

Effects of polydimethylsiloxane coating of Ni-MOF-74 on CH₄ storage

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Abstract—Ni-MOF-74 was prepared by microwave heating and coated with polydimethylsiloxane (PDMS) via vapor deposition. Both the pristine and the PDMS-coated Ni-MOF-74 samples were exposed to moisture in air (relative humidity of 75%) for different periods of time, and their methane storage capacities under 35 bar conditions were measured. The pristine sample had a Brunauer-Emmett-Teller (S_{BET}) surface area of $1,050 \text{ m}^2 \cdot \text{g}^{-1}$, with a CH₄ uptake capacity of $113.8 \text{ mg} \cdot \text{g}^{-1}$ at 300 K and 35 bar. After exposure to moisture for seven days, the BET surface area and CH₄ uptake capacity declined drastically, whereas the PDMS-coated sample maintained its original BET surface area ($1,018 \text{ m}^2 \cdot \text{g}^{-1}$) and CH₄ uptake capacity ($107.7 \text{ mg} \cdot \text{g}^{-1}$). After exposure to moisture in air for 30 days, however, even the PDMS-coated sample lost almost 60% of its CH₄ storage capacity. All the methane storage capacity data were linearly correlated with the BET surface areas of the Ni-MOF 74 samples.

Keywords: Ni-MOF-74, Methane Storage, Polydimethylsiloxane, Moisture Stability

INTRODUCTION

Natural gas, which is mainly composed of methane (>95%), is abundant, environmentally friendly, and has higher hydrogen content than other hydrocarbon fuels. Because of the low volumetric energy density of natural gas, adsorbed natural gas (ANG) storing natural gas using porous adsorbents such as zeolites, activated carbons, and metal-organic frameworks (MOFs) is being investigated [1].

MOFs are porous crystalline hybrid materials composed of inorganic metal ions or metal clusters linked by multifunctional organic ligands in well-ordered porous structures with large surface areas and pore volumes. They have been intensively studied for their potential applications in high-density methane storage [2]. High methane storage capacities have been reported for HKUST-1 [3], PCN-11 [4], PCN-14 [5], and Ni-MOF-74 [6].

One of the strategies for enhancing methane uptake is to improve the methane binding energy in the MOF by coordinatively unsaturated open metal sites, in which the metal sites can strongly interact with CH₄ molecules through Coulomb interactions [7]. Among the MOFs with open metal sites, members of the M-MOF-74 series (M: Mg, Mn, Co, Ni, or Zn) have been constructed with 2,5-dioxido-1,4-benzenedicarboxylate (DOBDC) linkers in a 1 D arrangement of parallel hexagonal channels, with dimensions of $10.3 \times 5.5 \text{ \AA}^2$ [8]. These have been shown to have methane adsorption capacity, ranging from 149 to $190 \text{ cm}^3_{\text{STP}} \cdot \text{cm}^{-3}$ at 298 K and 35 bar. However, recent studies have reported that the gas adsorption capacity of M-MOF-74 decreases sharply when H₂O molecules are present [9].

Recently, a strategy of applying a polydimethylsiloxane (PDMS)

coating to the surfaces of MOF-5, HKUST-1, and ZnBT by chemical vapor deposition was reported [10]. The coated MOFs were tested for CO₂ adsorption at 1 bar condition and heterogeneous catalysis after exposure to humidity. Huang et al. [11] prepared a Pd/UiO-66 nanocomposite coated with PDMS to improve catalytic activity in the styrene hydrogenation. Zhang et al. [12] reported PDMS/MIL-101 and PDMS/MOF-199 immobilized onto a stainless steel wire through sol-gel technique for a solid-phase microextraction fiber. The prepared fibers were used for the extraction of polycyclic aromatic hydrocarbons from river and lake water samples. Park et al. [13] prepared a mesoporous silica coated by PDMS using a thermal deposition method, and used it as an adsorbent for various chemical warfare agent simulants in gas phase.

In this work, we prepared a Ni-MOF 74 sample with good textural properties by microwave heating, and methane adsorption capacities of the pristine Ni-MOF-74, and measured the PDMS-coated Ni-MOF-74 under both low- and high-pressure conditions to evaluate the effectiveness of the hydrophobic coating on gas storage for extended period of time.

