requirements of industrial application was prepared. Through ion exchange modification and molding process control, the acid and alkali active sites on the surface of the adsorbent were successfully weakened while effectively maintaining the specific surface area of the adsorbent. A deep purification adsorbent for oxygen-containing compounds with high adsorption capacity and promising regeneration performance was obtained.

2. Experimental

2.1. Materials

The raw powder of 3A, 4A, and 5A zeolites and NaX and NaY zeolites were purchased from Luoyang Jianlong Micro-nano New Materials Co., Ltd. (Luoyang, China), and ammonium chloride, sodium chloride, magnesium acetate, nitric acid, and sesbania gum were purchased from Sinopharm Reagent Co., Ltd. (Shanghai, China). Pseudoboehmite (Al₂O₃, dry basis 70.1%) was purchased from Shandong Aluminium Co., Ltd. (Zibo, China).

2.2. Samples Preparation

2.2.1. Preparation of Na-Type Ultra-Stable Y Zeolite (NaUSY) Powder

100 g ammonium chloride was dissolved in 1000 mL deionized water and stirred until clear, and then 100 g NaY zeolite was added and stirred at 80 °C for 2 h. After the exchange was completed, the mixture was filtered, washed, and dried at 100 °C for 12 h. The exchange process was repeated three times to completely remove the Na⁺ ions from the zeolite framework. The exchanged NH₄⁺ Y zeolite was treated with 100% steam at 800 °C for 5 h to obtain the USY zeolite.

A total of 20 g sodium chloride was dissolved in 200 mL deionized water and stirred until it was clear. Then, 20 g USY zeolite was added and stirred at room temperature for 12 h. After suction filtration and washing, the filter cake was dried in an oven at 100 °C for 12 h and calcined at 500 °C for 4 h to obtain NaUSY zeolite.

2.2.2. Preparation of Magnesium Ion Exchange X Zeolite Powder

80 g magnesium acetate was dissolved in 800 mL deionized water and stirred until clear, then 200 g NaX zeolite was added and stirred at 80 °C for 2 h. After the exchange is completed, the obtained suspension is divided into two equal parts: one is filtered, the filter cake is dried at 100 °C for 12 h, and calcined at 500 °C for 4 h to obtain the ion exchange sample MgNaX zeolite; another half was washed three times with deionized water, then dried at 100 °C for 12 h and calcined at 500 °C for 4 h to obtain the washed ion exchange sample wMgNaX zeolite.

2.2.3. Extrusion Molding of Adsorbent

The zeolite and pseudo-boehmite powder were weighed, respectively, to ensure that the dry base ratio of zeolite and Al₂O₃ was 1:1. The 0.2% sesbania gum of the total weight of zeolite and pseudo-boehmite was weighed. After the above three were mixed evenly, the dilute nitric acid with a concentration of 1% was added in batches and kneaded until sticky. The strip-formed adsorbent is continuously extruded using a 1.5 mm mold (the formed adsorbent is not easily broken, indicating good strength). The extruded strip adsorbent was dried naturally for 8 h, then dried in an oven at 100 °C for 12 h and calcined at 500 °C for 4 h to obtain the formed adsorbent sample. The formed adsorbents were named as NaX–Al₂O₃, MgNaX–Al₂O₃, and wMgNaX–Al₂O₃, corresponding to NaX, MgNaX, and wMgNaX zeolite powders, respectively.

2.3. Adsorption Capacity Evaluation

The evaluation of the adsorption capacity of the sample was carried out on a custom-made continuous-flow fixed-bed tube (Figure 1), and the inner diameter of the adsorber was 10 mm. The formed sample was crushed to obtain 16–20 mesh particles and then loaded into the adsorber with a loading dose of 4 mL. The standard gas containing dimethyl ether (dimethyl ether 2000 ppm, the rest is nitrogen) was mixed with high-purity nitrogen by a mass flowmeter to control the concentration of dimethyl ether at the inlet of the adsorber to 400 ppm, and it was then sent to the top of the adsorber to contact with the sample bed for adsorption experiments. The adsorption conditions were 40 °C, 6000 h^{−1}, and atmospheric pressure. Before the adsorption evaluation, the sample needs to be heated to 290 °C in a flowing nitrogen atmosphere to remove the adsorbed impurity on the surface. The gas phase chromatograph (Agilent 6890; DIMA TCEP Capillary column: 60 m × 0.25 mm 10 μm; Column temperature: 40 °C; Flame Ionization Detector, Detection temperature: 250 °C) was used to detect and analyze the airflow at the outlet of the adsorber every 15 min, and the change in dimethyl ether concentration was monitored. When the outlet concentration is consistent with the raw material concentration, the adsorption experiment is stopped.

