Separation of naphtha on a series of ultramicroporous MOFs: A comparative study with zeolites

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ABSTRACT

Naphtha separation is of significant importance for refineries to make full use of oil and to reduce the cost of refining. In the recent years, scientists have devoted great efforts to developing novel porous materials such as metal-organic frameworks (MOFs) for the separation of naphtha. However, previous investigations have been limited to single-component or 3- to 5-component model systems. Separation of full range hydrocarbon mixture such as naphtha has rarely been explored. In this work, we carry out a comprehensive study on the separation of alkane isomers as well as full range naphtha mixture by a series of robust microporous MOFs, e.g., Zr-abtc, Al-bttotb, Co-fa, in comparison with representative zeolite materials, e.g., ZSM-5 and zeolite 5A. We find that Al-bttotb and Co-fa, which can separate monobranched and dibranched alkanes through complete molecular exclusion, show superior separation performance for naphtha mixtures. This work may shed light on strategies for developing adsorbents with optimal performance for naphtha separation and ultimately realizing the industrialization of MOF-based separation technologies.

1. Introduction

Efficient separation of oil mixture is an important task in petro-chemical industry. The separation of naphtha components is crucial for optimizing the feed for steam cracking and catalytic reforming, as well as for producing high-octane gasoline [1]. Zeolite 5A is the primary adsorbent for industrial naphtha separation [2]. It is currently used in adsorptive separation processes such as MaxEne (the world's first industrialized process for adsorptive separation of naphtha jointly developed by UOP and Sinopec), and Molex and Isosiv for C5/C6 isomerization. Zeolite 5A adsorbs only linear alkanes, thus it can sepa-rate linear alkanes from their branched isomers [3]. However, the adsorption capacity of zeolite 5A is relatively low, with a theoretical maximum adsorption capacity of only 1.75 mmol/g (15 wt% for n-hexane) [4]. In addition, normal alkanes only account for 22–36% of typical naphtha components [1], and therefore it can hardly meet the current requirements for high-quality raw materials for ethylene

production by steam cracking. Furthermore, with high concentration of monobranched alkanes, the remaining components have relatively low octane number and are not suitable for use as gasoline components.

In this context, separation of normal and monobranched alkanes from their dibranched isomers would be more ideal, as monobranched alkanes could serve as high quality ethylene cracking feed and the remaining products are expected to have a higher octane number. However, zeolite 5A is not capable of fulfilling this task as it adsorbs essentially no branched alkanes. While ZSM-5 is able to discriminate mono-branched and di-branched alkanes, its adsorption capacity for monobranched hexanes is relatively low (2.4 wt% for 2-methylpentane at 298 K [5]). To this end, it is imperative to develop novel adsorbent materials which are capable of efficient separation of branched alkanes so as to efficiently split naphtha. Metal-organic frameworks (MOFs) hold particular promise in hydrocarbon separations [6] such as ethylene mixtures [7] and propene mixtures [8], especially for separating naphtha in light of their structural diversity as well as highly tunable

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pore shape and pore dimensions. Tremendous advancements have been made in using MOFs for the separation of alkane isomers over the past few years.

