Preparation of mannitol-based ketal-linked porous organic polymers and their application for selective capture of carbon dioxide

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Abstract

Four kinds of mannitol-based ketal-linked porous organic polymers (**MKPOPs**) were successfully synthesized through condensation reaction between aromatic acetyl monomers and mannitol, catalyzed by *p*-toluenesulfonic acid. The structure of resulting polymers was confirmed by Fourier transform infrared and solid-state ^{13}C nuclear magnetic resonance spectrum measurements. The porosities of **MKPOPs** were investigated by gas adsorption experiments and the results indicate high carbon dioxide uptake (up to 11.5 wt% at 273 K and 1.0 bar) for **MKPOPs** due to the predominant microporous and hydroxyl-rich structures. Remarkably, **MKPOPs** exhibit excellent selective adsorption performances for carbon dioxide over methane (9.9–14.2, IAST at 273 K and 1.0 bar). These studies are of significant importance for **MKPOPs** and their potential application in selective gas adsorption.

Keywords: porous organic polymers; mannitol; ketal-linkage; carbon dioxide capture; selective adsorption

1. Introduction

In recent years, the humanity faces greatest danger from global warming as the surge emissions of greenhouse gases (GHG) like carbon dioxide (CO_2) or methane (CH_4). Pollution from cars and industry is one of the leading causes of GHG becoming trapped in our atmosphere. Global warming can disrupt nature's equilibrium and has lead to more droughts, floods, and other calamities. Scientists have been working hard to develop effective methods for capturing GHG. CO_2 as a major GHG, not only bring damage to atmosphere, but also jeopardize the quality of natural gas that can significantly reduce the gas capacity even lead to corrosion of gas piping [1,2]. The current utilization of amine solutions to chemically capture CO_2 from natural gas still has drawbacks such as energy dissipation during regeneration and the considerable hazard of volatile amine solutions. Consequently, development of new adsorbent material for selective capture of CO_2 from CH_4 has become a great challenge. Efforts employing porous organic polymers (POPs) have attracted considerable attentions. Porous organic materials such as metal organic frameworks (MOFs) [3–6] can exhibit efficient uptake for CO_2 with large polar pore surfaces, while chemical or hydrothermal instability make them vulnerable for application. Given the aforementioned defect, POPs composed of organic building blocks and linkages are more competitive owing to their high stability and simple synthesis. Especially the organic polymers with permanent microporosity, they have wide potential applications in many fields such as gas storage [7–10], selective adsorption [11,12], organic vapor capture [13,14], and

heterocatalysis [15,16]. Several POPs such as hyper-cross-linked polymers (HCPs) [17,18], polymers of intrinsic microporosity (PIMs) [19], and conjugated microporous polymers (CMPs) [20–22] and their performances on CO₂ capture have been reported recently.

The heteroatoms (oxygen, sulphur or nitrogen) in POPs were reported to play an important role in efficient capture of polar gases and adsorption selectivity of CO₂ over nitrogen or CH₄ [23–26]. Based on this strategy, efficient selective sorption of CO₂ over nitrogen was achieved by employing microporous organic polymers synthesized from heterocyclic aromatic monomers [27]. Sulfonate-grafted porous polymer networks exhibit significant adsorption selectivity for CO₂ over nitrogen at low pressure [28]. Particularly, nitrogen-rich POPs such as BILPs [3,29], Azo-COPs [30,31], and PSNs [32,33] possess high Brunauer–Emmet–Teller (BET) specific surface area along with good CO₂/N₂ or CO₂/CH₄ adsorption selectivity. Herein, we utilized mannitol to construct several ketal-linked porous organic polymers (**MKPOPs**). Mannitol [34–36], a polyol derived from mannose, is a cheaply available raw material with broad applications in both food and pharmaceutical industries. Combined with its polyhydroxy structure, mannitol can be promising candidate for constructing desirable POPs. **MKPOPs** are structurally confirmed by Fourier transform infrared (FT-IR) and solid state ¹³C nuclear magnetic resonance (NMR) spectrum measurements. The predominant microporosities of **MKPOPs** are further verified by gas adsorption measurements. Owing to the high hydroxyl contents stem from polyhydric mannitol, **MKPOPs** exhibit

high CO₂ uptake (up to 11.5 wt% at 273 K and 1.0 bar) and considerable selectivity over CH₄ (9.9–14.2, IAST at 273 K and 1.0 bar). These studies open up the possibilities for ketal-linked polymers in further industrial application, especially in gas separation.

