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Regulation of isobutane/1-butene adsorption behaviors on the acidic ionic liquids-functionalized MCM-22 zeolite☆

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ABSTRACT

The adsorption ratio of isobutane/1-butene on the catalyst surface is one of the most important factors for the C_4 alkylation process. Regulation of isobutane/1-butene adsorption ratio on the zeolite-supported acid catalyst is a big challenge for catalyst preparation. To regulate the isobutane/1-butene adsorption ratio, four types of ionic liquid (i.e., IL) with different alkyl chain lengths and different acid group numbers were synthesized and were subsequently immobilized onto the MCM-22 zeolite. The as-synthesized IL-immobilized MCM-22 (i.e., MCM-22-IL) was characterized by FTIR, TGA, BET, XPS and XRD, and their adsorption capacities and adsorption molar ratios of isobutane to 1-butene (I/O) were investigated to correlate with surface features of MCM-22-IL. Results showed that the immobilization of ILs led to a decrease of specific surface area and pore volume. But the surface density of acid groups was increased and the adsorption molar ratio of isobutane/1-butene (I/O) was significantly improved by the immobilization of ionic liquids. The adsorption molar ratio of I/O is substantially improved from 0.75 to above 0.9 at 300 kPa upon immobilizing ILs. Although the alkyl chain length of ILs was found to have little effect on the adsorption molar ratio of I/O, the increase of acid group numbers led to a dramatic decrease in the adsorption I/O ratio. The results illustrated that immobilizing ionic liquids is an effective way to modify the textural, chemical and morphological properties of MCM-22. Accordingly, the immobilization of ionic liquids provides a novel and a feasible way to regulate the adsorption I/O ratio on an adsorbent or a solid catalyst.

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1. Introduction

The adsorption property is one of the most important fundamental characteristics for an adsorbent or a catalyst. The adsorption selectivity, which depends on the adsorption capacity difference between different substrates, is a crucial factor for the adsorption separation [1]. For example, an adsorbent with a large difference in adsorption capacity for propane and propylene is very useful for the challenging paraffin/olefin separation process. For a solid catalytic reaction, the ideal adsorption property is a stoichiometric ratio of reactant adsorption capacities. For example, the selectivity and catalyst life of the alkylation process between isobutane and 1-butene on a solid acidic catalyst are significantly controlled by the adsorption isoparaffin/olefin ratio (I/O). However, preferential adsorption of olefin on the solid acid catalyst usually takes places owing to the polarity difference between isoparaffin and olefin. Unfortunately, the excess of olefin on the catalyst surface results in

many undesirable side reactions, rapid deactivation of catalysts and low selectivity of objective products. It is therefore of great significance to achieve an equivalent adsorption capacity of isoparaffin and olefin for the improvement of C_4 alkylation reaction and the prolongation of catalyst life.

The adsorbent–adsorbate interactions have a strong effect on the adsorption behavior. One of the effective ways to modulate the catalyst/adsorbent adsorption property is to alter adsorbent–adsorbate interactions by surface modification. Inorganic adsorbents have been incorporated with transition metal ions (such as Cu or Ag) as adsorbent to separate olefin/paraffin, in which a π -complexation is formed between the unsaturated bond in the olefin and the metal ion on the adsorbent surface [2]. This strong interaction leads to a preferential adsorption of the olefin. Examples of this preferential olefin adsorption include ethane/ethylene and propane/propylene separation on an Ag(1) immobilized metal–organic framework (Cr)-MIL-101- SO_3Ag [3]. An increase in adsorption selectivity of ethylene over ethane is also observed on ordered mesoporous carbon CMK-3 modified with cuprous chloride (CuCl) [4]. Aluminum methylphosphonate polymorph α (AlMePO- α) has been synthesized as adsorbent to separate olefin/paraffin [5], and exhibits a preferential adsorption of paraffin due to an enhanced interaction between paraffin and methyl groups of AlMePO- α [6].

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Consequently, an alternative surface modification technique is highly desired to enhance the adsorption capacity of paraffin on the surfaces of adsorbents or solid acid catalysts.

Alkylation of isobutane with various olefins is an important reaction of gasoline production in the petroleum industry. Concentrated sulfuric acid (H_2SO_4) and hydrofluoric acid (HF) are usually used as acid catalysts in the industrial alkylation processes. However, the disadvantages of a large amount of waste acid, dangerously stable aerosols at the ground level, equipment corrosion and environmental liability impede the wide usage of liquid acid catalysts in the alkylation process. Solid acids provide a promising environmentally-benign alternative to mineral acids. However, solid acid catalysts often suffer from rapid deactivation due to fouling of the pores, thus resulting in low product yield and reaction selectivity [7]. On the other hand, the preferential olefin adsorption on the solid acid catalyst surface inevitably results in a low molar ratio of isoparaffin/olefin (I/O), which is much lower than the stoichiometric ratio of the objective alkylation reaction. The redundant olefin easily causes the occurrence of side reactions such as oligomerization or polymerization reaction under the acid environment. Therefore, the alkylation reaction of isobutane only takes place at a low reaction selectivity and the catalyst life is significantly shortened. In order to inhibit the side reactions of oligomerization, polymerization, disproportionation, cracking and self-alkylation, the adsorption I/O ratio at the active sites must increase to the stoichiometric ratio of the objective alkylation reaction.

Ionic liquids (ILs) have attracted considerable interests over the past decades, due to their unique properties, such as high thermal and chemical stability, negligible volatility, designable structures, tunable chemical properties [8,9], wide liquid ranges, good conductivity and large electrochemical windows. They have been extensively used as catalysts for organic reactions [10–13], media for gas and liquid separations [14–16], entrainers in the extractive distillation [17], nonconventional reaction media [18] and advanced functionalization materials [19–21] in a variety of chemical processes. The immobilization of ILs on a support material is an effective way to modify the structural, chemical and morphological properties of the support [12,22,23]. The change of surface properties of adsorbents has a significant effect on the adsorption properties [24]. Examples include activated carbon loaded with 1-ethyl-3-methylimidazolium acetate [25] and imidazolium-based IL-functionalized porous silica gel particles for SO_2 separation in air [26], amino acid-based IL-immobilized activated carbons for CO_2 separation [15], room temperature IL-immobilized silica gel or Merrifield resin for adsorption removal of thiophenic compounds from fuel [24,27]. It has been reported that the structures of ILs, such as the alkyl chain length and anions, are associated with their adsorption selectivity to adsorbate gases [28]. To improve adsorption and catalytic properties of an adsorbent or a catalyst, ionic liquids have been used to modify their surfaces for different reactions [20,29], such as Friedel-Crafts reactions, nitration, alkylation [30], oligomerization, esterification, transesterification and condensation reactions [11].

Extensive previous studies have reported that a binary mixture of mineral acid and ionic liquid as a catalyst in the isobutane/butene alkylation can substantially improve the product yield and catalyst life [31–34]. The ILs are believed to change the interfacial properties and the solubility of hydrocarbon in the catalyst system, which are favorable for the alkylation reaction. In our previous study, we found that the structures of ILs have a significant effect on the isobutane solubility [35]. We also immobilized a specific dual acidic IL, 3-sulfobutyl-1-(3-propyltriethoxysilane)-imidazolium hydrogen sulfate, on the MCM-22 zeolite to improve the adsorption I/O ratio and the alkylation reaction. Results demonstrated a superior adsorption ability in tuning the adsorption ratio of ethane/ethylene at a level of 0.97–1.01 [36]. However, to the best of our knowledge, few studies have documented to address the effect of the molecular structure (such as alkyl chain length and acid group number) of ILs on the adsorption ratio.

