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Angewandte Chemie International Edition
2018 57 (34), pp. 10971-10975
which has been published in final form at
https://doi.org/10.1002/anie.201806732
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Accepted Article

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201806732
Angew. Chem. 10.1002/ange.201806732

Link to VoR: http://dx.doi.org/10.1002/anie.201806732
http://dx.doi.org/10.1002/ange.201806732
Robust Ultramicroporous Metal-Organic Frameworks with Benchmark Affinity for Acetylene


Abstract: Highly selective separation and/or purification of acetylene from various gas mixtures is a relevant and difficult challenge which currently requires costly and energy intensive chemisorption processes. Herein, we demonstrate that two ultramicroporous metal-organic framework physisorbents, NKMOF-1-M (M = Cu or Ni), offer high hydrolytic stability and benchmark selectivity towards acetylene vs. several gases at ambient temperature. We attribute the performance of NKMOF-1-M to their exceptional acetylene binding affinity as revealed by modeling and several experimental studies: in situ single crystal X-ray diffraction and FT-IR; gas mixture breakthrough tests. NKMOF-1-M exhibit better low pressure uptake than existing physisorbents and possesses the highest selectivities yet reported for C2H2/CO2 and C2H2/CH4. This study introduces a new strategy for the design of porous materials for acetylene separation since the performance of NKMOF-1-M is not driven by the same mechanism as current benchmark physisorbents that rely on pore walls lined by inorganic anions.

Acetylene (C2H2) is not only an important fuel gas, but also an industrial commodity that is widely used for production of plastics (e.g. PVC and PVDF), acrylic derivatives, vinyl compounds, and α-ethyl alcohol.[1] The production of C2H2 usually generates methane (CH4) and carbon dioxide (CO2) due to insufficient combustion of methane or the nature of the steam cracking process in petroleum refining.[5] Therefore, developing highly efficient and energy-efficient approaches to purify acetylene from C2H2/CH4 and C2H2/CO2 mixtures is of industrial relevance.[12,13] Besides the production of high purity C2H2, elimination of trace amounts of C2H2 is also of industrial importance. For instance, in polyethylene production acetylene is a trace contaminant that must be removed because it poisons the polymerisation catalyst by formation of solid metal acetyldes that can block the fluid stream and even lead to explosions.[14] Currently, there are two major technologies to remove trace C2H2: (i) solvent extraction using a large volume of solvent (e.g. DMF or acetonitrile); (ii) partial hydrogenation of C2H2 into ethylene using noble metal catalysts. These two approaches suffer from high cost and low efficiency,[15] so new strategies for separation/purification of C2H2 are needed.

Metals-organic frameworks (MOFs) can offer crystallinity, ultra-high surface area (>6000 m2/g) and tunable pore size because of their compositional diversity, control over pore chemistry.[16] In the past two decades, MOFs have been studied with respect to gas storage,[11-13] and/or separation,[14-22] catalysis,[23] drug delivery,[24] conductivity,[25,26] and magnetism.[27,28] In principle, MOFs have the potential to surpass many traditional porous materials such as zeolites, silica and activated carbon as they can be designed to offer features to enhance C2H2 capture: (i) open metal sites for strong interactions between C2H2 and pore walls, e.g. Long et al. reported that MOF-74 materials exhibit high uptake of C2H2 and strong C2H2 separation selectivity thanks to a high density of open metal sites and large specific surface areas.[19] (ii) Functional groups (e.g. NH2, SiF62−, TiF62− and NbOF5) on the pore walls of MOFs can afford strong sorbent-sorbate interactions.[20] For example, we recently reported that a member of the SIFSIX family of hybrid ultramicroporous materials, SIFSIX-2-Cu,[19,20] can exhibit benchmark C2H2/C2H4 and C2H2/CO2 separation performance. The key feature of the SIFSIX family is the MF62− (M = Si, Ti, etc) moiety which allows for strong sorbate-sorbent (F−−HC=CH−−F interactions) with C2H2,[21] (iii) Tailored pore sizes can endow MOFs with a sieving effect. For instance, although SIFSIX-14-Cu i (pore size: ~3.4 Å) exhibits high C2H2 uptake, it does not adsorb ethylene and it superceded SIFSIX-2-Cu-i with respect to C2H2/C2H4 selectivity.[22] Herein, we report two ultramicroporous MOFs (NKMOF-1-M, M = Cu, Ni) that offer a new type of binding site for C2H2 that results in the highest selectivities yet reported for C2H2/CO2 and C2H2/CH4.