2. Experimental

2.1. Materials

Ferrocene, biphenyl, mannitol, *p*-toluenesulfonic acid monohydrate (TSA), acetyl chloride, and *o*-dichlorobenzene were purchased from Beijing Chemical Reagent Corp. Ferrocene was purified by sublimation beforehand. Dichloromethane, acetone, petroleum ether, and ethyl acetate were analytical reagents and used without further purification, unless otherwise noted. 1,3,5-Triphenylbenzene and tetraphenylmethane were synthesized according to the published procedures, respectively [37,38]. Acetyl substituted aromatic monomers 1,1'-diacetylferrocene (**M1**), 4,4'-diacetylbiphenyl (**M2**), 1,3,5-tris(4-acetylphenyl)benzene (**M3**), and tetrakis(4-acetylphenyl)methane (**M4**) were synthesized respectively using the reported methods [18]. All condensation reactions were conducted using the standard Schlenk-line technique.

2.2. Preparation of **MKPOPs**

A mixture of **M1** (35.1 mg, 0.13 mmol), mannitol (23.7 mg, 0.13 mmol), and TSA (500 mg, 2.63 mmol) was suspended in *o*-dichlorobenzene (4.00 mL). After ultrasonication for 0.5 h, the mixture in a Pyrex tube was degassed by at least three freeze–pump–thaw cycles. The Pyrex tube was frozen at 77 K (liquid nitrogen bath)

and evacuated to high vacuum and flame-sealed. The reaction mixture was heated at 180 °C for 72 h affording a black solid. This product was collected by filtration, washed with water, ethanol, acetone, and dichloromethane and then dried *in vacuo* at 120 °C for more than 12 h to obtain **MKPOP-1** in 93% isolated yield. Elemental analysis for $C_{20}H_{24}O_6Fe$: Calculated. C, 57.71%; H, 5.81%. Found. C, 55.93%; H, 2.78%.

Similar to the preparation of **MKPOP-1**, **M2** (31.0 mg, 0.13 mmol), **M3** (37.5 mg, 0.087 mmol), or **M4** (31.8 mg, 0.065 mmol) was used to react with mannitol (23.7 mg, 0.13 mmol) to give **MKPOP-2** (95% isolated yield. Elemental analysis for $C_{22}H_{24}O_6$: Calculated. C, 68.74%; H, 6.29%. Found. C, 70.12%; H, 3.96%), **MKPOP-3** (93% isolated yield. Elemental analysis for $C_{39}H_{39}O_9$: Calculated. C, 71.87%; H, 6.03%. Found. C, 74.55%; H, 4.73%), and **MKPOP-4** (90% isolated yield. Elemental analysis for $C_{45}H_{48}O_{12}$: Calculated. C, 69.22%; H, 6.20%. Found. C, 63.00%; H, 3.67%), respectively.

2.3. Instrumental Characterization

Solid-state ^{13}C cross-polarization/magic-angle-spinning (CP/MAS) NMR spectra of polymers were collected by a Bruker Avance III 400 spectrometer (Bruker, Germany). Thermogravimetric analysis (TGA) was carried out using a Pyris Diamond thermogravimetric/differential thermal analyzer (PerkinElmer Instruments Co. Ltd., USA) by heating the samples to 800 °C under an atmosphere of nitrogen (heating rate 10 °C min⁻¹). FT-IR spectra of the **MKPOPs** were recorded on KBr pellets using a Spectrum One FT-IR spectrometer (PerkinElmer Instruments Co. Ltd., USA). The