Accordingly, the aim of this study is to systematically investigate the effect of ILs structure, including different alkyl chain lengths and different acid group numbers, on the adsorption behaviors of isobutane and 1-butene on MCM-22 zeolites modified by ILs, and to further regulate the adsorption ratio of isobutane/1-butene on MCM-22. As schematically shown in Figs 1 and 2, five types of triethoxysilyl-terminated ILs were synthesized for subsequent immobilization on the MCM-22 zeolites. Success in the immobilization of ILs was ascertained by FT-IR, TGA, BET, XPS and XRD, respectively. Static adsorption experiments were performed to determine the adsorption capacities of isobutane and 1-butene, and further regulated the ILs immobilized on the MCM-22 to achieve the desired adsorption ratio of isoparaffin/olefin (I/O).

2. Experimental

2.1. Chemicals and materials

Na-MCM-22 zeolite precursor was obtained from Dalian University of Technology (Dalian, China). 3-Chloropropyltriethoxysilane (99%) and 1,4-butane sultone (99%) were purchased from Shanghai Nuotai Chem. Co. (Shanghai, China). The protonic forms of the MCM-22 (H-MCM-22) were obtained by ion-exchange of the material with 1 M NH_4NO_3 solution as described elsewhere [37]. 1-butene (99.9%) was purchased from Tianjin Summit Specialty Gases Ltd. and isobutane (99.5%) used in adsorption behaviors experiments was purchased from Chengdu HaoYun Gases Co., Ltd. All solvents used in this study were strictly redistilled and dried according to standard operations and stored over 5 Å molecular sieves.

2.2. Synthesis of ionic liquids

Three types of novel triethoxysilyl-terminated ILs, including 1-methyl-3-(3-triethoxysilyl)propyl imidazolium chloride ([TPMIm][Cl]), 1-ethyl-3-(3-triethoxysilyl)propyl imidazolium chloride ([TPEIm][Cl]) and 1-butyl-3-(3-triethoxysilyl)propyl imidazolium chloride ([TPBIm][Cl]), were synthesized using a similar procedure described in detail previously [38]. Typically, equal molar of 3-chloropropyltriethoxysilane and 1-methylimidazole were reacted at 110 °C in a round-bottom flask under continuous stirring. The reaction was allowed to proceed overnight under nitrogen atmosphere. After the reaction, the resultant product was washed thrice with 50 ml diethyl ether, and a light yellow transparent liquid of [TPMIm][Cl] was obtained. Similar synthesis procedures were used to obtain the [TPEIm][Cl] and [TPBIm][Cl] ILs. The as-synthesized acidic ILs were subsequently characterized by NMR (Bruker-Alt, Switzerland).

^1H NMR (400 MHz, DMSO) of [TPMIm][Cl]: 0.59 (2H, SiCH_2), 1.22 (9H, CH_3), 2.00 (2H, $\text{CH}_2\text{--CH}_2\text{--CH}_2$), 3.82 (6H, OCH_2), 4.13 (3H, NCH_3), 4.31 (2H, NCH_2), 7.32 (1H, NCH), 7.56 (1H, NCH), 10.62 (1H, NCHN).

^1H NMR (400 MHz, CDCl_3) of [TPEIm][Cl]: 0.63 (2H, SiCH_2), 1.21 (9H, CH_3), 1.59 (3H, CH_3), 2.00 (2H, $\text{CH}_2\text{--CH}_2\text{--CH}_2$), 3.80 (6H, OCH_2), 4.34 (2H, NCH_2), 4.45 (2H, NCH_2), 7.35 (1H, NCH), 7.50 (1H, NCH), 10.70 (1H, NCHN).

^1H NMR (400 MHz, CDCl_3) of [TPBIm][Cl]: 0.62 (2H, SiCH_2), 0.95 (2H, CH_3), 1.21 (9H, CH_3), 1.38 (2H, $\text{CH}_3\text{--CH}_2$), 1.91 (2H, $\text{CH}_2\text{--CH}_2\text{--CH}_2$), 2.02 (2H, $\text{CH}_2\text{--CH}_2\text{--CH}_2$), 3.82 (6H, OCH_2), 4.38 (4H, NCH_2), 7.35 (1H, NCH), 7.42 (1H, NCH), 10.68 (1H, NCHN).

3-Sulfobutyl-1-(3-propyltriethoxysilane)imidazolium hydrogen sulfate ([TPBSIm][HSO_4]) was synthesized and characterized according to the procedure as described in our previous work [36].

2.3. Immobilization of ionic liquids onto the MCM-22

The immobilization of ILs onto MCM-22 was performed using a similar procedure described in our previous work [36]. Briefly, the as-synthesized [TPMIm][Cl] (6.0 g), [TPEIm][Cl] (6.0 g) and [TPBIm][Cl]

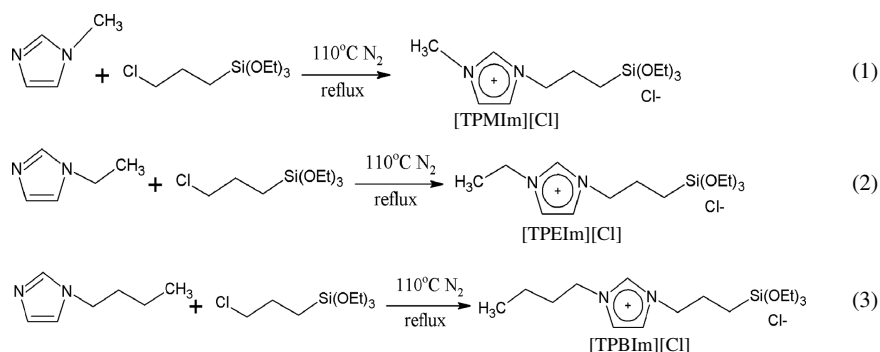


Fig. 1. Synthesis routes of [TPMIm][Cl], [TPEIm][Cl] and [TPBIm][Cl].

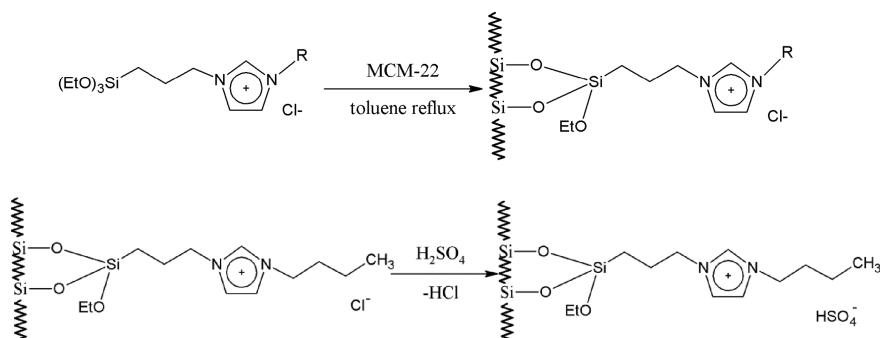


Fig. 2. Schematic illustration of the immobilization of ILs onto MCM-22.