Figure 1. (a) The [M(pdt)2]−, M = Cu, Ni, metaloligands in NKMOF-1-M. (b) the crystal structure of NKMOF-1-M viewed along the c axis.

NKMOF-1-M (Cu[M(pdt)2]), M = Cu, Ni) materials are based on pyrazine-2,3-dithiol (pdt) and were prepared via previously reported procedures with slight modification.[24,33,34] Figure 1 reveals that NKMOF-1-M possess a 3D framework with one-dimensional (1D) square channels along the c direction. Cu or Ni ions exhibit 4-coordinate square planar geometry with four sulfur atoms to form 4-connected [M(pdt)2] (M = Cu, Ni) building units (Figure 1a) linked by 4-connected square planar Cu centers, to generate isostructural 4,4-connected pts topology networks. Cu,
NKMOF-1-Cu or Ni, NKMOF-1-Ni, atoms from [M(pdth)]
building units line the walls of the 1D channels which possess
square pores of 5.75 Å (Cu···Cu distance after subtracting van
der Waals radius) (Figure 1b). The combination of
ultramicropores and open metal sites endow NKMOF-1-M with
the potential for high C2H2 binding affinity.

The ubiquity and small kinetic diameter of water vapour
means that sorbents must exhibit hydrolytic stability in order
to have utility. NKMOF-1-M are stable in water for at least six
months at room temperature or in pH = 1 or 12 water for one
week as verified by PXRD and surface area measurements
(Figure S1, S2 and S3). Variable temperature PXRD of
NKMOF-1-Ni (Figure S4) revealed that it exhibits thermal stability to 240
°C whereas NKMOF-1-Cu loses crystallinity above 60 °C. In order to
assess porosity of NKMOF-1-M, N2 sorption isotherms were collected at 77K. NKMOF-1-Ni showed a typical type I
isotherm and a BET surface area of 382 m2/g after activation
under vacuum at 90 °C without solvent exchange (Figure S5).
NKMOF-1-Cu was activated using CO2 supercritical drying and afforded a BET surface area of 280 m2/g. Considering the less
convenient activation conditions, lower thermal stability and
lower BET surface area of NKMOF-1-Cu, NKMOF-1-Ni became the primary focus of further study.

Single-component adsorption isotherms for C2H2, C2H4, C2H6,
CO2, CH4, and N2 were collected for NKMOF-1-Ni at 273 K, 288
K and 298 K (Figure S6). NKMOF-1-Ni was found to adsorb 61.0 cm3/g of C2H2, 47.3 cm3/g of C2H4, 51.1 cm3/g of CO2, 33.5
cm3/g of C2H6, 22.2 cm3/g of CH4 and 7.3 cm3/g of N2 at 1 bar
and 298 K (Figure 2a and S6). Gas mixture selectivity generally
correlates with the adsorption behavior of single-component
gases in the low-pressure region. In NKMOF-1-Ni, we compared the adsorption capacity of each single component (C2H2, C2H4,
C2H6, CO2 and CH4) gas at low-pressure and 298 K (Figure 2a and 2b).
NKMOF-1-Ni displayed strong uptake of C2H2 at low pressure.
Indeed, C2H2 uptake of NKMOF-1-Ni is the highest (33.7 cm3/g)
yet observed at 0.003 bar and 298 K and can be compared with the current benchmark material SIFSIX-14-Cu (25.4 cm3/g)
(Figure 2c and Table S1). Although the surface area of NKMOF-1-Cu is lower than that of NKMOF-1-Ni, it also displayed a high
takeup capacity of 25.8 cm3/g (Figure 2c and S7) at 0.003 bar
and 298 K. This exceptional C2H2 adsorption performance in the ultra-low-pressure region indicates strong C2H2-sorbent interactions in NKMOF-1-M. We focused further upon the following separations because of their practical relevance: C2H2/C2H4, C2H2/CO2 and C2H2/CH4.