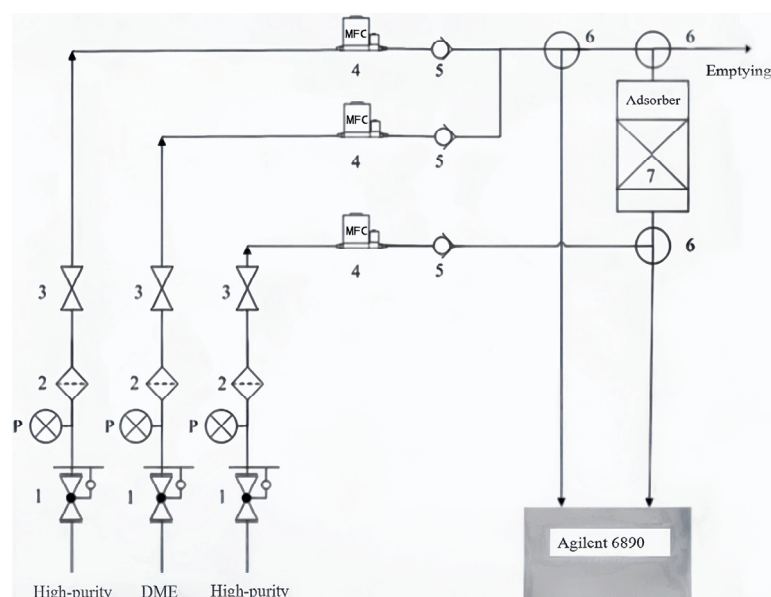


Figure 1. Schematic diagram of adsorption experiment process: 1, Raw gas; 2, Filter; 3, Stop valve; 4, Mass flow meter; 5, Check valve; 6, Three-way valve; 7, Adsorber; P, Pressure gauge.

The adsorption capacity of dimethyl ether is calculated according to the following calculation Formula (1):

$$q = M \cdot 10^{-6} \cdot \int_0^t \left(\frac{QP}{RT} \right) / m_s \cdot (C_0 - C_t) dt \quad (1)$$

where q is the adsorption capacity on the unit mass adsorbent (mg/g); M is the molecular weight of DME; t is time (min); Q is the flow rate (mL/min); P is pressure (Pa); R is the ideal gas constant (8.314 J/(mol·K)); T is temperature (K); m_s is the mass of adsorbent (g); C_0 and C_t is the impurity content (ppm) of the raw material and the outlet, respectively. The breakthrough time was defined as the time when the outlet dimethyl ether concentration was 1 ppm, and the corresponding adsorption capacity was q_b (mg/g). The time when the outlet concentration is equal to the inlet concentration is the equilibrium time, corresponding to the equilibrium adsorption capacity q_e (mg/g). The adsorption capacity mentioned below is the breakthrough adsorption capacity, unless otherwise specified.

2.4. Sample Characterization

XRD: Powder X-ray diffraction (XRD) was performed on a Bruker D8 Advance X-ray diffractometer using a Cu K α 1 ray source ($\lambda = 0.15405$ nm) and a graphite monochromator (Bruker, Karlsruhe, Germany). The tube pressure was 40 kV, the tube current was 50 mA, and the scanning range was 5–35°. Eight characteristic peaks between 14 and 35° were selected, and the relative crystallinity was obtained by comparing the area of the eight characteristic peaks with that of the standard samples.

SEM: Using Hitachi S-4800 acquisition with a working voltage of 3 KV (Hitachi, Tokyo, Japan). The morphology of the catalyst sample was observed, and the EDS surface scan was measured by an X-ray energy spectrometer (Oxford X-MaxN 150 EDS) (Oxford Instruments, Oxford, UK).

XRF: The elemental composition and content of the adsorbent were determined by S4 Pioneer X-ray fluorescence spectrometer (Bruker, Karlsruhe, Germany).

N₂ adsorption and desorption: N₂ adsorption–desorption was performed on a specific surface area and porosity analyzer (Micromeritics ASAP 2020M, Micromeritics, Norcross, GA, USA). The sample was extracted at 300 °C, and the adsorption–desorption curve of N₂ was measured at liquid nitrogen temperature. The specific surface area of the sample

was calculated by the BET formula, and the pore size distribution curve of the sample was calculated by the BJH method.

NH₃-TPD and CO₂-TPD: Ammonia temperature-programmed desorption (NH₃-TPD) and carbon dioxide temperature-programmed desorption (CO₂-TPD) tests were performed on a chemical adsorption instrument (Altamira AMI-3300, Altamira Instruments, Pittsburgh, PA, USA). After pretreatment, the samples were adsorbed with NH₃ or CO₂, and the desorption process was performed at 100–550 °C to measure the acid-base amount and strength of the zeolite.

Determination of crushing strength of shaped adsorbent: The radial strength test of the sample was carried out on the DL III intelligent particle strength tester (Dalian Penghui Technology Development Co., Ltd, Dalian, China), and the sample was measured continuously 10 times, and the average value was taken.