(6.0 g) were dissolved in absolute toluene (30 ml), respectively, and reacted with dried H-MCM-22 (4.0 g) under nitrogen atmosphere. The reaction was allowed to proceed at 80 °C under refluxing for 24 h. After the reaction, the solids were isolated by filtration and washed thrice with 30 ml ethanol, followed by ultrasonic washing in copious amounts of ethanol for 5 min, and further washed thrice with 30 ml ethanol to remove the physically-adsorbed ionic liquid, if any. Then resultant IL-immobilized MCM-22 were defined as MCM-22-MPIm Cl, MCM-22-EPIIm Cl and MCM-22-BPIIm Cl, respectively.

The immobilized hydrogen sulfate acidic ILs was accomplished by ion exchange of MCM-22-BPIImCl with concentrated H₂SO₄ using the previously-reported procedures [39]. Briefly, the MCM-22-BPIImCl was introduced to dichloromethane and the reaction was carried out under 60 °C under continuous stirring for 24 h. After reaction, the reaction mixture was filtrated and the filter cake was washed thrice with 30 ml ethanol to remove Cl⁻. A slightly yellow powder was obtained after drying, and the resultant [TPBIm][HSO₄]-immobilized MCM-22 was named as MCM-22-BPIIm HSO₄. The synthesis and characterization of the MCM-22-BPIIm HSO₄ were described in detail in our previous study [36].

2.4. Characterizations

Fourier transform infrared (FTIR) spectra were measured in the region 4000–400 cm⁻¹ on a Perkin Elmer Fourier transform infrared spectra spectrometer (FTIR-850, Spectrum Two System, L1600300). The sample was prepared using a KBr disc technique. X-Ray photoelectron spectroscopy (XPS) measurements were recorded on a XSAM800 spectrometer (XSAM800, Kratos, UK) with a monochromatized Al K α X-ray source radiation at constant dwell time of 100 ms and a pass energy of 40 eV. The C 1s (binding energy (BE), 284.6 eV) spectrum was used as internal reference to compensate the surface charging effect. X-ray powder diffraction (XRD, DX-2700, Dandong, China) was used to

measure the crystalline structures of MCM-22 and MCM-22-IL. The voltage and anode current were 40 kV and 30 mA, respectively. The thermal stability of MCM-22 and MCM-22-IL was characterized by thermogravimetric analysis (TGA, HTG-2, Beijing, China). The samples were heated from about 25 °C to 650 °C at a heating rate of 10 °C·min⁻¹. The N₂ adsorption/desorption isotherms were measured on a commercial pore and surface analyzer (Quantachrome NOVA 1000e). The surface acid amounts of MCM-22 and MCM-22-IL were titrated by *n*-butylamine as described in detail previously [36].

2.5. Adsorption behaviors of isobutane/1-butene on MCM-22 and MCM-22-ILs

The adsorption properties of gas adsorbates on MCM-22 and MCM-22-IL were evaluated in a static adsorption apparatus as schematically illustrated in Fig. 3, which resembles the method mentioned in our previous work [40]. The apparatus mainly consists of a stainless steel equilibrium cell, a gas reservoir, pressure sensors with pressure transducer (0–689.5 kPa, $\pm 0.03\%$, Omega Industrial Measurements, USA), a vacuum pump and a water bath system. During the static adsorption experiment, a predetermined amount of isobutane (or 1-butene) was filled in gas reservoir, the equilibrium pressure and temperature were recorded and the adsorbate mass was calculated by the Peng–Robinson (P–R) equation. Subsequently, the valves 4 and 5 were opened to let the gas into the equilibrium cell pre-filled with adsorbent. The adsorbate mass in the gas phase was calculated on the basis of the equilibrium pressure and the total volume (including equilibrium cell, gas reservoir and the pipelines, and excluding the adsorbent volume). Hence, the adsorption capacity of the gas on the MCM-22-ILs was obtained in terms of the decrease of adsorbate mass in the gas phase. The precision of the pressure sensor $u(P)$ was 0.2 kPa, while the temperature was controlled by a thermostatic bath with an accuracy of 0.1 K.

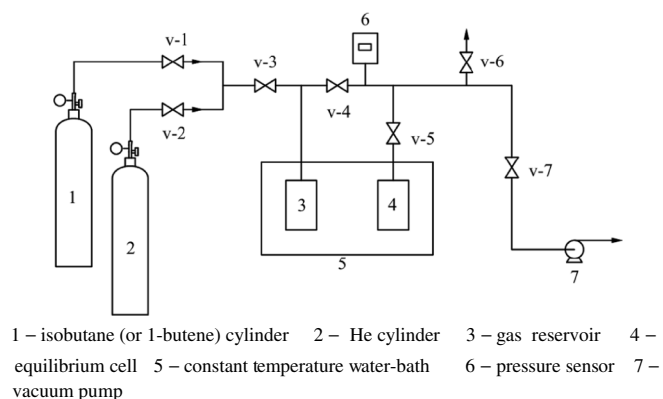


Fig. 3. Schematic diagram of static adsorption apparatus.

The volume from valve 5 to the equilibrium cell (V_1) was determined by injecting ethanol to the system at 25 °C for five times. The volume was 11.05 ml with an uncertainty $u(V)$ of 0.01 ml. The volume between valve 1, valve 2 and valve 7, including the gas reservoir and pipes (V_2), was determined by a volume increasing method described as follows. Valves 1, 2, 5, 6 and 7 were closed after the total system was degassed. Helium was first filled into the gas reservoir, then valve 2 was closed. The mass of filled Helium was calculated based on the equilibrium temperature, pressure and known gas reservoir volume by the Peng–Robinson (P–R) equation. Then valve 5 was opened to let the equilibrium cell filled with the Helium from the gas reservoir and the equilibrium temperature and pressure were recorded. On the basis of the variation of pressure and known equilibrium cell volume and Helium mass, we were then able to calculate the V_2 volume of the device

by the P–R equation. This process was repeated five times, and the volume was 93.69 ml with an uncertainty $u(V)$ of 0.01 ml.

To determine the adsorption behaviors of isobutane and 1-butene on the MCM-22 or MCM-22-IL, the precisely-weighed MCM-22 (or MCM-22-IL) was filled into the equilibrium cell, followed by eliminating gaseous impurities from the gas reservoir using vacuum pump until the pressure in the equilibrium cell was less than 1 Pa. The temperature was controlled at a pre-set value by using water bath. Thereafter, the valves 5 and 7 were closed and Helium was introduced to the gas reservoir to obtain the equilibrium temperature and pressure. Then valve 5 was opened and then the equilibrium temperature and pressure were recorded. Similarly, with the calculation of V_2 , the volume of the equilibrium cell excluding the filled adsorbent was calculated by P–R equation. Then, the Helium was degassed by the vacuum pump at a pressure < 1 Pa. Using isobutane or 1-butene as adsorbate to replace Helium, the procedures described above were repeated to get the equilibrium pressure variation. The adsorption capacity of isobutane or 1-butene was calculated by P–R equation. Changing equilibrium pressure by complementing adsorbate into gas reservoir, the adsorption capacities at different equilibrium pressure were measured.