Barcia et al. reported a zinc based MOF $Zn_2(bdc)_2(dabco)$ (bdc = 1,4-benzenedicar-boxylate, dabco = 1,4-diazabicyclo [2,2,2]octane), which exhibits a much higher adsorption capacity for n-hexane (5.5 wt%, 313 K, 33 kPa) than that of 3-methylpentane (1.5 wt%) and 2,2-dimethylbutane (1 wt%) [9]. In a follow-up study, Ling et al. developed $Zn_2(hbdc)_2(dmtrz)_2$ (H_2bdc = 1,4-benzenedi-carboxylate acid, Hdmtrz = 3,5-dimethyl-1H, 1, 2, 4-triazole) through ligand functionalization. It adsorbs similar amounts of n-hexane (13.3 wt% at 298 K) and 3-methylpentane (12.1 wt%) but much less 2,2-dimethylbutane (3.5 wt%) [10]. Ferreira et al. found that while ZIF-8 adsorbs n-hexane, 3-methylpentane and a small amount of 2,3-dimethylbutane, 2,2-dimethylbutane was completely excluded [11]. Belarbi et al. investigated the separation performance of MIL-101(Cr) for hexane isomers and the order of adsorption capacity follows n-hexane > methylpentane > 2,3-dimethylbutane = 2,2-dimethylbutane [12]. In one of our recent studies, we designed a series of Zr based MOFs, including $Zr_6O_4(OH)_4(bptc)_3$ (Zr-bptc, bptc = 3,3′,5,5′-biphenyltetracarboxylate) and $Zr_6O_4(OH)_4(abtc)_3$ (Zr-abtc, abtc = 3,3′,5,5′-azobenzene-tetracarboxylate). Zr-bptc can separate linear and branched C6 isomers through size exclusion, with a n-hexane adsorption capacity 70% higher than zeolite 5A. Zr-abtc is capable of separating monobranched and dibranched hexanes through thermodynamically-controlled mechanics [13]. Herm et al. investigated the separation of hexane isomers by $Fe_2(bdp)_3$ (bdp^{2-} = 1,4-benzenedipyrazolate). Its triangular pores can accommodate all types of hexane isomers, but the adsorption strength is different leading to a thermodynamic separation [14]. In a more recent study, we developed a series of MOFs that can well separate monobranched alkanes from their dibranched isomers. Ca (H_2tcpb) (tcpb = 1,2,4,5-tetrakis(4-carboxyphenyl)-benzene) featuring flexible framework is capable of splitting hexane isomers as a degree of branching as a result of its breathing behavior [15]. Al-bttotb ($H_3bttotb$ = 4,4′,4″-(benzene-1,3,5-tri-yltris (oxy))tribenzoicacid) [16] and $Co_3(HCOO)_6$ (Co-fa) [17] represent the first porous adsorbents that can fully separate monobranched and dibranched alkanes through selective molecular exclusion under ambient conditions.

However, the aforementioned studies have been mostly focused on the evaluation of separation capability for model mixtures of 3–5 components of hexane isomers, while the separation of full range naphtha involves ~200 components [17]. To further evaluate the capability of the reported benchmark MOF adsorbents for the separation of naphtha and to explore what is the optimal pore structure for the separation process, in this study we carry out a comprehensive comparative study of Zr-abtc, Al-bttotb, Co-fa, ZSM-5, and zeolite 5A for the adsorption and separation of hexane isomers and full range naphtha mixtures.

2. Experimental

2.1. Materials

Chemical precursors for the synthesis of the organic linker H_4abtc: 5-nitroisopthalic acid (95% purity, AK Scientific), zinc powder (97.5% purity, Alfa Aesar), sodium hydroxide (97% purity, Honeywell), hydrochloric acid (38%, VWR). Chemicals for the synthesis of the Zr-abtc were purchased in bulk as follows: zirconium (IV) oxychloride octahydrate ($ZrOCl_2·8H_2O$, 99%, Sinopharm Chemical Reagent), formic acid (99.5%, Sinopharm Chemical Reagent), N,N-dimethylformamide (99.8%, Sinopharm Chemical Reagent). Chemicals for the synthesis of the Al-bttotb were purchased in bulk as follows: $Al(NO_3)_3·9H_2O$ (99.0%, Sinopharm Chemical Reagent); $H_3bttotb$ (98%, Yanshen Technology). ZSM-5 was purchased from Nakai University Catalyst Co. Ltd. (NKF-5, Si/Al = 38); 5A was purchased from Sinopharm Chemical Reagent. All organic solvents and precursors were used as is without further purification after receiving from the chemical supplier. Naphtha mixture was

obtained from the CNPC Urumqi Petrochemical. It is the atmospheric straight run naphtha after hydrogenation to remove sulfur, nitrogen and arsenic.

2.2. Synthesis

2.2.1. Synthesis of Zr-abtc

Zirconium (IV) oxychloride octahydrate ($ZrOCl_2·8H_2O$, 32.2 mg, 0.1 mmol) was ultrasonically dissolved in a mixed solvent of N,N-dimethylformamide (DMF, 8 mL) and formic acid (6 mL) in a 20 mL scintillation vial. H_4abtc (35.8 mg, 0.1 mmol) was then added to the solution which was sonicated for 5 min before being moved to a pre-heated oven at 120 °C. The reaction was kept at 120 °C for 3 days and light orange solids were observed in the reaction glass vial upon cooling. These solids are either microcrystalline or crystals large enough for single crystal X-ray diffraction analysis. The solid samples were collected by centrifuge (or vacuum filtration). The materials were washed with DMF and methanol with a Soxhlet extractor for 2 and 3 days, respectively, prior to the adsorption study. Yield: 74% (based on Zr).