EXPERIMENTAL

1. Synthesis of Ni-MOF-74 and PDMS Coating

A detailed synthesis procedure of Ni-MOF-74 is provided in Supplementary information (SI). PDMS coating of the Ni-MOF-74 was carried out using a vapor deposition technique [10]. A given amount of Ni-MOF-74 powder was spread in a thin layer on a glass dish placed inside a Teflon container with a fresh PDMS stamp. The glass container was then heated to, and maintained at, 503 K for 6 h in the oven. Following the vapor deposition for 6 h, the container was allowed to cool naturally to room temperature to obtain a PDMS-coated Ni-MOF-74.

2. Characterization

X-ray powder diffraction (XRD) patterns of the Ni-MOF-74

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samples were recorded using a Rigaku diffractometer with CuK α radiation ($\lambda=1.54 \text{ \AA}$) at a scan rate of $0.5^\circ \cdot \text{min}^{-1}$. N₂ adsorption and desorption isotherms were obtained using a BELSORP-max instrument (BEL, Japan) at 77 K. Prior to the sorption measurements, the samples were activated at 423 K for 12 h in a vacuum. The morphology of the samples was examined by scanning electron microscopy (SEM, Hitachi S-4300), and energy dispersive spectroscopy (EDS) was conducted to verify the Si dispersion status of PDMS-coated Ni-MOF-74. Fourier transform infrared spectroscopy (FT-IR, Bruker VERTEX 80v) was performed on a KBr disk at room temperature. X-ray photoelectron spectroscopy (XPS) was performed using a monochromatic Al K α X-ray source (Thermo Scientific, USA) and a hemispherical analyzer.

3. CH₄ Adsorption

Relative humidity (H) is the ratio of the vapor pressure (e) of the moist air to its saturation vapor pressure (e_s) at the given temperature, which is expressed in %.

$$H = (e/e_s) \times 100\%$$

Before high pressure CH₄ adsorption experiments in this work, the MOF samples on glass dish were transferred into the constant temperature humidity chamber, where water bath was placed in the bottom and the relative humidity was checked by using wet and dry bulb thermometer.

CH₄ adsorption isotherms of the pristine Ni-MOF-74 and PDMS-coated Ni-MOF-74 under static conditions were obtained using a BELSORP-mini II at 298 K and 1 bar. High-pressure CH₄ adsorption isotherms (0–35 bar) were obtained at 300 K using a magnetic suspension balance (Rubotherm, Germany) with *in situ* density measurements in a closed system. Before the CH₄ adsorption capacity was measured, the buoyancy effect was corrected in ultra-high-purity He (99.999%), and the sample was activated.

RESULTS AND DISCUSSION

Microwave irradiation accelerates the nucleation rate, and consequently produces small uniform crystals in a short synthesis time [14]. Microwave heating enabled the preparation of uniform Ni-MOF-74 crystals in just 120 min, compared with the 24 h for conventional means [15]. The smaller particles obtained by micro-

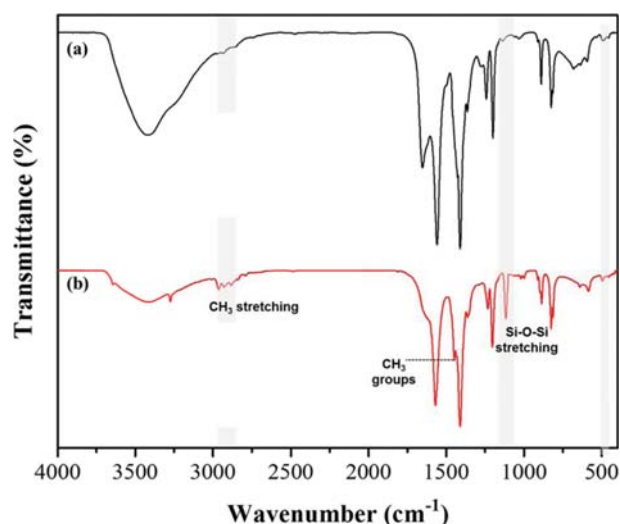


Fig. 1. FT-IR spectra of pristine Ni-MOF-74 (a) and PDMS-coated Ni-MOF-74 (b).

wave heating can also enable more uniform surface coating.