3. Results and Discussion

3.1. The immobilization of the ionic liquids onto MCM-22

As schematically illustrated in Fig. 4, the immobilization of ILs onto MCM-22 zeolite is accomplished by self-assembly reaction between triethoxysilyl groups of ILs and hydroxyl groups of MCM-22 zeolites. Successful immobilization of ILs onto the MCM-22 was ascertained by FTIR and XPS characterization, as described in detail as follows.

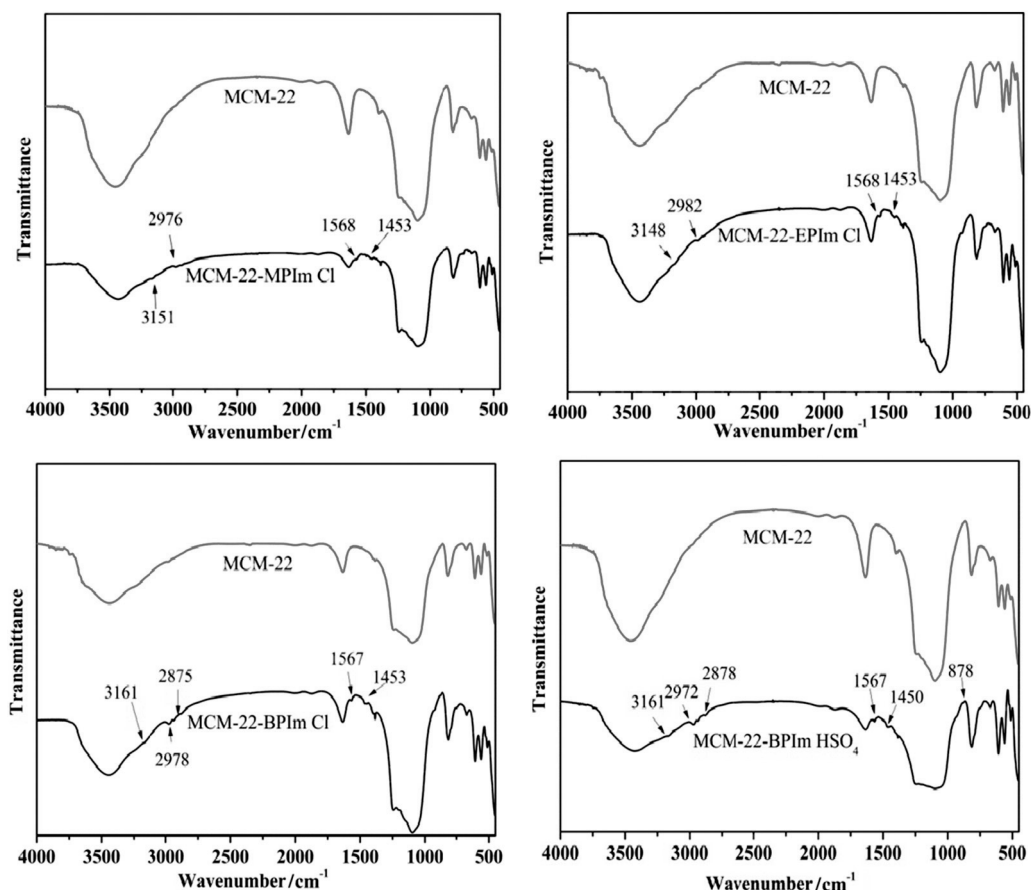


Fig. 4. FTIR spectra of the pristine MCM-22 and MCM-22-IL.

3.1.1. FTIR spectra

Fig. 4 shows the respective FTIR spectra of the pristine MCM-22 and MCM-22-ILs. In comparison with the FTIR spectrum of MCM-22, two additional characteristic peaks at about 1568 and 1453 cm^{-1} , attributable to the C–N and C–C stretching vibrations of the imidazole ring, are observed on those of MCM-22-MPIm Cl, MCM-22-EPIm Cl, MCM-22-BPIm Cl and MCM-22-BPIm HSO_4 . The bands in the range of 2800–3200 cm^{-1} are associated with the C–H stretching vibrations and the deformation vibrations of the imidazole moiety and alkyl chain. These peaks are all characteristic peaks of imidazolium ILs. An additional strong peak at 878 cm^{-1} , attributable to HSO_4^- stretching vibration

[36], is observed in the FTIR spectrum of the MCM-22-BPIm HSO_4 . These results are consistent with the fact that the acidic ILs have been successfully immobilized onto the MCM-22 zeolites.

3.1.2. XPS spectra

To further confirm the successful immobilization of ILs, XPS analyses of the surface compositions of the MCM-22-MPIm Cl, MCM-22-EPIm Cl, MCM-22-BPIm Cl and MCM-22-BPIm HSO_4 were performed. Fig. 5 shows the wide scan, curve-fitted C 1s core-level, Cl 2p and S 2p core-level XPS spectra of the MCM-22-IL. Compared with the XPS spectra of MCM-22 described in our previous work [36], two additional