2.2.2. Synthesis of Al-bttotb

$Al(NO_3)_3·9H_2O$ (200 mg) and $H_3bttotb$ (125 mg) was added to a mixed solvent of DMF/formic acid (20/10 mL) and the mixture was stirred at room temperature for 30 min before being transferred to a 100 mL Teflon bomb. The bomb was placed at an oven preset at 150 °C for 5 days. Colorless crystals were obtained after the reaction was cooled to room temperature Yield: 65 % (based on the organic ligand).

2.2.3. Synthesis of Co-fa

$Co(NO_3)_2·6H_2O$ (2.0 g) and formic acid (1.0 mL) was dissolved in 10 mL DMF in a 20 mL glass vial and the mixture was sonicated until a clear solution was achieved. The solution was put in an oven kept at 100 °C for 24 h. After the reaction was cooled naturally to room temperature, the formed pink powder was collected by filtration and dried in air. Yield: 78% (based on Co).

2.3. Characterization

The crystallinity and phase purity of MOF samples were monitored and analyzed by powder X-ray diffraction (PXRD) using a Rigaku Ultima-IV X-ray diffractometer with a scan speed of 1° min^{-1} with a copper $k_α$ radiation source (λ = 1.5406 Å).

2.4. Vapor adsorption experiments

Single component adsorption isotherms for hexane isomers were tested using a volumetric gas sorption analyzer, Vstar (Quantachrome Instruments Corp). The temperature for the adsorption experiments was controlled through a circulating water bath connected to a temperature control system. For each isotherm, approximately 80 mg of the sample was solvent exchanged and then activated immediately before data collection. Kinetic curves were extracted from the adsorption kinetics of the first pressure point of the vapor adsorption measurements.

2.5. Column breakthrough experiments

Column breakthrough measurement was performed with a lab-scale fix-bed reactor at 30 °C. In a typical experiment, 0.5–1 g of MOF material was packed into a quartz column (5.8 mm I.D. × 150 mm) with silane treated glass wool filling the void space. The MOF powder was thermally activated overnight and the flow of helium was then turned off while another dry helium flow at a rate of 1 mL/min was bubbled through a mixture of hexane isomers according to the following volumes (the volumes were determined through trial and error and calculated by GC: the experiment was run without any sample and the vapor phase ratios

were optimized to an equimolar mixture): 5.84 mL of nHEX, 4.12 mL of 3MP, and 2.57 mL of 22DMB for nHEX/3MP/22DMB ternary mixture. The effluent from the column was monitored using an online GC equipped with HP-PONA column and FID.

2.6. Separation test of naphtha

Naphtha separation experiments were performed with 50 mL glass tubes (15 mm I.D. × 480 mm). The bottom tips of the glass tubes was filled with glass wool, and the adsorbents were packed above them. The adsorbents were first pressured and screened to 20–40 mesh particles, and then activated at 150 °C overnight. 17 g of each adsorbent was packed in the glass tube and naphtha was pumped to the it through sealed pipe. The products after adsorption were collected into chromatogram vials drop by drop separately and then diluted by 2,2-dimethylbutane with weight recorded and then analyzed by GC (Agilent 7890B) with PONA analysis software developed by Sinopec Research Institute of Petroleum Processing. The component of the naphtha feed was directly analyzed by GC and PONA software. The components of the products were determined by deleting the 2,2-dimethylbutane peak in the GC and then analyzed with PONA software.

3. Results and discussion

3.1. Crystal structure of the selected adsorbent materials

Zr-abtc: Zr-abtc is built on 8-connected $Zr_6O_4(OH)_4(COO)_8$ and 4-connected $abtc^{4-}$ linker, featuring a 4, 8-c scu topology. It is derived from ftw topology where 1/3 of the linkers are missing, forming a framework with a BET surface area of ~1300 m^2/g possessing 1D channels with a diameter of ~7 Å [13].