Initially, PDMS-coated Ni-MOF-74 was characterized using various instrumentations. In the FT-IR spectra, a single peak $\sim 1,450 \text{ cm}^{-1}$ and a doublet feature at $\sim 2,900 \text{ cm}^{-1}$ attributed to the different vibrational modes of CH₃ groups in PDMS [13] were detected as shown in Fig. 1(b). Also, a band at $\sim 1,200 \text{ cm}^{-1}$ due to the Si-O-Si stretching frequency of PDMS was observed. The XPS of the pristine and the coated Ni-MOF-74 samples was also taken, and a clear signal of Si 2p after PDMS coating was revealed (Fig. 2). The binding energy of Ni 2p³ in Ni-MOF-74 exhibits an obvious shift after PDMS coating, indicating bond formation between the unsaturated Ni centers and O atoms from the PDMS layer. In Fig. 3, cross-sectional elemental analysis of PDMS-coated Ni-MOF-74 shows that the Si signal from PDMS slightly decreased from the surface to the pore inside of the Ni-MOF-74, supporting that PDMS vapor diffused into the inside of the micropores of Ni-MOF-74. As shown in Table S1 and Fig. S1, the pore size and pore volume of Ni-MOF-74 slightly decreased after PDMS coating. Since the MOF is microporous, the total PDMS content that can be accommodated without affecting the textual properties is expected to be

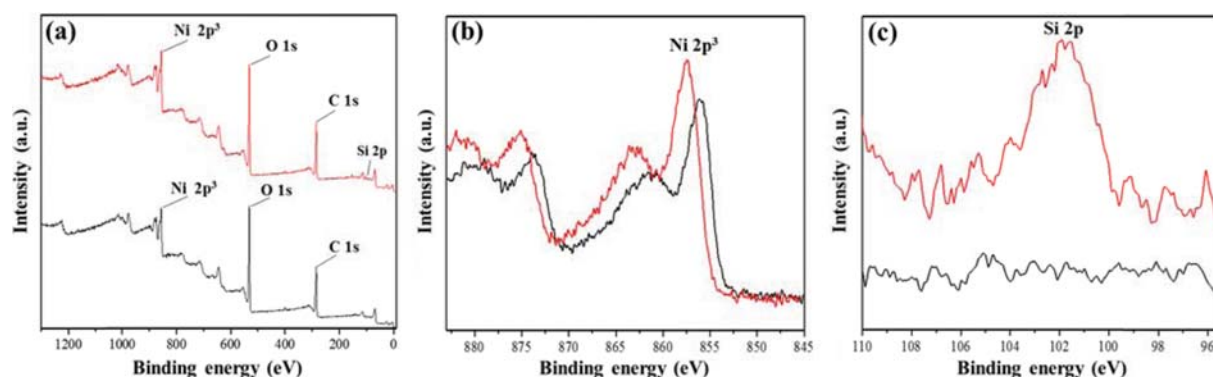


Fig. 2. XPS survey spectra (a) and high-resolution spectra of Ni 2p³ (b) and Si 2p (c) of the pristine Ni-MOF-74 (black) and PDMS-coated Ni-MOF-74 (red).