3. Results and Discussion

3.1. Preliminary Screening of Zeolite Adsorption Materials

As the main active component of the adsorbent, the structural properties (pore structure, composition, etc.) of the zeolite will affect the adsorption performance of the adsorbent. The most basic structural units of zeolites are silicon oxygen tetrahedra and aluminum oxygen tetrahedra. These tetrahedra are interconnected by oxygen atoms at their vertices, forming the three-dimensional framework structure of the zeolite. This three-dimensional crystal structure constructs regular polyhedral cavities or cages, such as cubic cages, beta cages, and gamma cages, which are connected to each other through specific windows to form the pore system of zeolites. This spatial structure provides zeolites with a large amount of internal surface area and adsorption space, enabling zeolites to adsorb a large number of molecules. Commercially, A, X, Y type zeolites are mainly used for adsorption and ion exchange. Among them, 3A, 4A, and 5A zeolites all have LTA topology and the framework Si/Al ratio is basically close to 1.0, but the types of metal cations in the zeolite framework are different. The 4A zeolite is a typical NaA zeolite with a pore size of about 0.4 nm. The 3A zeolite (KNaA) is an A-type zeolite with a pore size of about 0.3 nm, formed by K⁺ exchange of Na⁺ in the framework. The 5A zeolite (CaNaA) is an A-type zeolite with a pore size of about 0.5 nm, formed by using Ca²⁺ exchange with Na⁺. X and Y zeolites have FAU topology, and the framework contains 12-membered ring pores (about 0.78 nm in size) and a supercage. However, the Si/Al ratio of the NaX zeolite is low (Si/Al = 1.0–1.5), while the silicon–aluminum ratio of the NaY zeolite is basically between 1.5 and 2.5. The NaUSY zeolite is a special type of Y zeolite with a high Si/Al ratio (Si/Al > 2.5). It can be seen from Figure 2 that each zeolite has its own characteristic diffraction peaks, and the corresponding diffraction peak intensity is high, and the peak shape is complete, indicating that the zeolite crystal is perfect and the crystallinity is high. For A-type zeolites, the change in metal cations in the framework did not lead to significant changes in the position and shape of the zeolite diffraction peaks; for NaX, NaY, and NaUSY zeolites with FAU topology, with the increase in Si/Al ratio, the diffraction peak corresponding to the (533) crystal plane (vertical position in the figure) gradually shifts to a high angle, owing to the different lengths of silicon–oxygen bond and the aluminum–oxygen bond.

The SEM images of zeolites with different topologies are shown in Figure 3. It can be seen that the 3A zeolite (KNaA) has an obvious cubic morphology, and the particle size of the zeolite is not uniform. The large particle size is about 1–3 µm, and the small particle size is about 0.5–1.0 µm. The 4A zeolite is an NaA zeolite without ion exchange, while the 5A zeolite is a zeolite after Ca²⁺ exchange, and its morphology is similar to that of 3A. It can be seen from the scanning electron microscope image of the A-type zeolite that the morphology of the zeolite remains unchanged after ion exchange. In addition, it can be seen from Figure 3 that the NaX zeolite has a standard octahedral morphology (particle size of 1–3 µm), complete crystal structure, and without an obvious impurity crystal. With the increase in framework Si/Al ratio, the particle size of NaY and NaUSY zeolites is smaller than that of NaX zeolite, which is about 0.5–1.0 µm.

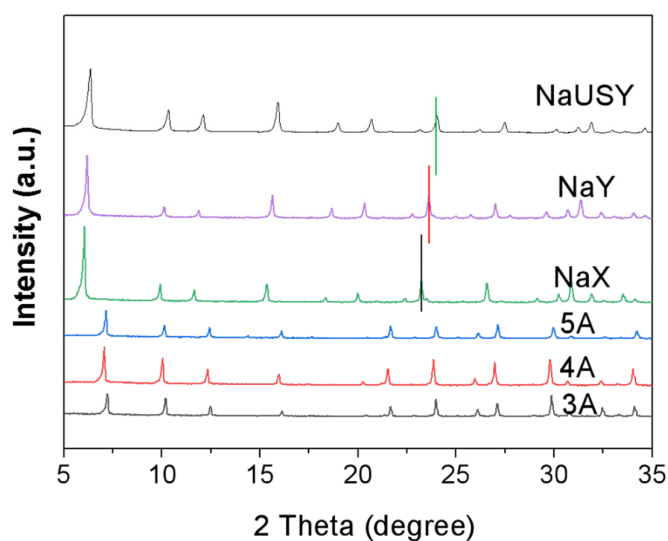


Figure 2. XRD patterns of different zeolites (the vertical lines in the pattern represent (533) the crystal plane of zeolites NaX, NaY, and NaUSY).