Al-bttotb: Al-bttotb is consisted of 1D Al-O arrays of octahedrally coordinated Al centers, which are interconnected by $bttotb^{3-}$ linkers. The formed 3D network possesses a BET surface area of ~600 m^2/g and features two types of 1D channels with a square-shaped cross section around 5.6 Å [16].

Co-fa: Co-fa is built exclusively on Co^{2+} and formate ($HCOO^-$). It features a 3D framework containing 1D channels with pore diameter of 5.5 Å [17]. The BET surface area of Co-fa is ~350 m^2/g.

ZSM-5: ZSM-5 framework contains two intersecting channel systems, one sinusoidal channel is parallel to [1 0 0] with cross section 5.1 Å × 5.5 Å and the other straight channel is parallel to [0 1 0] with cross section 5.4 Å × 5.6 Å.

Zeolite 5A: Zeolite 5A features LTA topology, and the entrance to the sodalite cage is blocked by Ca^{2+} cations which are located at the center of the six-membered ring window. The large supercage has a diameter of 11.4 Å and is accessible through eight-membered ring apertures with a diameter of 5 Å.

The crystal structures of the five selected microporous materials are shown in Fig. 1 and the structure comparison is listed in Table 1. In general, Zr-abtc, Al-bttotb and Co-fa have 1D channels with Zr-abtc having the largest channel diameter. ZSM-5 has 2D channels with diameter similar to Al-bttotb and Co-fa. While 5A has the cage-like pores with the narrowest aperture size. In terms of porosity, Zr-abtc has the largest surface area while ZSM-5 has the smallest surface area. N_2 sorption isotherms at 77 K were collected for all five materials to confirm their porosity (Figure S13-S17).

3.2. Single-component adsorption properties

In order to compare the adsorption and separation properties of the selected adsorbents under identical conditions, we re-evaluated the adsorption capability of all five adsorbents. Single-component adsorption isotherms of three representative hexane isomers, n-hexane (nHEX), 3-methylpentane (3MP), and 2,2-dimethylbutane (22DMB) with different degrees of branching were collected at 30 °C on all five adsorbents. The isotherms are shown in Fig. 2 and related results are summarized in Table 2.

As the channel diameter of Zr-abtc is larger than the kinetic diameters of all three isomers, they were all adsorbed with considerable amounts, including the largest isomer 22DMB. Its adsorption preference follows the sequence of nHEX > 3MP > 22DMB and the adsorption capacity for nHEX reaches 285 mg/g which is substantially higher than that of the other adsorbents. In comparison, 22DMB was barely adsorbed by the rest four materials, as a result of their limiting pore aperture (≤5.6 Å). As expected, zeolite 5A adsorbs nHEX only and fully excludes both 3MP and 22DMB (the negligible uptake should be attributed to surface adsorption, adsorption on pore mouth or at defect sites). While
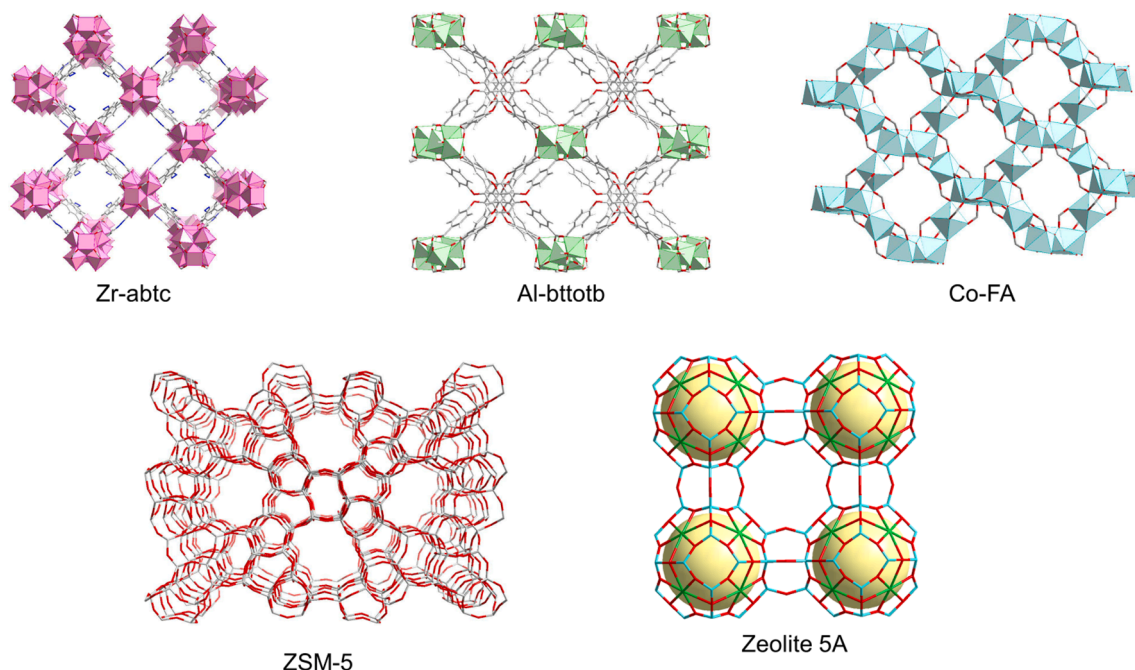