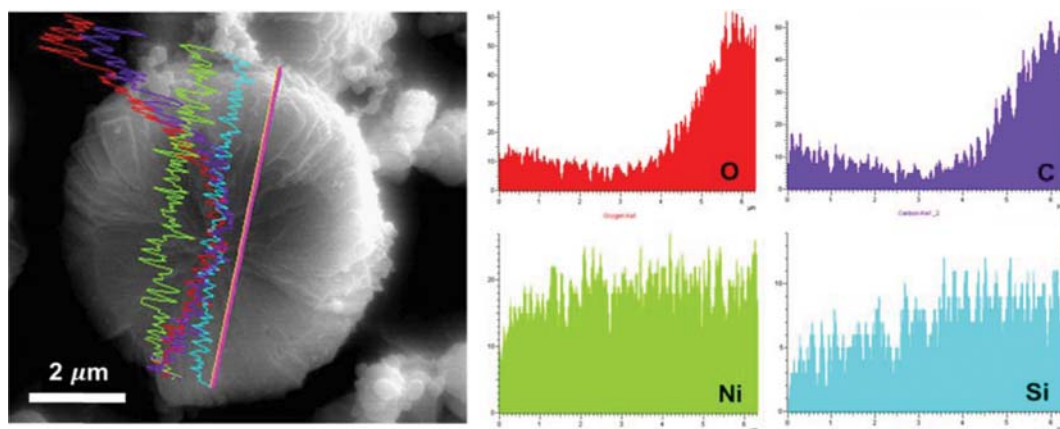


Fig. 3. SEM image of the cross-section of PDMS-coated Ni-MOF-74 with EDX line-scans and element mapping.

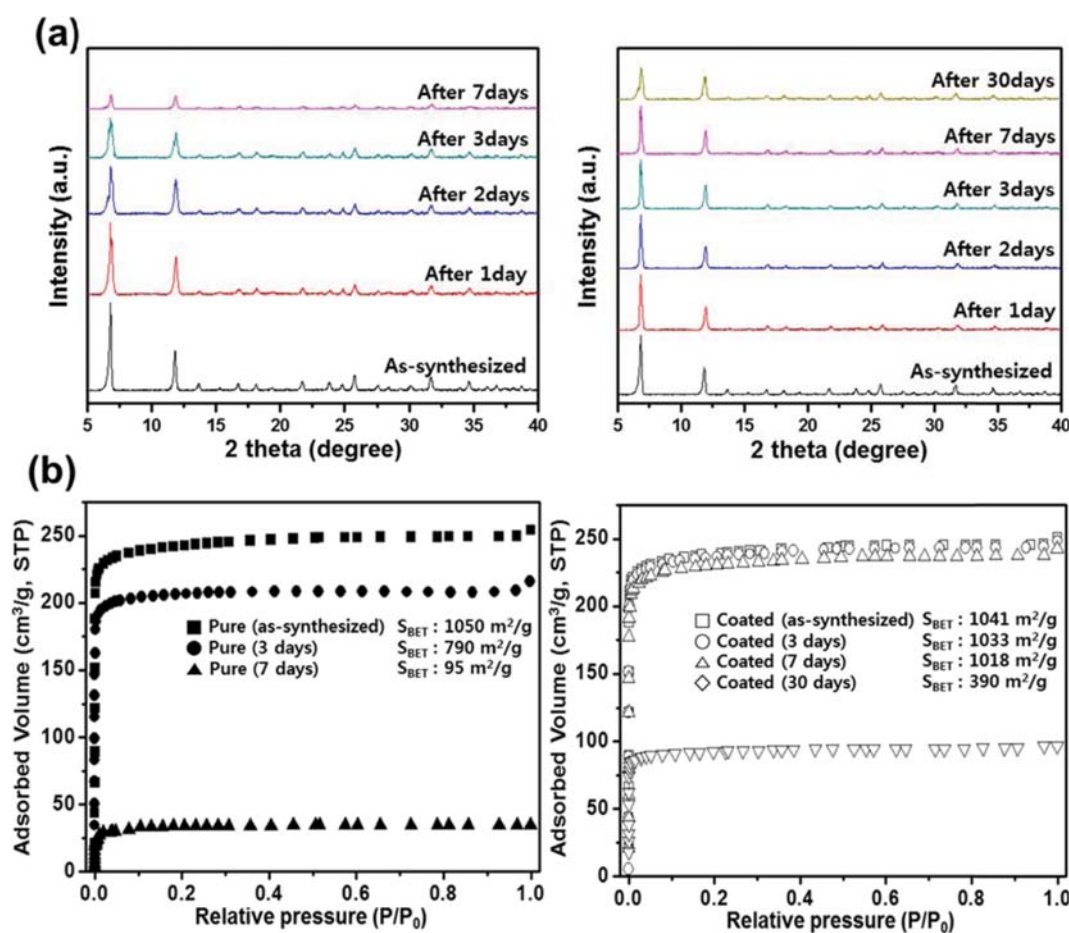


Fig. 4. (a) XRD patterns, (b) N₂ adsorption isotherms of Ni-MOF-74 (left) and PDMS-coated Ni-MOF-74 (right) exposed to moist air for different time intervals.