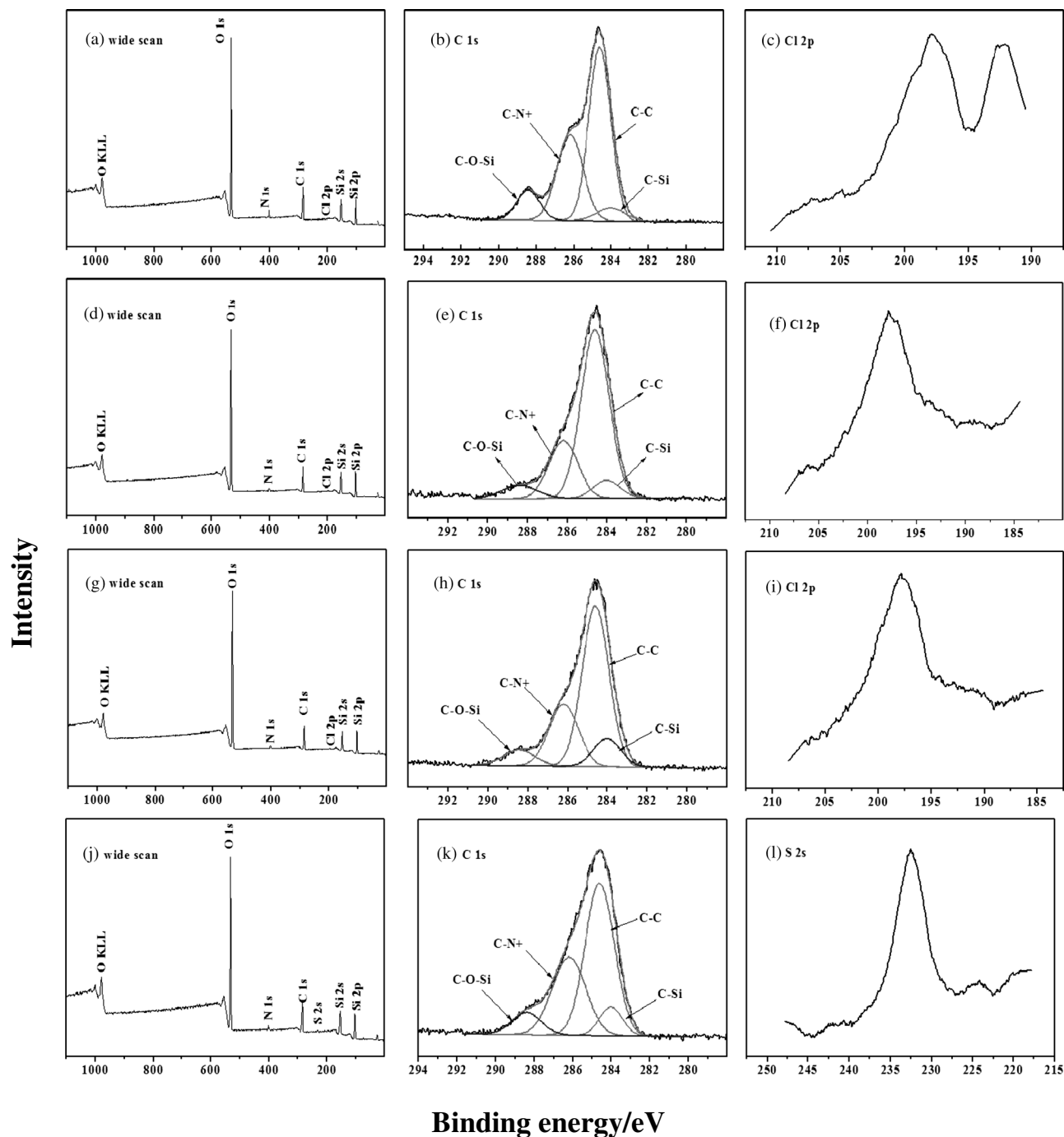


Fig. 5. XPS spectra of the MCM-22-MPIm Cl (a, b, c), MCM-22-EPIm Cl (d, e, f), MCM-22-BPIm Cl (g, h, i) and MCM-22-BPIm HSO_4 (j, k, l).

photoelectric signals with binding energies (BEs) at 401.2 and 197.5 eV, attributable to the N 1s and Cl 2p species, respectively, appear in the wide scan spectra, indicative of successful immobilization of [TPMIm][Cl], [TPEIm][Cl] and [TPBIm][Cl] (Fig. 5a, d, g). The successful immobilization of [TPBSIm][HSO₄] can be deduced from the appearance of a new peak at 232.5 eV, attributable to S 2s species [41]. The curve-fitted C 1s core-level peaks of MCM-22-MPIm Cl, MCM-22-EPIm Cl and MCM-22-BPIm Cl consists of four peak components with BEs at 284.6 eV for the C–C species, 286.2 eV for the C–N⁺ species [42], 284.0 eV for the C–Si species [43], and 288.4 eV for the C–O species respectively [44]. The peak area ratio of [C–O]:[C–Si] (about 1:1) is consistent with the chemical structure of the immobilized ionic liquid (theoretical component ratio of 1:1). The curve-fitted C 1s core-level spectrum of the MCM-22-BSPIm HSO₄ is composed of C–C, C–N⁺, C–S, C–Si and C–O species, similar to that reported previously [36]. Taken together, these above results further confirm that the acidic ILs have been successfully immobilized onto MCM-22 via covalent bonds.

3.2. Determination of structural features of MCM-22-IL

3.2.1. XRD pattern

XRD patterns of the MCM-22 before and after the immobilization of ILs were characterized to determine the change of crystal structures. Fig. 6 shows the respective XRD patterns of the MCM-22 and MCM-22-MPIm Cl, MCM-22-EPIm Cl, MCM-22-BPIm Cl and MCM-22-BPIm HSO₄. In comparison with the XRD pattern of the pristine MCM-22, the location of XRD peaks of the MCM-22-IL is clearly unchanged, albeit of a slight decrease in the peak intensity. This phenomenon is probably ascribed to the immobilization of the ILs. The XRD spectra of MCM-22-BSPIm HSO₄ are consistent with the previously-reported results [36]. Thus, the above results indicate that the crystal structure of MCM-22 remains unchanged after the immobilization of ILs.

3.2.2. TGA and thermostability of MCM-22-IL

The loading amount of ILs onto the MCM-22 can be calculated from the mass difference before and after immobilization, as determined by TG analysis:

$$\text{SIL} = \frac{(W_b - W_a) / M}{W_a} \quad (1)$$

where SIL represents the loading amount of the immobilized ILs onto the MCM-22 surface (mmol·g^{−1}), W_a is the mass of the pristine MCM-22, W_b is the mass of MCM-22-IL, they were all measured before and after the immobilization by a precise analytical balance, and M stands for the molecular weight of the immobilized ILs. The mass percent of the immobilized ILs on the MCM-22-MPIm Cl, MCM-22-EPIm Cl, MCM-22-BPIm Cl and MCM-22-BPIm HSO₄ was calculated to be circa 10.5 wt%, 10.2 wt%, 10.9 wt% and 10.4 wt% respectively, corresponding to circa 0.46, 0.42, 0.40 and 0.31 mmol·g^{−1} of ILs immobilized onto the MCM-22 substrate.

To further determine the thermostability of MCM-22-IL, TGA curves were recorded as shown in Fig. 7. Based on the results reported in our previous study, MCM-22 is stable under 600 °C [36]. In light of the TGA curves of MCM-22-IL zeolites, the mass losses before 200 °C are caused by the evaporation of the adsorbed water, as well as the loss of C₂H₅OH upon further condensation of unreacted ethoxy groups [36]. The loss of the covalently attached organic compounds is observed in the temperature range of 230 to 500 °C with a mass loss of 8.60%, 8.61% and 8.57%, 8.39%, respectively, for the MCM-22-MPIm Cl, MCM-22-EPIm Cl, MCM-22-BPIm Cl and MCM-22-BPIm HSO₄, which is consistent with the mass difference of MCM-22 before and after the IL immobilization. These above results further confirm that the IL-immobilized acid catalyst is thermally stable up to about 220 °C.