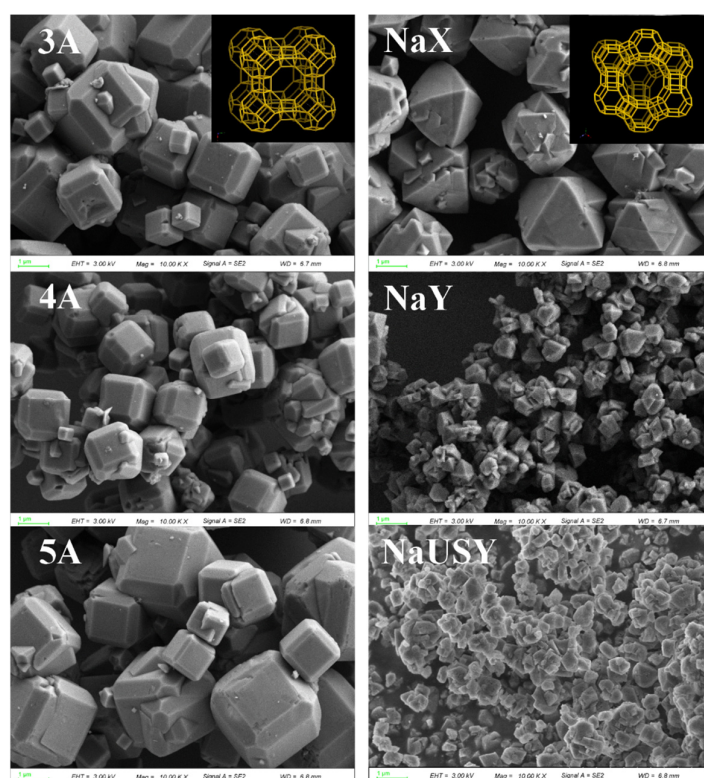


Figure 3. SEM images of different zeolites (scale bar: 1 µm).

The pore structure and composition properties of zeolites with different topologies are shown in Table 1. It can be seen from the table that the 3A, 4A, and 5A zeolites have the same framework, but the metal cations inside the framework are different. The Si/Al ratio of the three zeolites is the same by XRF detection. Among them, the 4A zeolite is a sample without ion exchange, and the metal cation is only Na^+ , and the sodium–aluminum molar ratio (Na^+/Al) is close to 1.0. The Na^+/Al molar ratio of 3A and 5A zeolites obtained after ion exchange is reduced to 0.58 and 0.25, respectively. The excess negative charge of the zeolite framework is balanced by K^+ ions and Ca^{2+} ions for 3A and 5A zeolites, respectively. Due to the limitation of pore size, nitrogen molecules cannot diffuse into

the pores of 3A and 4A zeolites at an ultra-low temperature (77 K). Therefore, the specific surface area and pore volume of 3A and 4A zeolites cannot be determined by nitrogen adsorption–desorption isotherms [32]. Different from this, the pore size of the 5A zeolite and the FAU zeolite is large enough. At 77 K, nitrogen molecules can diffuse and adsorb in the pores of zeolites. It can be seen from Table 1 that the specific surface area of the 5A zeolite is 619.4 m²/g. The Si/Al ratios of NaX, NaY, and NaUSY are 1.09, 2.33, and 4.80, respectively. The NaY zeolite has the highest specific surface area, followed by the NaX and NaUSY zeolites. The NaUSY zeolite has the lowest specific surface area, because of partial skeleton collapse in the process of dealuminization.

Table 1. Pore structure parameters, element composition properties, and adsorption performances for dimethyl ethers of different zeolite samples.

Sample	S _{BET} (m ² /g)	S _{Ext} (m ² /g)	V _{Total} (cm ³ /g)	V _{Micro} (cm ³ /g)	Si/Al β	Mn ⁺	Na ⁺ /Al	Adsorption Capacity q _b (mg/g) γ
3A	-- α	--	--	--	0.89	Na ⁺ /K ⁺	0.58	0
4A	-- α	--	--	--	0.89	Na ⁺	1.15	100.9
5A	619.4	19.8	0.30	0.28	0.89	Na ⁺ /Ca ²⁺	0.25	95.1
NaX	726.7	26.6	0.34	0.33	1.09	Na ⁺	1.13	154.3
NaY	752.4	38.7	0.36	0.33	2.33	Na ⁺	1.16	116.2
NaUSY	654.0	34.0	0.37	0.24	4.80	Na ⁺	0.09	10.9

α : N₂ adsorption–desorption could not detect the pore structure properties of 3A and 4A zeolites. β : The Si/Al ratio of zeolites is determined by XRF. γ : Evaluation conditions for dimethyl ether adsorption: impurity concentration, 400 ppm; adsorption temperature, 40 °C; atmospheric pressure; space velocity, 6000 h^{−1}.