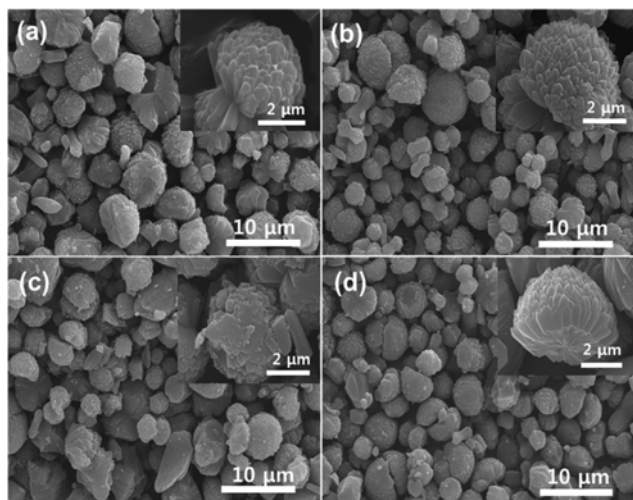
low, and the coated amount found was in good agreement with the range of the values reported by Zhang et al. [10].

Powder XRD (Fig. 4(a)) and N₂-adsorption isotherm measurements (Fig. 4(b)) showed the characteristic diffraction peaks of Ni-MOF-74 with a high surface area. The XRD peaks of the pristine Ni-MOF-74 sample, however, decreased steadily over one to seven days, as shown by the weakening of the major characteristic peaks

at 6.7° and 11.7°. The BET surface area of the Ni-MOF-74 was 1,050 m²·g⁻¹, which drastically decreased to 95 m²·g⁻¹ when the sample was exposed to the moisture in air (RH-75%) for seven days (Table 1). By contrast, the structural and textural properties of the PDMS-coated Ni-MOF-74 sample remained unchanged for seven days. Little reduction in intensity of the two main peaks at 6.7° and 11.7° was detected, and 97% of the BET surface area was found to be

Table 1. BET surface area and CH₄ uptake of Ni-MOF-74 and PDMS-coated Ni-MOF-74 after exposure to humid air for different durations

	BET surface area (m ² g ⁻¹)			CH ₄ uptake at 300 K, 35 bar (mg g ⁻¹)		
	As-synthesized	3 Days	7 Days	As-synthesized	3 Days	7 Days
Pristine Ni-MOF-74	1050	790	95	113.8	84.2	10.3
PDMS-coated Ni-MOF-74	1041	1033	1018	112.8	110.5	107.7

**Fig. 5.** SEM images of (a) Ni-MOF-74; (b) PDMS-coated Ni-MOF-74; (c) Ni-MOF-74 (after exposure to moist air for 7 days); and (d) PDMS-coated Ni-MOF-74 (after exposure to moist air for 7 days).

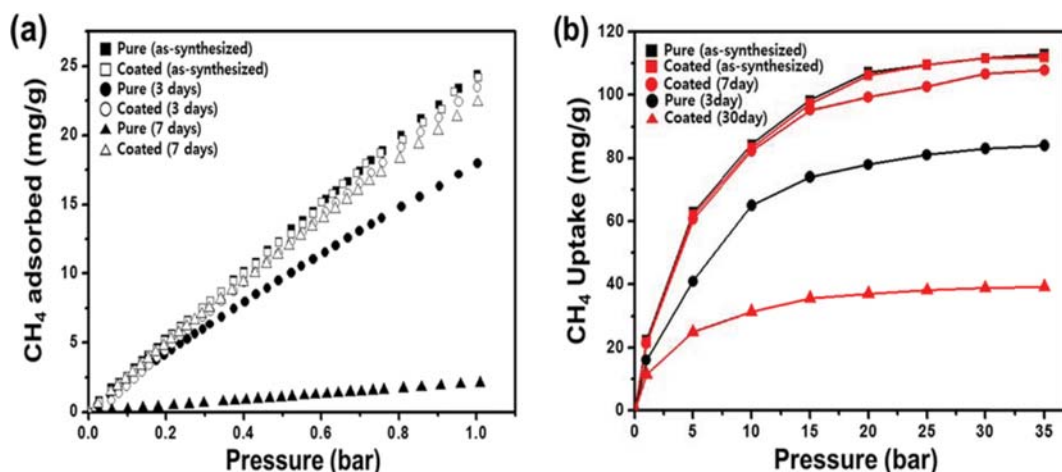
retained (1,018 m² g⁻¹), indicating that the inherent porous structure in the MOF remained intact after the cross-linked silicone molecules had covered the surface of pristine Ni-MOF-74 (Fig. 4(b) and Table 1).