Fig. 1. Crystal structures of selected MOFs and zeolites.

Table 1
Structure features of Zr-abtc, Al-bttotb, Co-fa, ZSM-5 and Zeolite 5A.

Structure	Topology	SBU	Channels	BET Surface Area (m^2/g)	Micropore Volumes (ml/g)	Reference
Zr-abtc	SCU	Zr$_6$(μ3-O)$_4$(μ3-OH)$_4$(COO)$_8$	1D channel 7 Å × 7 Å	1318	0.45	[13]
Al-bttotb	–	1D array of corner-sharing AlO6 polyhedra	1D channel 5.6 Å	572	0.22	[16]
Co-fa	–	–	1D channel 5.5 Å	365	–	[17]
ZSM-5	MFI	(TO)$_5$T	2D Channel 5.1 Å × 5.5 Å 5.4 Å × 5.6 Å	360	–	Nakai University Catalyst Co. Ltd.
Zeolite 5A	LTA	–	Cage with 5 Å aperture	650	0.25	[4]
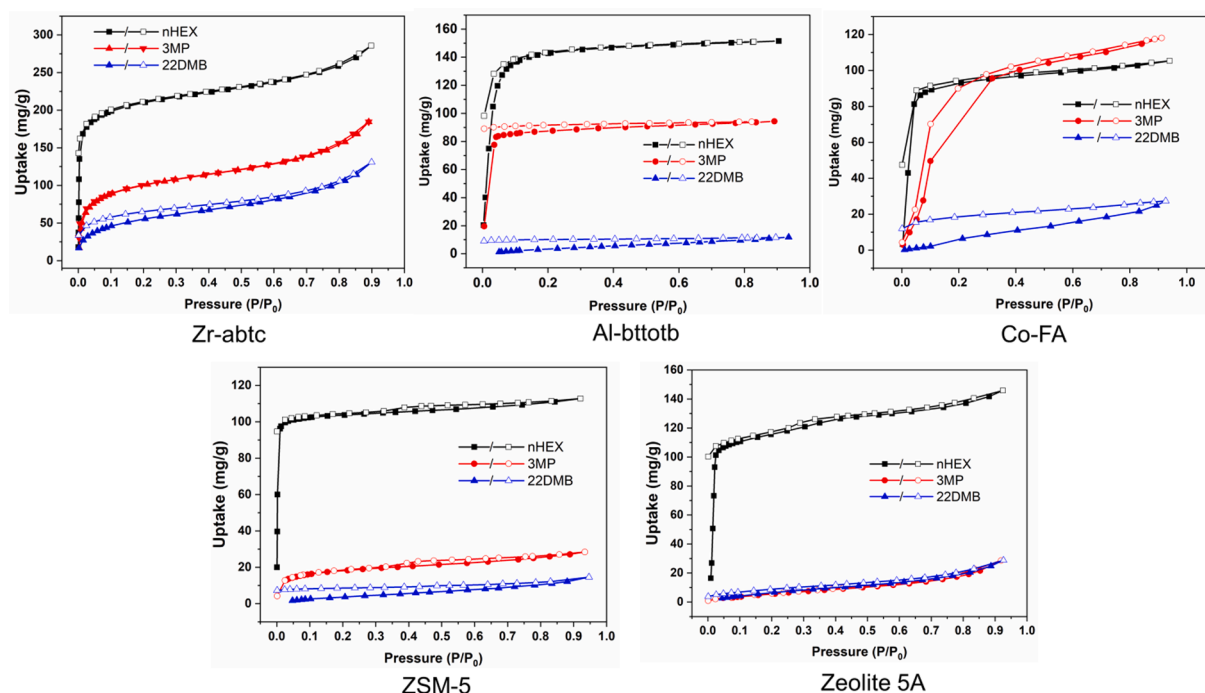
Fig. 2. Single-component adsorption-desorption isotherms of hexane isomers (nHEX, 3MP, and 22DMB) on selected adsorbents at 303 K.