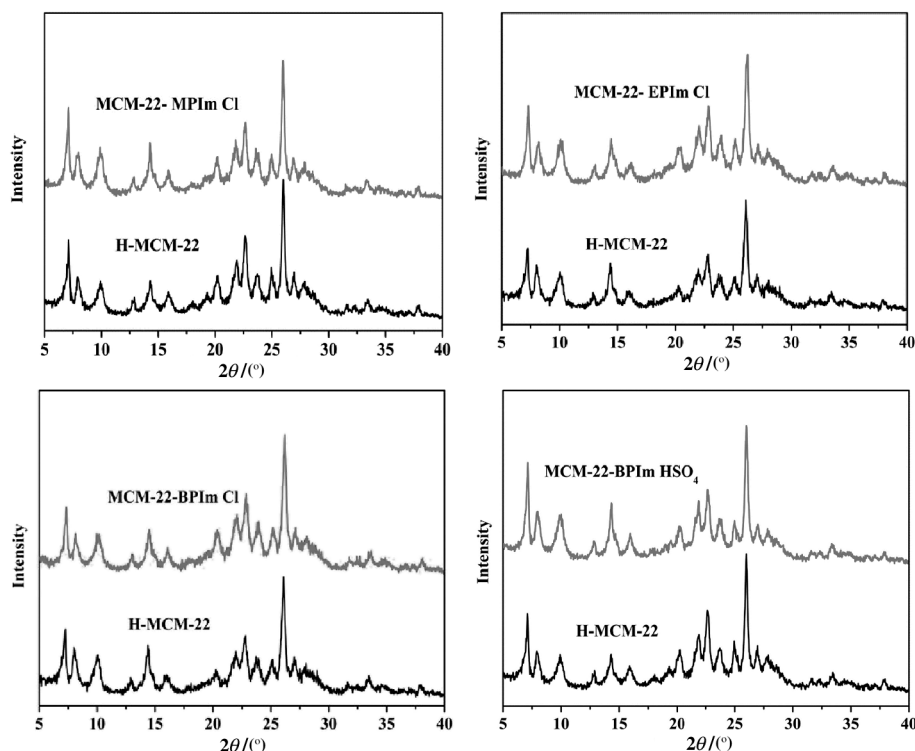


Fig. 6. X-ray powder diffraction patterns of MCM-22 and MCM-22-IL.

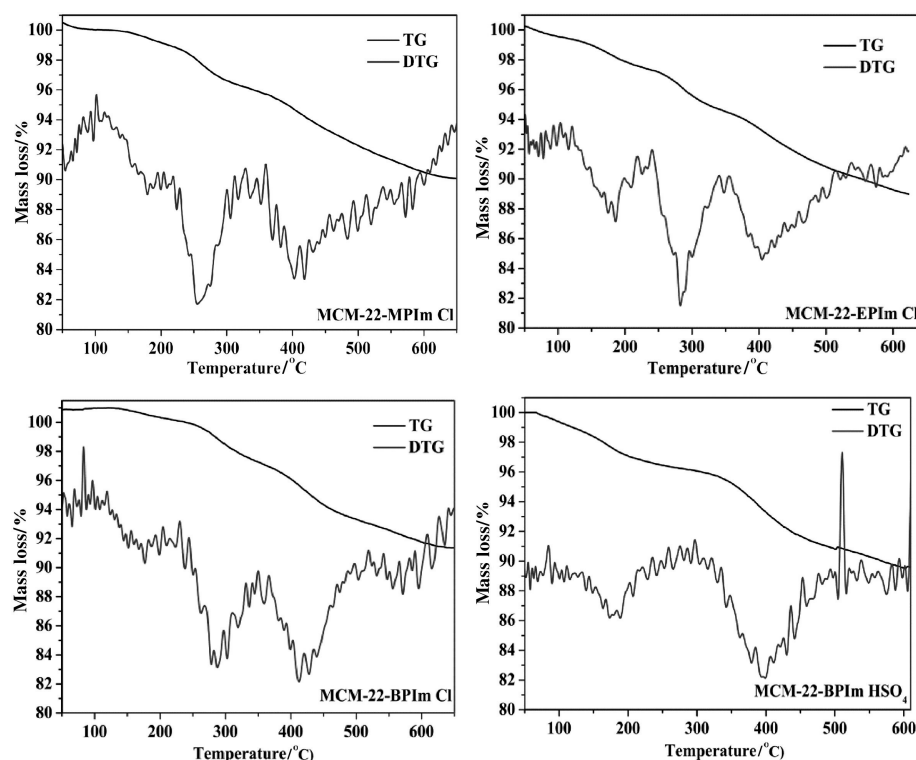


Fig. 7. TG analysis of MCM-22-MPIIm Cl, MCM-22-EPIIm Cl, MCM-22-BPIIm Cl and MCM-22-BPIIm HSO₄.

3.2.3. BET analysis

The BET analyses of the pristine MCM-22 and MCM-22-IL were performed to determine the change in the specific surface area and the average pore volume before and after the immobilization of ILs, and the results are summarized up in Table 1. After the immobilization of the as-synthesized ILs, the specific surface area of MCM-22 undergoes a dramatic decrease from $439.8 \text{ m}^2 \cdot \text{g}^{-1}$ to 174.7, 237.6, 190.8, 216.4 and $155.1 \text{ m}^2 \cdot \text{g}^{-1}$ for the MCM-22-MPIIm Cl, MCM-22-EPIIm Cl, MCM-22-BPIIm Cl, MCM-22-BPIIm HSO₄ and MCM-22-BSPIm HSO₄, respectively. The corresponding average pore volume decreases from $0.634 \text{ cm}^3 \cdot \text{g}^{-1}$ to 0.409, 0.476, 0.495, 0.324 and $0.297 \text{ cm}^3 \cdot \text{g}^{-1}$ respectively. The decrease in specific surface area and the average pore volume are associated with the coverage of a thin IL film on the surface of MCM-22 zeolites [36].

Table 1

BET analysis results of MCM-22 and MCM-22-IL

	Specific surface area/ $\text{m}^2 \cdot \text{g}^{-1}$	Average pore volume/ $\text{cm}^3 \cdot \text{g}^{-1}$
MCM-22	439.8	0.634
MCM-22-MPIIm Cl	174.7	0.409
MCM-22-EPIIm Cl	237.6	0.476
MCM-22-BPIIm Cl	190.8	0.495
MCM-22-BPIIm HSO ₄	216.4	0.324
MCM-22-BSPIm HSO ₄	155.1	0.297

3.2.4. Surface density of acid groups on the MCM-22 and MCM-22-IL

The surface acid amount on the MCM-22 and MCM-22-IL was determined by a well-established amine titration method [36], and the results are summarized up in Table 2. The surface acid amount of pristine MCM-22, MCM-22-MPIIm Cl, MCM-22-EPIIm Cl and MCM-22-BPIIm Cl is 1.129, 0.6677, 0.6604 and $0.6411 \text{ mmol} \cdot \text{g}^{-1}$, respectively. Due to the absence of acidic groups in the [TPMIIm][Cl], [TPEIm][Cl]

and [TPBIm][Cl] molecules, the immobilization of these ILs onto the MCM-22 surface results in the increase in the catalyst mass, but decrease in the total acid amounts of acidic groups. On the other hand, the [TPBIm] [HSO₄] molecule, contains an acidic sulfonate group HSO₄, hence the surface acid amount of MCM-22-BPIIm HSO₄ at around $0.6976 \text{ mmol} \cdot \text{g}^{-1}$ is slightly higher than those of the other three ILs without acidic groups. The [TPBSIm] [HSO₄] molecule containing two acidic groups of $-\text{SO}_3\text{H}$ and HSO_4^- , thus the MCM-22-BSPIm HSO₄ shows an evident increase in surface acid amount at $0.8269 \text{ mmol} \cdot \text{g}^{-1}$. These above results indicate that the surface acid amount of the IL-immobilized MCM-22 is positively correlated with the acid groups in the IL molecular structures.