All zeolite samples were compressed into sheets and crushed to 16–20 mesh, respectively, and their adsorption properties of dimethyl ether impurity molecules in nitrogen were evaluated in a fixed-bed reactor. The dynamic curve of dimethyl ether adsorption by each zeolite is shown in Figure 4. Due to the limitation of pore size, dimethyl ether molecules cannot diffuse into the pore of the 3A zeolite at room temperature, so its ability to adsorb dimethyl ether is almost zero. For 4A and 5A zeolites, due to the larger pore size, dimethyl ether can effectively diffuse into and adsorb in the channel of zeolites, and the penetration time of dimethyl ether is significantly prolonged. The dynamic diameter of the DME molecule is about 0.4 nm. The size relationship between the pore size of different zeolites and the dynamic diameter of DME is as follows: 3A < DME $\approx$ 4A < 5A < FAU. For zeolites with FAU topology, the pore size of zeolites is larger, and dimethyl ether can diffuse and adsorb freely in the pores of zeolites at room temperature, so dimethyl ether can be adsorbed effectively. The results of the breakthrough adsorption capacity of dimethyl ether calculated by the dynamic adsorption curve of dimethyl ether are shown in Table 1. Among the LTA zeolites, the breakthrough adsorption capacity of the 4A zeolite is higher than the 5A zeolite, while the equilibrium adsorption capacity of the 5A zeolite is better than the 4A zeolite. In the FAU zeolite, the adsorption capacity of dimethyl ether shows a higher correlation with the silica–alumina ratio of the zeolite. The NaX zeolite, with a lower Si/Al ratio, has a higher DME adsorption capacity (154.3 mg/g). The specific surface area of the NaUSY zeolite was only about 14% lower than that of NaY, but its dimethyl ether adsorption capacity was reduced by 90.6% (10.9 mg/g). This is owing to the fact that for zeolites with the same topology, although the specific surface area is an important factor affecting the adsorption capacity of zeolites, the metal cations (electron acceptors) in the zeolite framework that balance the negative charge of the zeolite framework also play an important role in the adsorption.

For the NaUSY zeolite, Na/Al is low and the number of metal cations in the zeolite skeleton is small, so the interaction with oxygen-containing compound impurities (electron donors) is weak. Furthermore, the collapse of the part skeleton during the process of dealuminization for the NaUSY zeolite also leads to a significant reduction in adsorption capacity.

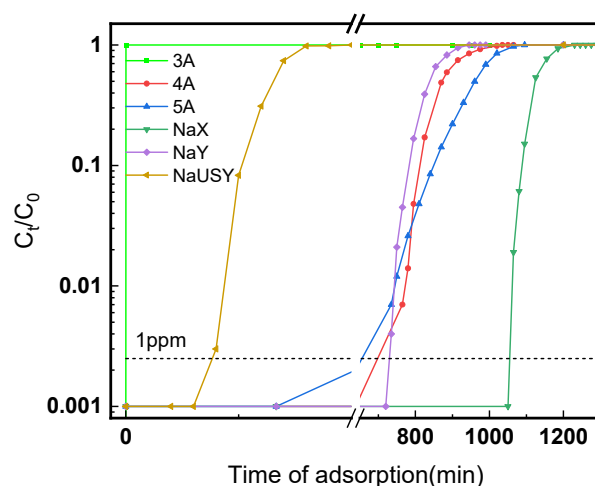


Figure 4. Kinetic curves of dimethyl ether adsorption by different zeolites. Evaluation conditions: impurity concentration, 400 ppm; adsorption temperature, 40 °C; atmospheric pressure; space velocity, 6000 h^{−1}.

3.2. Ion Exchange Modification of the NaX Zeolite

It is thought that the adsorption of oxygen-containing or sulfur-containing compound impurities by zeolites is a process of electron donor–electron acceptor interaction [33]. In other words, the metal cation in the framework that balances the negative charge of the silica–alumina zeolite framework acts as an electron acceptor, which can form a weak interaction with the lone pair electrons of oxygen atoms or sulfur atoms (electron donors) in oxygen-containing and sulfur-containing compound, thereby these oxygen-containing or sulfur-containing compound can be adsorbed inside the zeolite pores. Therefore, by means of ion exchange or impregnation, the modification of metal cations in the framework can change the charge distribution of the zeolite and the electrostatic field strength of the zeolite pores, which can adjust the adsorption of impurity molecules by the zeolite [34]. Based on this, we selected the NaX zeolite with the highest adsorption capacity of dimethyl ether as the precursor, and modified it by magnesium ion (Mg²⁺) exchange. The dimethyl ether adsorption performance of zeolite powder and the extruded adsorbent after ion exchange was investigated.

From Table 2, it can be seen that the crystallinity of the MgNaX zeolite obtained after ion exchange can be well retained with magnesium acetate as the magnesium precursor. The nitrogen adsorption–desorption isotherm (Figure 5) shows that the adsorption capacity of the exchanged sample at low pressure is lower than that of the NaX zeolite powder. Moreover, the adsorption curve of the zeolite after ion exchange still presents a type I isotherm, which indicates that there is no obvious mesoporous structure after ion exchange. However, compared with NaX raw powder, the BET specific surface area of zeolite after exchange decreased from 726.7 m²/g to 666.0 m²/g, which was mainly caused by the decrease in micropore specific surface area (from 700.1 m²/g to 639.3 m²/g). The above data indicate that there is a small amount of collapse of the zeolite skeleton during the exchange process.