To understand the excellent acetylene adsorption performance of NKMOF-1-M we conducted detailed theoretical
ingvestigations using GCMC (Grand Canonical Monte Carlo
methods and first-principles DFT-D (dispersion-corrected density
functional theory) calculations. NKMOF-1-M exhibit two binding sites (I and II) for acetylene (Figure 3). The stronger site
(Site I) combines hydrogen bonding (HC≡CH···S(MOF)) and π-
π interactions between C2H2 and the pyrazine units in NKMOF-
1-M (Figure 3a and 3b). The static adsorption energies were calculated to be 52.6 kJ/mol and 51.8 kJ/mol for NKMOF-1-Ni
and NKMOF-1-Cu, respectively. The other binding site (Site II) is
located in the middle of two open metal sites of adjacent MS₂
units (Figure 3a and 3b). Acetylene is usually weak alkaline, so it
can readily be bound by Lewis acidic open metal sites (Cu, Ni).
The static adsorption energies for these sites were calculated to be
25.2 kJ/mol and 30.3 kJ/mol for NKMOF-1-Ni and NKMOF-1-
Cu, respectively. GCMC simulations indicate that saturation of
C2H2 in NKMOF-1-M is achieved at 3.5 molecules per unit cell
with 2 molecules at binding site I and 1.5 molecules at binding
site II (Figure S9 and S10). The experimental data for C2H2
uptake capacity of 25.8 cm3/g (Figure 2c and S7) at 0.003 bar

The isosteric enthalpy of adsorption (Qst) is a quantitative
measure of the binding affinity of NKMOF-1-Ni towards C2H2,
C2H4, CO2, and CH4. Qst values for various gases were calculated based on the single-component gas adsorption
isotherms fitted with the dual-site-Langmuir-Freundlich isotherm
model (Table S2, S3, S4 and S5). Qst values were then
calculated using Clausius-Clapeyron equation. The zero-
coverage Qst values of NKMOF-1-Ni are 60.3 kJ/mol, 44.9
kJ/mol, 40.9 kJ/mol and 31.7 kJ/mol for C2H2, C2H4, CO2, and
CH4, respectively (Figure 2d). The dual-site-Langmuir-Freundlich
(DSLF) method (Figure S8, Table S6) afforded similar results
(C2H2: 53.9 kJ/mol for site I &19.0 kJ/mol for site II; C2H4: 40.9
kJ/mol; CO2: 36.2 kJ/mol; CH4: 28.5 kJ/mol). These Qst values indicate that NKMOF-1-Ni offers potential to capture trace levels
of C2H2 from various gas mixtures (e.g. C2H2/C2H4, C2H2/CO2
and C2H2/CH4).

Figure 2. (a, b) Single-component gas adsorption isotherms of NKMOF-1-M at
298K; (c) C2H2 adsorption isotherms of various MOFs at 298 K; (d) Qst of
various gases for NKMOF-1-M.

Figure 3. Two binding sites (I, II) of C2H2 determined via modeling studies
conducted upon NKMOF-1-Ni (a) and NKMOF-1-Cu (b); single crystal
structure of C2H2@NKMOF-1-Cu viewed along the a or c axis (c).
Angewandte Chemie International Edition

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Our study reveals new opportunities for the design of MOFs with improved C2H2 separation performance. We report the synthesis and characterization of a new MOF, NKMOF-1-Ni, which exhibits excellent C2H2 separation performance. The crystal structure of NKMOF-1-Cu under C2H2/NKMOF-1-Cu was studied to determine binding sites. Activated NKMOF-1-Cu crystals suitable for single-crystal X-ray diffraction (SCXRD) were filled with C2H2 via a C2H2 balloon at room temperature and SCXRD data was collected at 120 K. C2H2 molecules with full site occupancy were located between the four pyrazine rings (Figure 3c), consistent with the strong binding site, site I, determined by modelling. C2H2 molecules form hydrogen bonds (H···C≡CH·S) with the eight sulfur atoms and C···H···S distances range from 3.86 Å to 3.92 Å. No C2H2 molecules were found at the weaker binding site (II). This result indicates that C2H2 molecules preferentially bind to site I at lower pressures at room temperature (2 molecules per unit cell according to the modelling study). The experimental zero-coverage Qst should be therefore approximate the static adsorption energy of binding site (I). The experimental gas adsorption data for NKMOF-1-Ni revealed that NKMOF-1-Ni sorbed ~2 molecules of C2H2 per unit cell at 0.05 bar and 298 K, which we ascribed to adsorption at site I. The Qst of NKMOF-1-Ni at site I calculated from experimental data (53.9 kJ/mol) is close to that determined by modelling. These results indicate NKMOF-1-M exhibits excellent C2H2 separation performance.