Fig. 5 shows the SEM images of the corresponding Ni-MOF-74 samples. The pristine Ni-MOF-74 shows a flower-like morphology and a particle size range of 2–6 μm, consisting of polyhedral

aggregates of small crystals (Fig. 5(a)) [15]. These underwent corrosion, with cracks and cavities appearing on the surfaces after exposure to moisture for seven days (see the inset, Fig. 5(c)). On the other hand, the PDMS-coated Ni-MOF-74 retained an identical flower-like morphology before (Fig. 5(b)) and after (Fig. 5(d)) seven-day exposure to the same humid conditions. As shown in Fig. S2, the Si/Ni ratio of the PDMS-coated Ni-MOF-74 was approximately 2.24%.

The CH₄ storage capacity of the pristine and PDMS-coated Ni-MOF-74 was measured before and after exposure to moist air over different time intervals. At 1 bar (Fig. 6(a)), the CH₄ uptake of the pristine Ni-MOF-74 samples after moisture exposure dropped from 24.4 to 2.1 mg g⁻¹ after 7 days. The CH₄ uptake for the PDMS-coated Ni-MOF-74 samples, on the other hand, remained almost identical to that of the freshly prepared one (24.2 to 22.4 mg g⁻¹ after seven days). CH₄ uptake performance measurements at 35 bar and 300 K showed more drastic differences: a huge drop from 113.8 to 10.3 mg g⁻¹ for the pristine sample, and only a small drop from 112.8 to 107.7 mg g⁻¹ for the PDMS-coated Ni-MOF-74 sample, after exposure to air for seven days (Fig. 6(b) and Table 1). In Fig. S3, the CH₄ uptakes of all the Ni-MOF-74 samples, under both 1 and 35 bar conditions, are plotted against MOF surface areas, showing the linear relationship between CH₄ uptake and the surface areas of the adsorbents. As reported [16], CH₄ storage on Ni-MOF-74 was governed by physical adsorption, which was proportional to the surface area of the adsorbent.

On other hand, the PDMS-coated Ni-MOF-74 sample exposed to moist air for 30 days lost almost 60% of its CH₄ uptake capacity (Fig. 6(b)) accompanied by a significant drop in its surface area to

**Fig. 6.** (a) CH₄ uptake of Ni-MOF-74 and PDMS-coated Ni-MOF-74 at 1 bar/298 K and (b) high-pressure CH₄ uptakes of Ni-MOF-74 and PDMS-coated Ni-MOF-74 at 835 bar/300 K.

390 m²·g⁻¹ (Fig. 4(b)). Therefore, the PDMS coating, despite providing strong resistance against moisture in the short term, could not be a long-term solution to the susceptibility of Ni-MOF-74 to moisture. To keep the CH₄ storage capacity by Ni-MOF-74 longer, we also extended the PDMS-coating time to 12 h. As a result, the Si/Ni of the sample increased from 2.24% to 5.4% (Fig. S2). However, the BET surface area of the coated material dropped to only 53 m²/g and could not be used for gas storage, since excessive PDMS on the outer surface of Ni-MOF-74 blocked the pore entries.