Table 2

Surface acid amount of MCM-22 and MCM-22-IL

	Surface acid amount/ $\text{mmol} \cdot \text{g}^{-1}$	Surface density of acid groups/ $\text{mmol} \cdot \text{m}^{-2}$
H-MCM-22	1.129	2.05×10^{-3}
MCM-22-MPIIm Cl	0.6677	3.82×10^{-3}
MCM-22-EPIIm Cl	0.6604	2.78×10^{-3}
MCM-22-BPIIm Cl	0.6411	3.36×10^{-3}
MCM-22-BPIIm HSO ₄	0.6976	3.22×10^{-3}
MCM-22-BSPIm HSO ₄	0.8269	5.33×10^{-3}

Based on the specific surface area, the surface densities of acid groups of the pristine MCM-22 is circa $2.05 \times 10^{-3} \text{ mmol} \cdot \text{m}^{-2}$, while those of the MCM-22-MPIIm Cl, MCM-22-EPIIm Cl, MCM-22-BPIIm Cl, MCM-22-BPIIm HSO₄ and MCM-22-BSPIm HSO₄ are circa 3.82×10^{-3} , 2.78×10^{-3} , 3.36×10^{-3} , 3.22×10^{-3} and $5.33 \times 10^{-3} \text{ mmol} \cdot \text{m}^{-2}$, respectively. Obviously, the surface densities of acid groups on the MCM-22-IL zeolites are all larger than that of the pristine MCM-22. The increase in surface density of acid groups on the catalyst may be favorable to prolong catalyst life and improve the reaction with high yield for the acid-catalyzed alkylation reaction.

3.3. Regulation of the adsorption ratio of isoparaffin/olefin

To regulate the adsorption ratio of isoparaffin/olefin on the MCM-22 by the immobilization of ILs, the adsorption behaviors of isobutane and 1-butene on the MCM-22-IL surface were determined by the aforementioned static adsorption experiments. The adsorption isotherms are obtained and are further fitted by Freundlich model. Fig. 8 shows the adsorption isotherms of isobutane and 1-butene on the pristine MCM-22 and MCM-22-IL at temperature of 298.15 K.

It is clear that the adsorption amount of isobutane and 1-butene increased with increasing pressure for all substrates, albeit different of the growth tendency. As shown in Fig. 8a, MCM-22 exhibits more rapid increase in the adsorption capacity of 1-butene than that of isobutane with increasing pressure. As for the MCM-22-ILs samples (exclusive of MCM-22-BSPIm HSO₄), the adsorption capacity of isobutane increases more steeply than that of 1-butene with increasing

equilibrium pressure. However, the adsorption behavior of isobutane and 1-butene on the MCM-22-BSPIm HSO₄ shows a similar tendency with that of MCM-22.

To compare adsorption behaviors of isobutane and 1-butene on the MCM-22 immobilized with different types of ILs, the adsorption I/O molar ratios are calculated. Fig. 9 shows the effect of alkyl chain length and the acid group numbers of ILs on the adsorption I/O ratio. It is clearly observed that the immobilization of 1-alkyl-3-(3-triethoxysilyl)propyl imidazolium chloride (alkyl-methyl, ethyl, butyl) on the MCM-22 substantially improves the adsorption I/O ratio, especially at the relatively high pressure (Fig. 9a). The adsorption molar ratio of I/O is substantially improved from 0.75 to above 0.9 at 300 kPa upon immobilizing ILs. However, it is found that the effect of alkyl chain length of ILs on the adsorption I/O ratio is indistinctive, because the IL amount immobilized on MCM-22 is different, and it is difficult to obtain MCM-22-IL with the same amount of ILs.

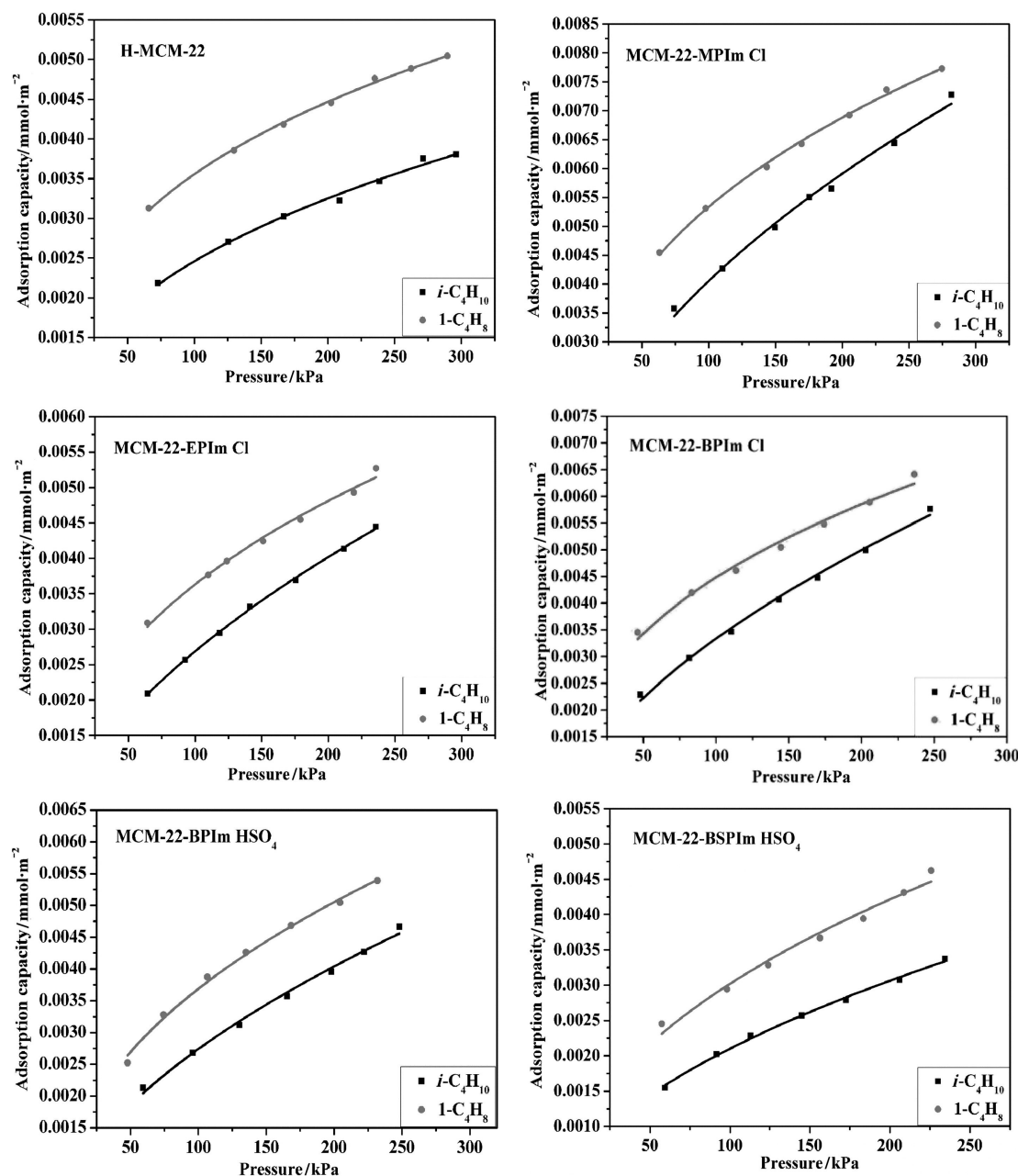


Fig. 8. The adsorption isotherms of isobutane/1-butene on the MCM-22 and MCM-22-IL zeolites at 298.15 K.