In the process of industrial application, when the olefin contacts with the porous adsorbent for the first time, the adsorption heat will be generated and accumulated rapidly, and the temperature rise in the adsorption tower can even reach more than 100 °C. At this time, the acid–base sites on the surface of the zeolite-type adsorbent will catalyze the polymerization, isomerization, and other side reactions of olefins. These by-products are adsorbed on the surface of the adsorbent and may be further converted into carbon deposition during the subsequent regeneration process [35,36], so that the adsorption capacity of the adsorbent is gradually lost. Therefore, we characterized the adsorbents by NH₃–TPD and CO₂–TPD to explore the changes in surface acid–base properties. The results

are shown in Figure 6. From Figure 6a, it can be seen that the NaX zeolite has continuous NH_3 desorption between 100 °C and 550 °C, and there are two obvious desorption peaks at 192.4 °C and 326.4 °C. After magnesium ion exchange, the desorption peak in the high temperature range disappeared, and only one desorption peak appeared at the low temperature of 191.2 °C, and the area of the desorption peak also decreased significantly, which indicated that magnesium ion exchange reduced the surface acid strength and acid amount of the zeolite. The CO_2 -TPD of Figure 6b shows that the CO_2 desorption peak of the NaX powder also moves to a low temperature after magnesium ion exchange, and the peak area decreases greatly, which indicates that the surface alkali strength and alkali amount of the NaX powder also decrease significantly after exchange.

Table 2. Structure, composition, and radial compressive strength of zeolite powders and zeolite formed adsorbents before and after ion exchange.

Sample	Crystallinity %	Si/Al α	Na/Al	S_{BET} (m^2/g)	S_{Micro}^β (m^2/g)	V_{Total} (cm^3/g)	Radial Compressive Strength (N/cm)
NaX	100	1.09	1.13	726.7	700.1	0.34	--
MgNaX	93	1.10	0.78	666.0	639.3	0.32	--
wMgNaX	93	1.10	0.68	645.0	611.1	0.33	--
NaX- Al_2O_3	--	0.32	0.31	503.1	312.4	0.36	25.5
MgNaX- Al_2O_3	--	0.30	0.20	499.4	312.2	0.35	31.8
wMgNaX- Al_2O_3	--	0.31	0.19	459.1	274.3	0.36	27.7
Al_2O_3	--	0	0	279.2	0	0.39	--

α : The Si/Al ratio of zeolites was determined by XRF. β : The micropore specific surface area was calculated by the t-plot formula.

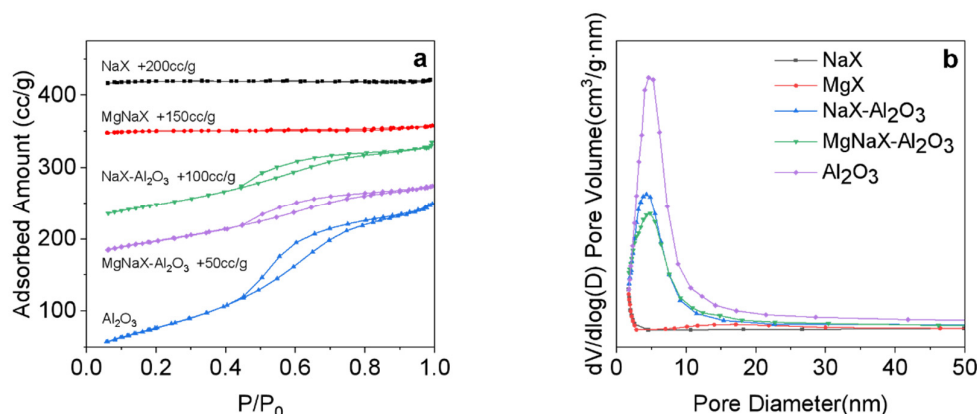


Figure 5. Nitrogen adsorption-desorption isotherms at 77K (a) and BJH pore size distribution curves (b) of the FAU zeolite and formed adsorbent.

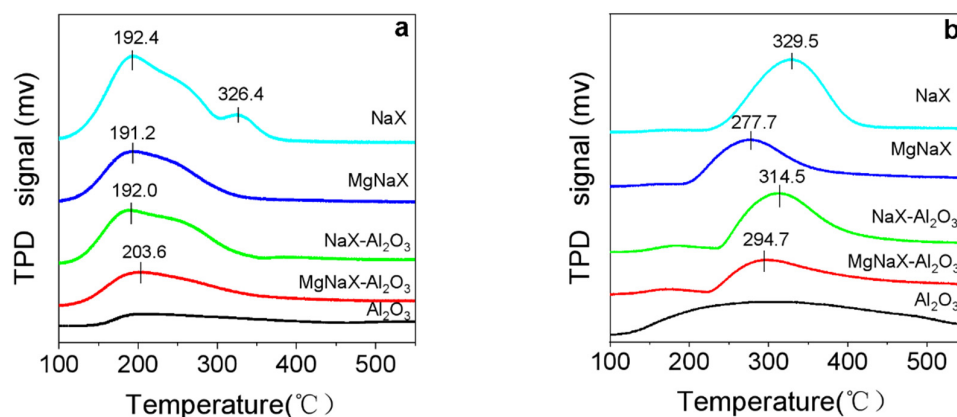


Figure 6. NH_3 -TPD (a) and CO_2 -TPD results (b) of the FAU zeolite and the formed adsorbent.