samples were prepared by pestling polymers in KBr and packing firmly to get transparent films, and 18 scans were signal-averaged. For scanning electron microscopy (SEM) images, samples were prepared by dropping ethanol suspensions of **MKPOP-1–4** on a silicon wafer and coated with gold after drying. Images were recorded on a Hitachi S-4800 microscope (Hitachi Ltd., Japan) operating at an accelerating voltage of 6.0 kV. Transmission electron microscopy (TEM) images were collected on a Tecnai G2 F20 U-TWIN microscope (FEI, USA) at an accelerating voltage of 200 kV. Prior to TEM measurement, **MKPOP-1–4** was ultrasonically dispersed in ethanol and dropped onto a copper grid coated with a carbon film, respectively. Nitrogen adsorption–desorption isotherms were recorded on an ASAP 2020 M+C accelerated surface area and porosity analyzer (Micromeritics Instrument Corporation, USA) at 77 K. **MKPOPs** were degassed at 120 °C for 12 h under vacuum before analysis. All the gas sorption experiments were carried out twice to ensure the reproducibility. There were no noticeable distinctions in the isotherm obtained from both experiments. The nitrogen adsorption–desorption isotherms were calculated to give the pore parameters, including Brunauer–Emmet–Teller (BET) specific surface area ($P/P_0 = 0.01–0.10$), pore size, and pore volume. The pore size distribution was calculated from the nitrogen adsorption isotherms by the non-local density functional theory (NLDFT) method using a cylindrical pore model. The pore volume was calculated from nitrogen adsorption–desorption isotherms at $P/P_0 = 0.99$. While the micropore surface area and micropore volume were calculated from nitrogen

adsorption–desorption isotherms using the *t*-plot method. CO₂ and CH₄ adsorption isotherms were measured up to 1.0 bar at 273 K, using a TriStar II 3020 accelerated surface area and porosity analyzer (Micromeritics Instrument Corporation, USA).

3. Results and Discussions

Scheme 1. (a) Reaction between mannitol and aromatic acetyl compound. (b) Synthesis routes to **MKPOPs**.

The ketal-linked microporous organic polymers **MKPOPs** were synthesized

using the condensation reaction of acetyl containing building blocks (**M1**, **M2**, **M3**, or **M4**) with mannitol. The preparation routes to **MKPOPs** are presented in Scheme 1. The sealed-tube polymerization method was used instead of the conventional flask method to get materials with desired properties according to our reported results [39,40]. The enclosed reaction condition without oxygen is favorable for high degree of polymerization. The acetyl containing compounds were dispersed in *o*-dichlorobenzene, and TSA as a catalyst was added into the reaction mixture. After polymerization in the sealed tube at 180 °C for 3 days, four polymers (**MKPOP-1–4**) were obtained in quantitative yields. Normally, the ketal-linkages in **MKPOPs** are formed through a connection between an acetyl group and two hydroxyl groups in ortho-carbon atoms in mannitol. There are also cases that acetyl group can react with two hydroxyl groups from different mannitols (Fig. S1, Supplementary Information), thus leading to the coexistence of two kinds of structures in **MKPOPs**. Since it is important to design CO₂ absorbents that can be mass-produced at a low cost, the synthetic method we adopted here has several advantages including cheaply available raw material and avoidance of metal catalysts. The obtained **MKPOPs** are stable and insoluble in most common organic solvents, such as ethanol, dichloromethane, and *N,N*-dimethylformamide, indicating their high degree of cross-linked structures.

Fig. 1. TGA curves of the polymers **MKPOP-1–4**.

The thermal stabilities of the obtained polymers were investigated using TGA measurement from 30 to 800 °C under nitrogen atmosphere (Fig. 1). The weight loss in the initial stages (< 200 °C) of heating is due to the evaporation of adsorbed water or trapped gas molecules in the organic porous network. No drastic weight loss occurs as the temperature increases up to 300 °C indicating the excellent thermal stability of the obtained ketal-linked networks. All the polymers show the residual mass varying from 70 to 60%. SEM observations were utilized to investigate **MKPOPs** morphologies (Fig. S2, Supplementary Information). The SEM images reveal uniform microspheres of 2–5 μm in diameters for **MKPOP-2–MKPOP-4**, while no obvious morphology can be observed in case of **MKPOP-1**. These polymers show amorphous nature owing to the irregular nanoparticles and nanoplatelets within their structures. The high-resolution TEM images of **MKPOPs** further confirm their intrinsic microporous structure (Fig. S3,

Supplementary Information).

Fig. 2. FT-IR spectra of **M3**, mannitol, and **MKPOP-3**.

Fig. 3. Solid-state ¹³C CP/MAS NMR spectrum of **MKPOP-3**.