Table 2
Adsorption capacities* of hexane isomers on the 5 structures.

Structure	n-hexane (mg/g)	3MP (mg/g)	22DMB (mg/g)
Zr-abtc	285	184	130
Al-bttotb	151	94	12
Co-fa	105	118	27
ZSM-5	113	28	15
Zeolite 5A	146	28	28

* Adsorption amount at 298 K, 0.9 P/P$_0$.

ZSM-5 can accommodate certain 3MP, the adsorption capacity is very limited (<30 mg/g). In comparison, Al-bttotb and Co-fa represent the only adsorbents that take up substantial amounts of both nHEX and 3MP but fully exclude 22DMB, indicating their capability of separating monobranched and dibranched alkanes through selective molecular exclusion.

In general, all of the five materials can adsorb nHEX without notable diffusion restrictions, and the adsorption capacities are in trend with their surface areas (Figure S6). It is also noted that the trade-off between adsorption capacity and selectivity is present for the adsorbents. Materials showing selective size-exclusion typically possess modest

adsorption capacity. Adsorption mechanisms of the five adsorbents toward hexane isomers have also been confirmed by adsorption kinetics (Figure S7-S11). However, it should be noted that the adsorption capacities of 3MP for Al-bttotb and Co-fa are substantially higher than that for ZSM-5. This should be attributed to the fact that the diffusion of 3MP in ZSM-5 is largely restricted.

3.3. Breakthrough experiments of hexane isomers

Multicomponent column breakthrough measurements of nHEX, 3MP, and 22DMB are commonly used to evaluate the separation capability of an adsorbent for alkane isomers and naphtha. In this work we also carried out the three-component column breakthrough experiments under identical conditions. In general, the breakthrough curves for all five adsorbents are fully consistent with their single-component vapor adsorption results (Fig. 3). For zeolite 5A, both 3MP and 22DMB eluted out from the column at the very beginning of the measurements indicating no retention in the column. In contrast, nHEX was retained in the column for a notable duration (~122 min/g). This confirms that zeolite 5A adsorbs nHEX only and fully excludes 3MP and 22DMB, indicating it is not capable of discriminating between branched alkane isomers. Zr-abtc is the only one among the five adsorbents that is able to
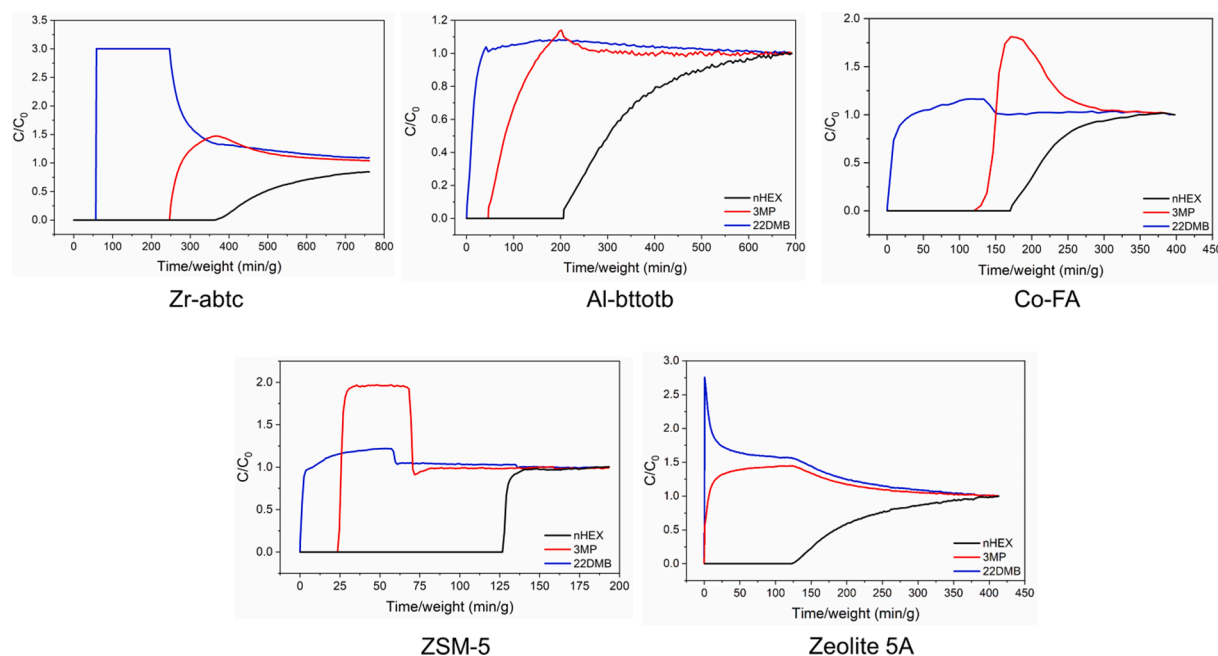
Fig. 3. Column breakthrough curves for hexane isomers (nHEX, 3MP, and 22DMB) on selected adsorbents at 303 K.