CONCLUSIONS

Ni-MOF-74 was synthesized by microwave heating and subsequently coated with PDMS to enhance its moisture resistance. The CH₄ storage capacity under both low- and high-pressure conditions was measured, and dependence on the PDMS coating and the resulting textural properties was examined. The PDMS-coated Ni-MOF-74 retained its structural stability and intrinsic textural properties after seven days of exposure to moisture in air. Whereas the pristine Ni-MOF-74 showed a catastrophic reduction in BET surface area to 95 m²·g⁻¹, the PDMS-coated Ni-MOF-74 maintained the initial surface area. The amount of methane stored by the Ni-MOF-74 samples was linearly dependent on the surface areas of the samples. PDMS-coated Ni-MOF-74 retained practically the same CH₄ uptake capacity after seven days exposure to air. These results confirmed that PDMS-coated Ni-MOF-74 is effective in maintaining stability against moisture. Prolonged exposure to moisture over 30 days, however, still led to a significant reduction both in the surface area and the methane storage capacity of Ni-MOF-74.

ACKNOWLEDGEMENTS

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SUPPORTING INFORMATION

Additional information as noted in the text. This information is

available via the Internet at <http://www.springer.com/chemistry/journal/11814>.

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Supporting Information

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EXPERIMENTAL

1. Chemicals

Nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (>99%, Aldrich), 2,5-dihydroxyterephthalic acid (H_2DOBDC) (>98%, TCI), PDMS (Aldrich), *N,N*-dimethylformamide (DMF) (99.9%, Aldrich), and ethanol (99.9%, DUKSAN) were purchased and used without further purification.

2. Synthesis of Ni-MOF-74

Ni-MOF-74 was prepared by microwave heating, as proposed by Wu et al. [15] with modification. A substrate solution for Ni-MOF-74 was prepared by dissolving $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.902 g, 6.54 mmol) and H_2DOBDC (0.382 g, 1.92 mmol) in a 1 : 1 : 1 (v/v/v) mixture of DMF, ethanol, and water (53.3 mL each). After 1 h stirring, the prepared solution was transferred to a 35 mL glass tube sealed with a rubber septum, placed in a microwave oven (Discover S-class, CEM), and heated by microwave irradiation at 200 W for 2 h. Following the synthesis, the mother liquor was decanted and replaced with methanol for 3 days at room temperature. The final brown-colored product was obtained by filtration and washed thoroughly with methanol.

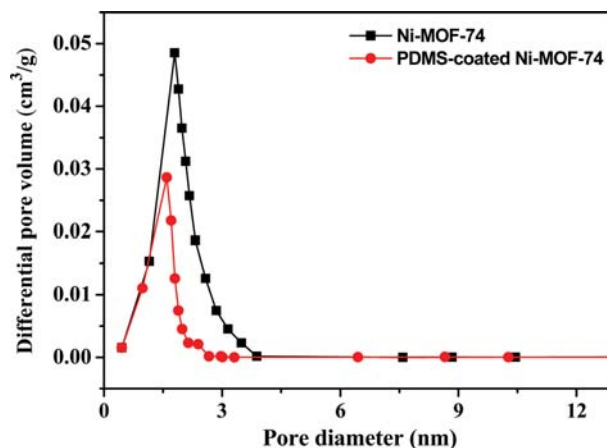


Fig. S1. Pore size distribution of pristine Ni-MOF-74 and PDMS-coated Ni-MOF-74 calculated by Horvath-Kawazoe (HK) method.

Table S1. Textural properties of Ni-MOF-74 and PDMS-coated Ni-MOF-74

	BET surface area (m^2/g)	Average pore diameter (nm)	Pore volume (cm^3/g)
Pristine Ni-MOF-74	1050	1.8	0.47
PDMS-coated Ni-MOF-74	1041	1.6	0.39