The formation of the ketal linkage was verified by FT-IR spectroscopic measurement (Fig. 2 and Fig. S4–S6, Supplementary Information). The consumption of the carbonyl group can be evidenced by a significant decrease in the intensity at 1690 cm^{-1} . The broad bands that can be attributed to the stretching vibration of hydroxyl groups of mannitol around 3400 cm^{-1} reduce as well. These results confirm the cross-linking between acetyl monomers and mannitol. Remarkably, absorption peaks at around 1700 cm^{-1} assigned to the stretching vibration of the resulting ketal linkage with two oxygen atoms in the six member ring further prove the formation of desired polymers. Meanwhile, the characteristic aliphatic C–H and C–O absorption peaks at ca. 2900 and 1100 cm^{-1} are also seen for the polymers. The observed signals in the fingerprint region of the polymers indicate the reservation of aromatic structures in the corresponding monomers. Solid-state CP/MAS ^{13}C NMR spectroscopic measurement was also employed to further verify the formation of **MKPOPs**. The chemical shifts in the ^{13}C NMR spectra of **MKPOPs**, located at 78 ppm confirm the formation of the ketal-linked polymers (Fig. 3 and Fig. S7–S8, Supplementary Information). For **MKPOP-3**, the signal at 19 ppm is attributed to the methyl group originating from the acetyl monomer **M3**. Notably, the spectrum of **MKPOP-4** exhibits a distinct resonance at 65 ppm , which can be attributed to the quaternary carbon atoms derived from the tetraphenylmethane monomer **M4** (Fig. S8, Supplementary Information). The peaks for the carbon atom in the alkane backbones might overlap with that of the ketal-linkage carbon. Overall the desired structures of **MKPOPs** can be confirmed by the FT-IR and

solid-state ^{13}C NMR spectra.

Fig. 4. (a) Nitrogen adsorption–desorption isotherms of **MKPOPs** measured at 77 K. (b) Pore-size distribution profiles of **MKPOPs** calculated by NLDFT method.

The adsorption–desorption isotherm can provide additional information on both specific surface area and pore volume of microporous networks. The porous nature of the **MKPOPs** was evaluated by nitrogen adsorption–desorption isotherm measurements at 77 K on activated samples (Fig. 4a). The polymeric networks of **MKPOP-1–4** exhibit combination of type I and IV sorption isotherms [41]. A rapid nitrogen uptake at a low relative pressure ($P/P_0 < 0.05$) indicates the predominant microporosities of **MKPOPs**. There is also noticeable uptake at high relative pressure ($P/P_0 > 0.9$) especially in **MKPOP-1** and **MKPOP-2**. These phenomena might be owing to the interparticle voids resulting from random aggregation of some nanoparticles. The sorption hysteresis existing between adsorption and desorption branches of the isotherms can be interpreted as the swelling of polymer matrix or the limited release of trapped nitrogen molecules

from narrow pore channel [42]. The key porosity parameters obtained from the isotherms, such as the BET specific surface area, micropore surface area, micropore volume, and total pore volume are summarized in Table 1. The BET specific surface area was calculated from nitrogen adsorption isotherms (Fig. S9, Supplementary Information), and the highest BET specific surface area belongs to **MKPOP-3** ($590 \text{ m}^2 \text{ g}^{-1}$). The resulting isotherms of polymers were employed to estimate the pore size distribution (PSD) profile by utilizing NLDFT model (Fig. 4b). The dominant pore size distributions of **MKPOPs** are in the range of 0.68–1.25 nm. Several contiguous low peaks observed in mesopore and macropore regions especially in the PSD profiles of **MKPOP-1** and **MKPOP-2** are consistent with their nitrogen sorption isotherms. The pore volumes were estimated at $P/P_0 = 0.99$ and resulted in $0.16\text{--}0.55 \text{ cm}^3 \text{ g}^{-1}$ for **MKPOPs**.

Fig. 5. CO_2 adsorption isotherms of the obtained **MKPOPs** at (a) 273 K and (b) 298 K.