accommodate linear, monobranched, and dibranched isomers. Indeed this was supported by column breakthrough results. All the three isomers (nHEX, 3MP, and 22DMB) were retained in the column for a notably long time and the breakthrough time follows the sequence of 22DMB < 3MP < nHEX. This is consistent with the single-component adsorption results. It is noted that the breakthrough time for 3MP is substantially longer than that for 22DMB, indicating that Zr-abtc can efficiently separate monobranched and dibranched alkane isomers through thermodynamically-driven mechanism.

The results of breakthrough measurements suggest that Al-bttotb, Co-fa, and ZSM-5 show full separation between 3MP and 22DMB, that is, 22DMB is completely excluded by all the three materials while 3MP (and nHEX) is notably retained in the column. This is expected as the aforementioned adsorption results indicated they are capable of separating monobranched and dibranched alkane isomers through selective size exclusion. However, the separation efficiency for 3MP and 22DMB follows the sequence of ZSM-5 < Al-bttotb < Co-fa. The breakthrough time of 3MP for ZSM-5 is 24 min/g, notably shorter than that for Al-bttotb (48 min/g) and Co-fa (118 min/g), indicating that All-bttotb and Co-fa can separate monobranched and dibranched alkane isomers more efficiently than ZSM-5, primarily due to their higher adsorption capacity for 3MP while excluding 22DMB.

3.4. Naphtha separation on selected adsorbents

The aforementioned three-component column breakthrough measurements have been commonly applied to evaluate the separation capability of adsorbents for alkane isomers and for naphtha. However, a real naphtha mixture from oil refining typically consists of ~200 different components of C4-C12 hydrocarbons. While the main components are linear and branched alkanes, it also contains certain amounts of cycloalkanes and aromatics. Thus the separation performance of an adsorbent for three-component hexane isomers would not accurately reflect its capability for separating naphtha. For example, as illustrated in above sections, both Zr-abtc and Al-bttotb can separate hexane isomers as a function of branching, but through different mechanisms. Al-bttotb splits monobranched and dibranched hexane isomers through selective size exclusion. In contrast, Zr-abtc possesses pore opening that is large enough to accommodate all isomers and thus the separation is

thermodynamically controlled, and its adsorption capacity is notably higher than that of Al-bttotb. This raises an interesting question: Which of the two, Zr-abtc or Al-bttotb, is more ideal for the separation of real naphtha mixtures?