Adsorption selectivity is a critical factor to assess the separation performance for an absorptive material. We calculated the gas mixture selectivity of NKMOF-1-M using ideal adsorbed solution theory (IAST). As displayed in Figure 4a, the adsorption selectivities at 298 K were determined to be 1272.6, 249.3, 272.5, 6409.1 and 4949.2 for C2H2/C2H4 (1/99, v/v), C2H2/C2H4 (1/9, v/v), C2H2/CO2 (1/1, v/v), C2H2/CO2 (2/1, v/v), C2H2/CH4 (1/1, v/v) and C2H2/CH4 (2/1, v/v) at 298 K were conducted (Figure 4). For C2H2/C2H4 (1/99, v/v) and C2H2/C2H4 (1/9, v/v), C2H2 breakthrough occurred at 243.0 min and 48.0 min, respectively, and the concentration of C2H2 is <1 ppm before breakthrough (Figure S18). The purity of C2H4 (99.9999%) exceeds the specification for industrial polymerization of ethylene. For C2H2/CO2 (2/1, v/v) and C2H2/CO2 (1/1, v/v), breakthrough of C2H2 occurred after 10.5 min and 35.1 min, respectively. For C2H2/CH4 (2/1, v/v) and C2H2/CH4 (1/1, v/v) mixtures, breakthrough of C2H2 occurred at 17.6 min and 38.3 min, respectively. It is remarkable that the concentration of C2H2 is <1 ppm before C2H2 breakthrough (Figure S18). These results reveal that NKMOF-1-Ni selectively sorbs C2H2 in all tested conditions. In addition, we found that the breakthrough time correlates with the C2H2 concentration of each gas mixture; higher concentration of C2H2 leads to earlier C2H2 breakthrough. According to the breakthrough results, the selectivities of NKMOF-1-Ni for C2H2/C2H4 (1/99, v/v), C2H2/C2H4 (1/9, v/v), C2H2/CO2 (2/1, v/v), C2H2/CO2 (1/1, v/v), C2H2/CH4 (2/1, v/v) and C2H2/CH4 (1/1, v/v) are 43.6, 7.2, 1.8, 2.6, 8.8 and 6.6, respectively. Activated NKMOF-1-Ni powders were exposed to C2H2 gas mixtures at room temperature. Fourier Transform Infrared Spectroscopy (FT-IR) of NKMOF-1-Ni (Figure S19) demonstrated the characteristic stretching vibration of C2H2 at 3236.8 cm⁻¹ and 734.8 cm⁻¹. No signals for C2H4, CH4 and CO2 were detected, further validating high binding affinity towards C2H2 by NKMOF-1-Ni. Finally, NKMOF-1-Ni can be recycled at least five times (Figure S20 and S21).

![Figure 4: IAST adsorption selectivities (a) and breakthrough curves (b, c, d) of various C2H2 gas mixtures at 298K for NKMOF-1-Ni.](image)

In conclusion, we report that an ultramicroporous MOF, NKMOF-1-Ni, exhibits excellent water stability over a broad pH range and new benchmarks for C2H2/CO2 and C2H2/CH4 selectivity by more than an order of magnitude vs. current benchmark materials. Overall, NKMOF-1-Ni exhibits four new benchmark selectivity values: C2H2/CO2 (1/1), C2H2/CO2 (2/1), C2H2/CH4 (1/1) and C2H2/CH4 (2/1). We attribute the superior performance of NKMOF-1-Ni to a new type of specific binding site for C2H2 as verified by modelling and in situ SCXRD. This approach holds promise for the development of novel MOFs with improved C2H2 separation performance.
work not only provides a new approach to the design of porous materials with strong binding affinity for C2H2, but also promotes MOF physisorbent materials with potential to resolve industrial challenges related to C2H2 separation.

Acknowledgements

The authors acknowledge the support of National Natural Science Foundation of China (21601093, Science Foundation Ireland (13/RP/B2549 and 16/IA/4624), National Science Foundation of US (Awards 1607989, CHE-1531590), XSEDE Grant of US (No.TG-DMR090028) and American Chemical Society Petroleum Research Fund grant (ACS PRF 56673-ND6).

Keywords: Metal-organic frameworks, ultramicroporous materials, acetylene separation, gas breakthrough, acetylene binding site, hydrolytic stability

COMMUNICATION

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