A number of literatures indicate that the CO₂ capability can be enhanced significantly via the incorporation of heteroatoms (like N, S, and O) in the polymer networks [23–33]. Given the considerable microporosity and abundant hydroxyl groups in **MKPOPs**, we further evaluate their capability for CO₂ adsorption. The gas sorption measurements for CO₂ were performed for all **MKPOPs** by volumetric methods and the results demonstrate their relatively high CO₂ adsorption capability (Fig. 5 and Table 1; 6.3–11.5 wt% at 273 K and 1.0 bar; 4.7–7.4 wt% at 298 K and 1.0 bar). It is worth noting that the trend of the CO₂ capabilities of **MKPOPs** is basically consistent with their BET specific surface area. One possible explanation for the result is that the considerable micropore surface area in the polymer networks might be favorable to the CO₂ uptake [43]. To further investigate the binding affinity of **MKPOPs** for CO₂, we calculated the corresponding isosteric heat (Q_{st}) of CO₂ derived from adsorption data recorded at 273 and 298 K from 0 to 1.06 bar by using the Clausius–Clapeyron equation (Table 1, Fig. S10 and S11, Supplementary Information) [44]. The Q_{st} value of **MKPOP-3** is up to 27.1 kJ mol⁻¹, which is higher than that of **MKPOP-1** (23.5 kJ mol⁻¹), **MKPOP-2** (18.3 kJ mol⁻¹), or **MKPOP-4** (23.6 kJ mol⁻¹). The Q_{st} values practically remain constant over the whole CO₂ uptake range. The largest value is comparable to that of the most reported POPs but a little less than that of the nitrogen-rich networks such as PI-1 (34 kJ mol⁻¹) [45] or PECONFs (26–34 kJ mol⁻¹) [46]. As shown in Table S2 (Supplementary Information), when comparing with other CO₂ adsorbents, the CO₂ uptakes of the **MKPOPs** are comparable to that of adsorbents

with high surface area. The strong interactions play a crucial role in the good performing CO₂ uptake like –OH in POF1B, which greatly help the CO₂ capturing of the materials [47]. To sum up, the obtained results reveal that high surface area, microporosity, and hydroxyl-rich structure together contribute to stronger binding affinities of polymers toward CO₂.

Table 1. Porosity properties and gas uptake capacities of MKPOPs

MKPOPs	S_{BET}^a	S_{micro}^b	V_{micro}^c	V_{total}^d	CO ₂ at 1.0 bar ^e		
	(m ² g ⁻¹)	(m ² g ⁻¹)	(cm ³ g ⁻¹)	(cm ³ g ⁻¹)	273 K	298K	Q_{st}
MKPOP-1	510	340	0.14	0.55	8.7	6.2	23.5
MKPOP-2	160	130	0.05	0.16	6.3	4.7	18.3
MKPOP-3	590	410	0.17	0.43	11.5	7.4	27.1
MKPOP-4	480	350	0.14	0.31	8.5	5.8	23.6

^a Specific surface area calculated from the nitrogen adsorption isotherm using the BET method in the relative pressure (P/P_0) range from 0.01 to 0.10; ^b Micropore surface area calculated from the adsorption branch of the nitrogen adsorption–desorption isotherm using the t -plot method; ^c Micropore volume calculated from the nitrogen adsorption isotherm using the t -plot method. ^d Total pore volume at $P/P_0 = 0.99$; ^e CO₂ uptake in wt% and the isosteric enthalpies of adsorption (Q_{st}) in kJ mol⁻¹.

Table 2. Corresponding data of CO₂ separation for **MKPOPs**.

MKPOPs	CO ₂ /CH ₄ selectivity			CO ₂ /N ₂ selectivity	
	initial	IAST ^b	IAST ^c	initial	IAST ^d
	slope ^a			slope ^a	
MKPOP-1	19.4	12.8	4.4	75.2	21.9
MKPOP-2	13.5	9.9	3.6	60.0	17.2
MKPOP-3	16.6	10.8	4.3	104.3	29.8
MKPOP-4	21.8	14.2	4.7	105.2	33.8

^a Selectivity (mol mol⁻¹) was calculated by initial slope method at 273 K. ^b Selectivity (mol mol⁻¹, 1.0 bar) was calculated by IAST method at mole ratio of 5/95 for CO₂/CH₄ (natural gas model) at 273 K. ^c Selectivity (mol mol⁻¹, 1.0 bar) was calculated by IAST method at mole ratio of 50/50 for CO₂/CH₄ (shale gas model) at 273 K. ^d Selectivity (mol mol⁻¹, 1.0 bar) was calculated by IAST method at mole ratio of 15/85 for CO₂/N₂ at 273 K.