To address this question, we performed column separation tests for real naphtha mixtures. As the single-component adsorption results and the three-component breakthrough experiments of hexane isomers have already confirmed that zeolite 5A is not able to fulfill the target to isolate n-paraffins and monobranched-paraffins from others, the naphtha separation experiments are taken on Zr-abtc, Al-bttotb, Co-fa and ZSM-5 and the research octane number (RON) of the eluent was monitored to evaluate the separation efficiency. The RON of the naphtha feed is 69.41. As is known that Zr-abtc separate monobranched and dibranched hexane isomers by thermodynamic mechanism, while Al-bttotb, Co-fa and ZSM-5 separate them through selective size exclusion. Interestingly, it is observed that there is either short or long plateau on the RON curves for the latter three adsorbents (Fig. 4a). However, the curve for Zr-abtc shows continuous decrease as the increase of the eluent. Moreover, the initial RON of the eluent for Zr-abtc is lower than that of the other adsorbents. This suggests that adsorbents showing selective size-exclusion behavior for alkane isomers would be more ideal for the separation of naphtha compared to those separating alkanes thermodynamically.

Naphtha separation experiments displayed that Co-fa shows the highest product RON as well as the highest separation efficiency. This could be attributed to the fact that Co-fa adsorbs more monobranched alkanes than Al-bttotb and ZSM-5. It should be noted that while ZSM-5 shows complete separation for three-component hexane isomers, its naphtha separation efficiency is relatively low due to its relatively low adsorption ability toward monobranched alkanes. We further looked into the evolution a monobranched alkane, 2-methylpentane (2MP) throughout the naphtha separation experiments (Fig. 4b). 2MP broke out quite fast from the column filled with ZSM-5, however, it retained in the column of Al-bttotb much longer and then the concentration of 2-MP in the eluent increased slowly, indicating that Al-bttotb adsorbed more monobranched alkanes than ZSM-5, which is in accordance with their separation efficiency. PXRD analysis revealed that the crystallinity of the adsorbents were retained after the naphtha separation measurements (Figure S12).
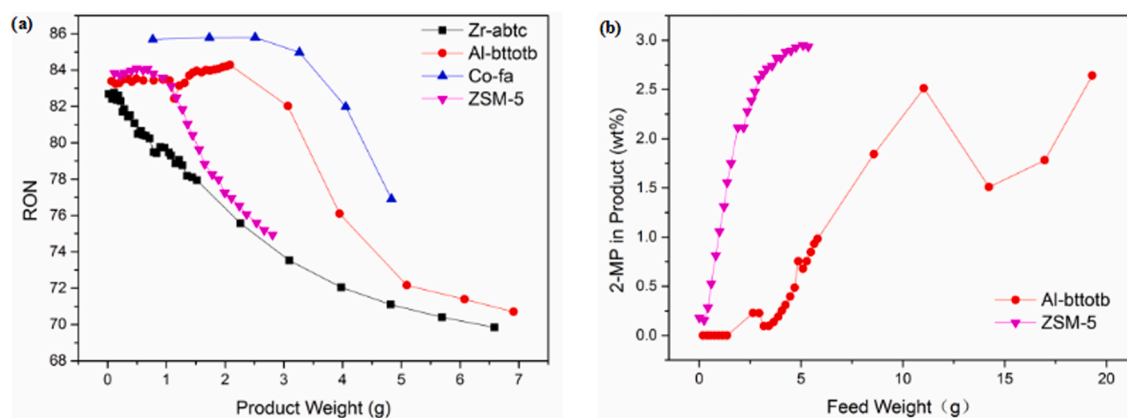
Fig. 4. Product RON curves for Zr-abtc, Al-bttotb, Co-fa and ZSM-5 (left) and 2MP breakthrough curve of Al-bttotb and ZSM-5 (right) from naphtha separation measurements.

4. Conclusion

In summary, we have performed a comprehensive comparison study of a series microporous MOFs and representative zeolites for the adsorption and separation of alkane isomers and naphtha mixtures. Our experiments indicate that adsorbents showing selective molecular exclusion behavior for monobranched and dibranched alkanes are more ideal for efficient separation of naphtha. As the first trial of systematic study for the separation of full range naphtha by MOFs, we believe this work provides important information for developing novel adsorbent materials for industrial naphtha separation.

CRediT authorship contribution statement

Qihan Gong: Investigation, Writing – original draft. **Liang Yu:** Investigation, Data curation. **Jiayu Ding:** Visualization. **Shang Zhang:** Formal analysis, Supervision. **Yawen Bo:** Validation. **Kebin Chi:** Formal analysis, Supervision. **Hao Wang:** Conceptualization. **Qibin Xia:** Supervision. **Shengbao He:** Funding acquisition. **Jing Li:** Supervision, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2022.121219.

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