3.3. FAU Zeolite Molding

The formed adsorbents, NaX- Al_2O_3 and MgNaX- Al_2O_3 , for industrial application scenarios were prepared by extrusion of NaX and MgNaX zeolite powders before and after exchange. Figure 7 shows the shape of the molded adsorbent. It can be seen that the extruded adsorbent has a uniform particle size and smooth surface. The radial crushing strength of NaX- Al_2O_3 and MgNaX- Al_2O_3 can reach 25.5 N/cm and 31.8 N/cm, respectively (Table 2), which meets the requirements of industrial application. SEM results for MgNaX- Al_2O_3 showed that the zeolite crystal inside the formed adsorbent was complete and the element distribution was uniform, which indicated that the forming step did not cause mechanical damage to the zeolite crystal, and the zeolite powder and the binder alumina were fully mixed. The nitrogen adsorption–desorption isotherms of NaX- Al_2O_3 and MgNaX- Al_2O_3 samples are shown in Figure 5a, and there are obvious hysteresis loops, indicating that different from the zeolite powder, the formed samples contain a rich mesoporous structure. It can be seen from the pore size distribution curve in Figure 5b that the mesopores in the adsorbent mainly come from the binder alumina, and the mesoporous size is basically the same as the pore size of pure alumina. Table 2 gives more texture information about the formed samples, from which it can be seen that although the specific surface area of MgNaX zeolite raw powder is significantly lower than that of NaX raw powder, MgNaX- Al_2O_3 and NaX- Al_2O_3 adsorbents formed according to the same zeolite–alumina ratio have almost the same specific surface area. This may be because the organic salt introduced in the preparation process of the MgNaX zeolite is decomposed at high temperature during the roasting stage, which is beneficial to the improvement of the specific surface area of the formed adsorbent.

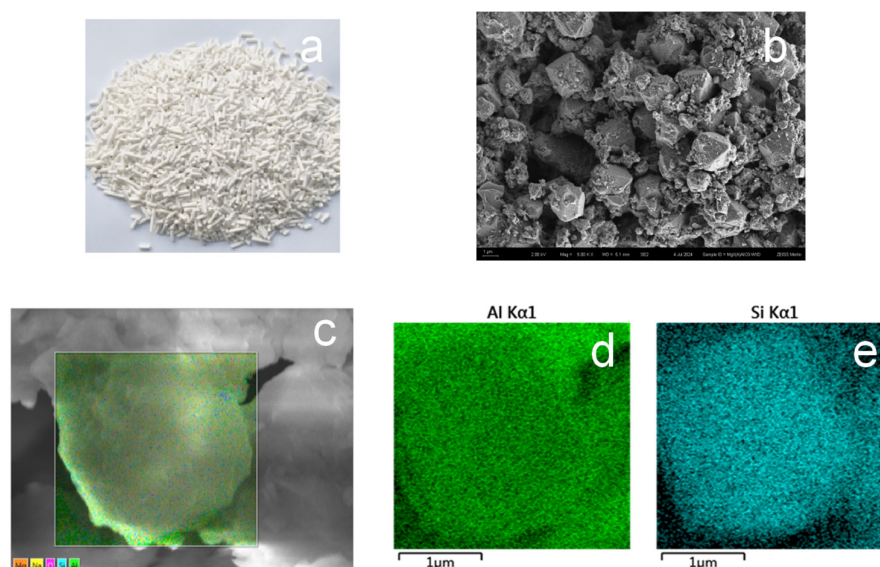


Figure 7. Photo of adsorbent MgNaX- Al_2O_3 (a), scanning electron microscope image (b), and the distribution of each element (c–e).

In order to verify the above inference, the zeolite powder wMgNaX was prepared by fully washing and removing organic anions after ion exchange. The corresponding molding sample, wMgNaX- Al_2O_3 , was also prepared. The characterization results (Table 2) showed that the specific surface area of wMgNaX was 645.0 m^2/g , which was close to that of MgNaX. But the specific surface area of wMgNaX- Al_2O_3 was 459.1 m^2/g , which was significantly lower than that of MgNaX- Al_2O_3 . It has been confirmed by repeated experiments that the residual organic salts on the surface of the zeolite-powder after ion exchange play an important role in the forming process, which can promote the specific surface area of the formed sample.

Figure 8 shows the adsorption evaluation results of the FAU zeolite and its formed adsorbent. From Figure 8a, it can be seen that the dimethyl ether adsorption capacity of the MgNaX zeolite and wMgNaX zeolite obtained after ion exchange is 117.3 mg/g and 117.5 mg/g, respectively, which is significantly lower than that of the NaX powder (154.3 mg/g). Due to the low adsorption capacity of the binder alumina (5.1 mg/g), the adsorption capacity of all the molded adsorbents decreased, but the adsorbent MgNaX- Al_2O_3 prepared with the original powder of the MgNaX zeolite had the smallest decrease (q_b -formed/ q_b -powder was the highest), which made it have the highest adsorption capacity in the molded sample, up to 68.0 mg/g. Figure 8b further correlated the adsorption capacity with the specific surface area of the sample. It can be seen that the adsorption capacity of dimethyl ether has a significant linear relationship with its specific surface area. For the MgNaX zeolite, although the specific surface area and adsorption capacity of the original powder were significantly lower than those of NaX zeolite, the organic salts introduced by ion exchange played an important role in the molding process, so that the adsorption capacity of the molding adsorbent MgNaX- Al_2O_3 was well maintained, even about 13% higher than that of NaX- Al_2O_3 . For the wMgNaX zeolite powder, although its specific surface area and adsorption capacity is close to that of the MgNaX zeolite, its corresponding molding adsorbent, wMgNaX- Al_2O_3 , has a low specific surface area and the lowest adsorption capacity.