CH₄/CO₂ mixed gas are widely found in natural gas, biogenic gas, and oil field gas, masses of CO₂ in the mixture can directly influence the combustion effect or the quality of the gas product. Based on the promising microporous properties resulted from **MKPOPs**, we decide to determine their CO₂ uptake selectivity over CH₄ to assess the potential application in gas separation. To investigate the CO₂/CH₄ selectivity, single component adsorption isotherms of CO₂ and CH₄ were collected at 273 K and 0–1.06

bar. CO_2/CH_4 selectivity was first calculated by use of the initial slope ratios estimated from Henry's law constants that derived from single-component adsorption isotherms in the low pressure range (Table 2 and Fig. S12, Supplementary Information). The calculated CO_2/CH_4 selectivity of **MKPOP-4** is 22 at 273 K. Notably, the CO_2/CH_4 selectivities of **MKPOP-1–3** are found to be in the range of 13–19, indicating possibilities of **MKPOPs** for further use in CO_2 removal from pre-combustion gases.

Fig. 6. IAST selectivity of **MKPOPs** for (a) 0.05/0.95 CO_2/CH_4 mixture (natural gas model) (b) 0.50/0.50 CO_2/CH_4 mixture (shale gas model) calculated at 273 K.

The ideal adsorbed solution theory (IAST) [48] is a generally applied method to evaluate the adsorption behavior of binary gas mixture in porous organic materials [49–52]. The CO_2 and CH_4 isotherms of **MKPOPs** collected at 273 K are well fitted by using the dual-site Langmuir model and the single-site Langmuir model, respectively (black lines in Fig. S14, Supplementary Information). The initial significant rise in uptake of CO_2 compared with CH_4 might be owing to the interactions of CO_2 with

accessible hydroxyl sites of mannitol. The resulting IAST data for **MKPOPs** are listed in Table 2. By specifying the natural gas composition as $\text{CO}_2/\text{CH}_4 = 0.05/0.95$, the selectivities of CO_2/CH_4 for **MKPOPs** are shown in Fig. 6a. Remarkably, **MKPOP-4** exhibits the highest CO_2 over CH_4 selectivity (14.2) among all **MKPOPs** at 273 K and 1.0 bar. When we simulate the shale gas composition as $\text{CO}_2/\text{CH}_4 = 0.5/0.5$, the IAST selectivities for **MKPOPs** were calculated varies from 3.6 to 4.7 at 273 K and 1.0 bar (Fig. 6b). It should be noted that the CO_2/CH_4 selectivities of **MKPOPs** (9.9–14.2) are comparable even superior to those of the reported POPs with higher BET specific surface area and CO_2 capability, such as PANs (7 and 10, 273 K, 1.0 bar) [33] and APOPs (5.3–6.7, 273 K, 1.0 bar) [52]. To sum up, the IAST data and the calculated initial slopes ratios give consistent results, i.e. **MKPOPs** exhibit satisfactory separation performance for CO_2 over CH_4 at 273 K (Table 2).

To further evaluate the selectivity of CO_2 over N_2 for **MKPOPs** under simulated flue-gas conditions (15% CO_2 , 85% N_2), IAST model was used to calculate the molar loadings of the polymers in CO_2 separation from gas mixtures. The experimental N_2 isotherms collected at 273 K for **MKPOPs** were fitted to the single-site Langmuir model (black lines in Fig. S15, Supplementary Information). The calculated IAST for **MKPOPs** is shown in Table 2 and Fig. S16 (Supplementary Information). At 273 K and 1.0 bar, **MKPOP-4** exhibits the highest CO_2 over N_2 selectivity (33.8) among all four polymers. The CO_2/N_2 selectivity calculated by the initial slope ratios (Fig. S13, Supplementary Information) is shown in Table 2, and the highest value of CO_2/N_2

selectivity for **MKPOPs** is 105 at 273 K.

4. Conclusions

In summary, we have prepared four new **MKPOPs** by classic acid catalyzed condensation between aromatic acetyl monomers and mannitol. This synthesis method is economical and environmentally friendly compared to traditional metal-catalyzed polymerization. The solid-state ^{13}C NMR spectroscopy and FT-IR confirm the anticipated structures of the obtained polymers. **MKPOPs** exhibit high CO_2 uptake (up to 11.5 wt% at 273 K and 1.0 bar) owing to their predominant microporous and hydroxyl-rich structures. Furthermore, **MKPOPs** show considerable CO_2 over CH_4 selectivity (9.9–14.2, IAST at 273 K and 1.0 bar) in a specified natural gas composition ($\text{CO}_2/\text{CH}_4 = 0.05/0.95$). These investigations render the ketal-linked microporous polymers promising candidates for selective gas adsorption.

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Graphic TOC