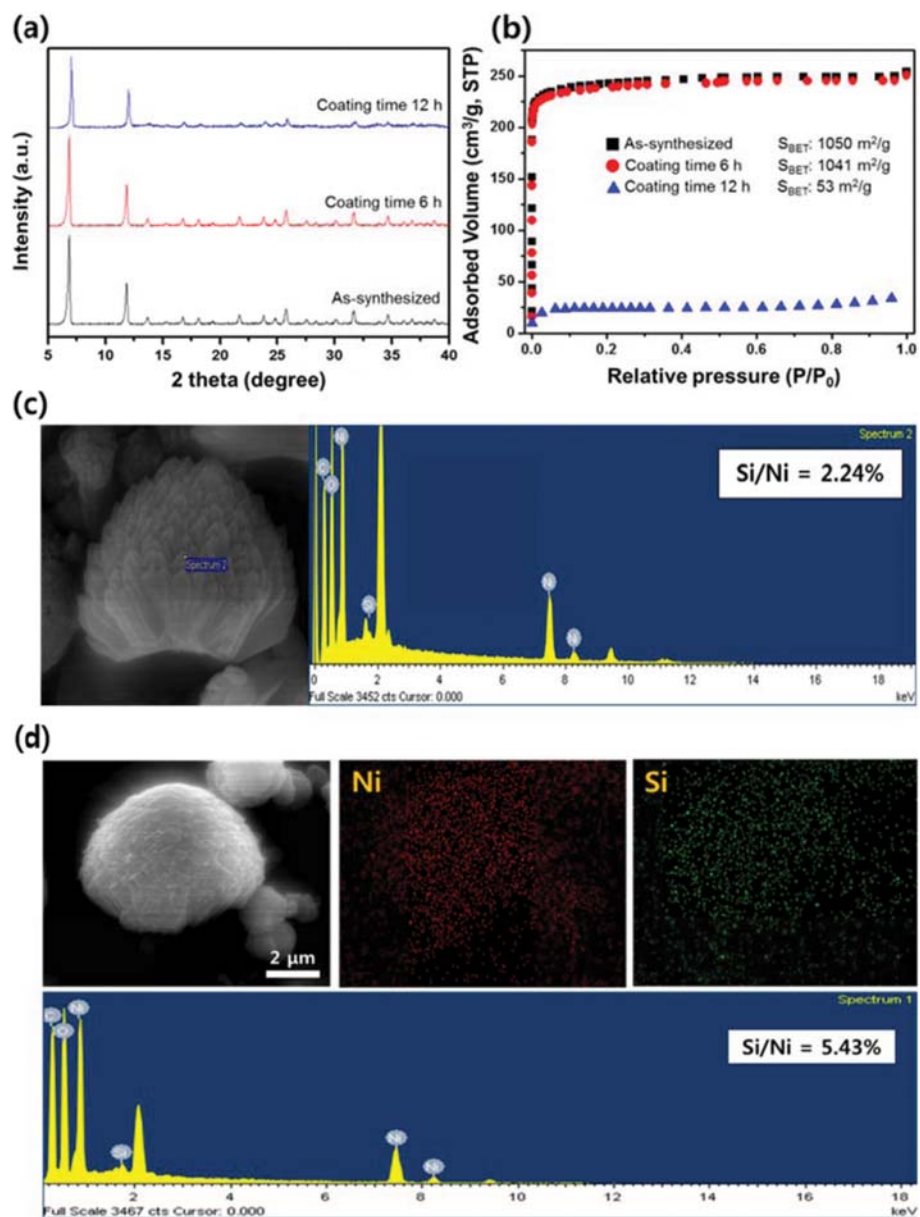


Fig. S2. XRD patterns (a), N_2 adsorption isotherms (b), SEM-EDS analysis of the PDMS-coated Ni-MOF-74 after 6 (c), and 12 h coating time (d).

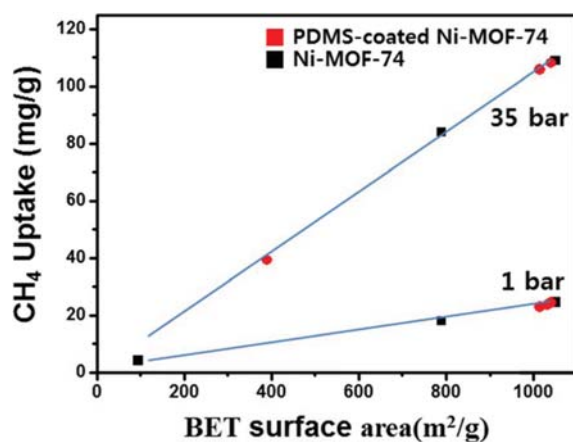


Fig. S3. Correlation between the BET surface area and CH_4 uptake of pristine Ni-MOF-74 and PDMS-coated Ni-MOF-74.