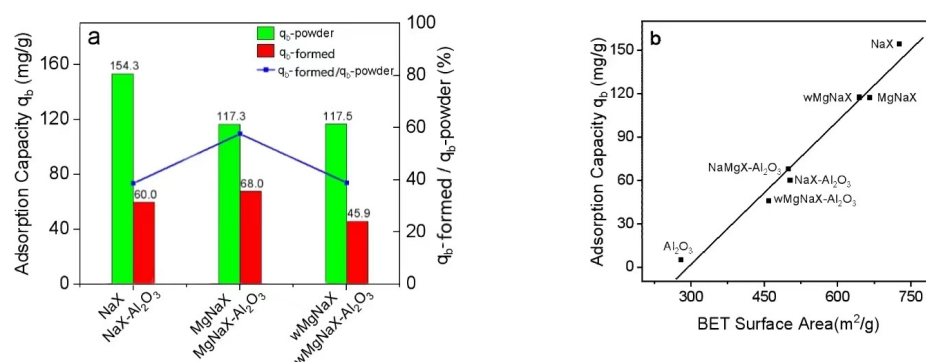


Figure 8. Adsorption performance of the FAU zeolite and formed adsorbent (a), and the relationship between specific surface area and adsorption capacity (b). Evaluation conditions: impurity concentration, 400 ppm; adsorption temperature, 40 °C; atmospheric pressure; space velocity, 6000 h^{-1} .

The surface acid–base properties of the shaped adsorbent are similar to those of the zeolite powder, as shown in Figure 6. The MgNaX- Al_2O_3 adsorbent prepared after ion exchange has lower acid/alkali strength and acid/alkali amount than that of the NaX- Al_2O_3 adsorbent. The weakening of the acid/base active sites on the surface of the adsorbent corresponds to the lower catalytic activity. It can be inferred that during the olefin purification process in the MTO industry, the catalytic side reactions caused by the adsorption heat on the surface of the MgNaX- Al_2O_3 adsorbent will also be less, which is more favorable for the retention of its adsorption capacity and cycle number.

The adsorption and regeneration performance of the formed adsorbent MgNaX- Al_2O_3 was further determined. The samples were named as MgNaX- Al_2O_3 -n, where n is the number of cycles. The results are shown in Figure 9. It can be seen that the adsorbent can be completely regenerated by high temperature nitrogen purging, and the adsorption performance is not significantly reduced after three regenerations, which means that MgNaX- Al_2O_3 is a potential adsorbent for removing dimethyl ether in the MTO industry.

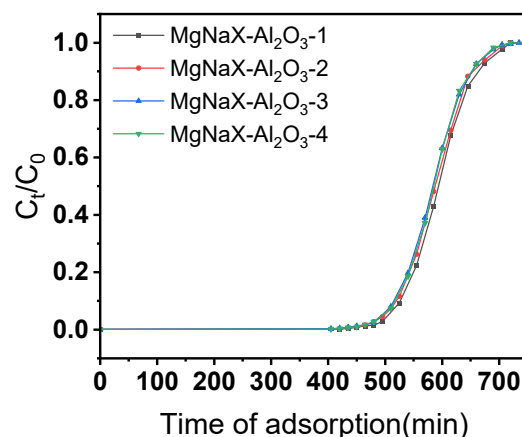


Figure 9. MgNaX-Al₂O₃ adsorption–regeneration curve. Evaluation conditions: impurity concentration, 400 ppm; adsorption temperature, 40 °C; atmospheric pressure; space velocity, 6000 h^{−1}; Regeneration conditions: regeneration atmosphere; high purity nitrogen; temperature, 290 °C; space velocity, 3000 h^{−1}; time, 2 h.

4. Conclusions

The adsorption performance of the FAU zeolite was much higher than that of the LTA zeolite because of its high specific surface area and pore size, and the adsorption capacity decreased with the increase in the Si/Al ratio for the FAU-type zeolite. The NaX zeolite, with a lower Si/Al ratio, had the highest adsorption capacity.

The strength of acid and alkali on the surface of zeolite becomes weaker after Mg ion exchange, which is beneficial to avoid the catalytic side reaction caused by the heat release during the adsorption process.

The residual organic salt on the surface of the zeolite powder after exchange promoted the specific surface area and adsorption capacity of the formed adsorbent. The adsorption capacity of the MgNaX-Al₂O₃ molding adsorbent for dimethyl ether can reach 68 mg/g, and the regeneration performance is excellent, which can meet the industrial requirements of high-precision removal of oxides in olefins.

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