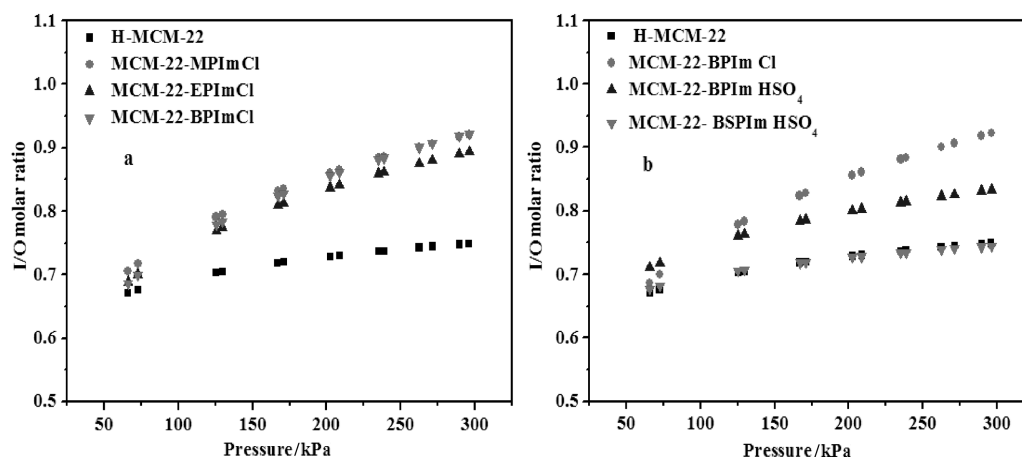


Fig. 9. The effects of the alkyl chain length (a) and the acid group number on the I/O molar ratio (b).

As shown in Fig. 9b, it is surprised to find that the improvement of adsorption I/O ratio is mainly associated with the acid group number. The [TPBIm][Cl], [TPBIm][HSO₄] and [TPBSIm][HSO₄] molecules contain the same cation alkyl chain of butyl, but have different acid group numbers of 0, 1 and 2 respectively. Among them, the [TPBIm][Cl]-immobilized MCM-22 shows best improvement in the adsorption I/O ratio from 0.75 to 0.92 at 300 kPa, while the [TPBSIm][HSO₄]-immobilized MCM-22 does not show any improvement on the adsorption I/O molar ratio. Because the polarity of MCM-22-IL increases with the increase in the acidic group number, it is readily concluded that the acid group numbers of ILs have a negative effect on the improvement of the adsorption I/O ratio. According to Pauli's exclusion principles, the higher polarity of 1-butene than isobutane facilitates the preferential adsorption of 1-butene on a polar adsorbent such as MCM-22-BSPIIm HSO₄. Furthermore, the increase in the acid group amount may promote the polymerization of olefin, thus resulting in the increase in the adsorption amount of olefin. Taken together, these above results demonstrate that the longer cation alkyl chains and less acid group numbers are favorable to improve the adsorption I/O ratio on the MCM-22-IL surfaces.

3.4. The proposed adsorption mechanisms of the MCM-22-IL

To deeply understand the adsorption mechanism of isobutane and 1-butene, it is necessary to analyze the regulation mechanism of adsorption I/O molar ratio on the ILs-immobilized MCM-22. As schematically illustrated in Fig. 10, the preferential adsorption of olefin on MCM-22 (see Fig. 10) is attributed to the interaction between C=C of 1-butene molecules with Si-OH, Al-OH and Si-OH-Al on the H-MCM-22 surface. Thus, the C=C...H-O and π coordination supermolecular complexes are formed. However, the only interaction between isobutane and Si-OH, Al-OH, Si-OH-Al on the H-MCM-22 surface is the

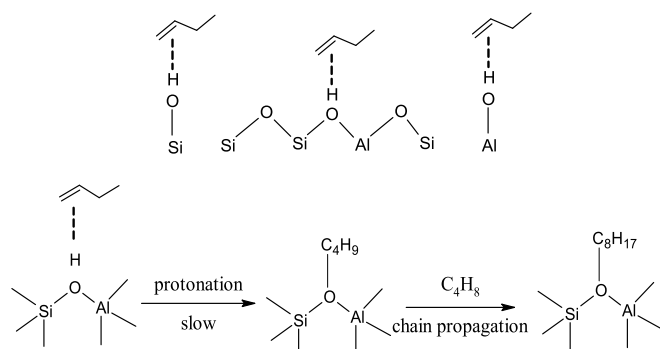


Fig. 10. The proposed adsorption mechanism of 1-butene on the H-MCM-22.

formation of C-C...H-O bond [45,46]. The covalent bonds of 1-butene on the MCM-22 are much stronger than the van der Waals' force of isobutane on the MCM-22, and thus leading to higher adsorption capacity of 1-butene than that of isobutane. Besides, the 1-butene can also react with acid protonic to form oligomerization or aggregation [47,48], thus leading to the increase in the adsorption capacity of 1-butene, while the decrease in the adsorption of I/O ratio.

As for the MCM-22-IL, the immobilization of ILs on the MCM-22 by covalent bonds results in the reduction of the surface density of OH groups. This results in the weakening in the interaction between OH and C=C. Thus, then decrease in adsorption capacity of 1-butene is expectable. On the other hand, the decrease in surface polarity by the immobilization of ILs is unfavorable for 1-butene adsorption on the MCM-22, while it is probably beneficial for the adsorption of isobutane. Hence, the improvement of the I/O ratio can be readily achieved by the immobilization of ILs on the MCM-22. At the same time, the increase in acid group number of ILs causes the increase in the surface polarity of MCM-22-IL. Therefore, regulation of adsorption I/O ratio can be achieved by adjusting the acid group numbers on the ILs-immobilized MCM-22.

4. Conclusions

Four types of ionic liquids (ILs) were synthesized to functionalize the surface of MCM-22 zeolite for regulation of the adsorption molar ratio of isobutane and 1-butene. Successful immobilization of ILs on the MCM-22 was ascertained by FTIR and XPS characterization. The structural and surface features of ILs-modified MCM-22 were determined by XRD, BET and TGA. Static adsorption experiment demonstrated that the immobilization of ILs have a significant effect on the adsorption capacity of isobutane and 1-butene. The immobilization of ILs on MCM-22 improved the adsorption molar ratio of I/O from 0.75 to above 0.9 at 300 kPa. With the number of acid group numbers increased, the acid amounts increased while the adsorption I/O ratio decreased. In conclusion, immobilizing ionic liquids is an effective way to modify the textural, chemical and morphological properties of MCM-22. Accordingly, the adsorption properties of MCM-22, such as the adsorption molar ratio of isoparaffin/olefin are tunable by immobilizing predesigned ionic liquids with a desired supporting amount. This study can be a guidance in modification the adsorbent or catalyst used in adsorption separation and other competitive adsorption reactions.

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