Hiden Analytical Ltd.
420 Europa Boulevard
Warrington WA5 7UN
England

T +44 [0] 1925 445 225
F +44 [0] 1925 416 518
E info@hiden.co.uk
W www.HidenAnalytical.com

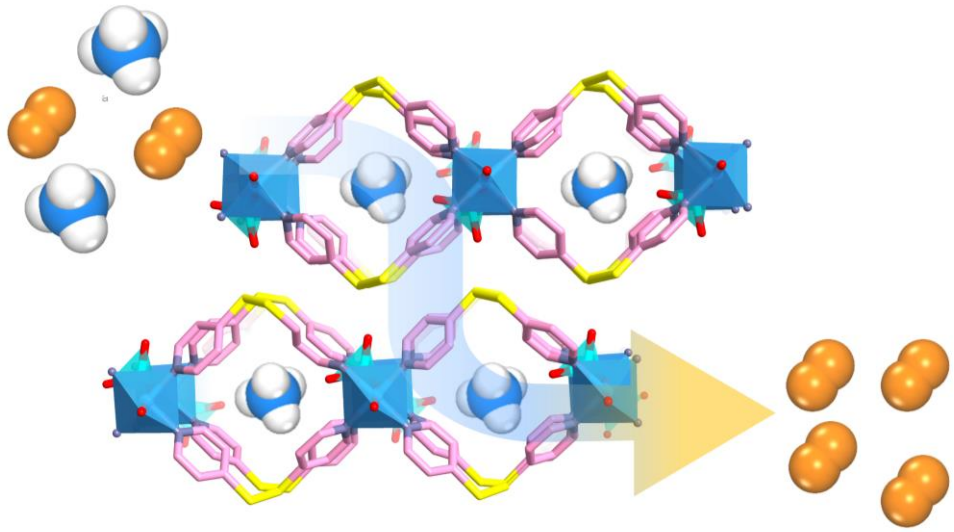
A Robust Two-dimensional Layered Metal-Organic Framework for Efficient Separation of Methane from Nitrogen

Fang Zheng[a], Lihang Chen[a, *], Rundao Chen[a], Zhiguo Zhang[a, b], Qiwei Yang[a, b], Yiwen Yang[a, b], Baogen Su[a, b], Qilong Ren[a, b], Zongbi Bao[a, b, *]

[a]*Key Laboratory of Biomass Chemical Engineering of the Ministry of Education, College of Chemical and Biological Engineering, Zhejiang University, 38 Zheda Road, Hangzhou 310027, P. R. China.*

[b]*Institute of Zhejiang University-Quzhou, Quzhou, 78 Jiuhua Boulevad North, Quzhou 32400, P. R. China.*

Selective capture and separation of methane (CH_4) from nitrogen (N_2) is a feasible approach to mitigate the effects of global warming and to improve the heating value of low-quality natural gas. However, the efficient separation of CH_4/N_2 is a challenge issue since their very close kinetic diameters and thermodynamic properties. In this work, we successfully combine twisted organic ligand (4-DPDS = 4,4'-dipyridyldisulfide) and angular inorganic anion (CrO_4^{2-}) forming a new class of robust two-dimensional (2D) layered rhomboid grids with ionic polar environment. This a new type of 2D layered metal-organic framework (MOF) with permanent rhomboid pore channels, denoted as $Ni(4\text{-}DPDS)_2CrO_4$, was synthesized for the first time and used for CH_4/N_2 separation. Such a 2D layered material is rarely used for methane and nitrogen separation and shows high affinity towards CH_4 thereby affording admirable methane adsorption and separation performance. Specifically, it not only performs high stability as outstanding as or even better than previously reported 3D MOFs but also exhibits a relatively high CH_4 adsorption capacity of 0.95 mmol/g. $Ni(4\text{-}DPDS)_2CrO_4$ has a high affinity towards CH_4 with the highest reported Q_{st} value of 28.4 kJ/mol as well as a high CH_4/N_2 selectivity of 7.3, which is comparable to the state-of-the-art MOF materials reported so far.



By DFT-D calculations, it was found that twisted organic ligand plays a vital role in delivering a relatively rigid structure and the angular inorganic anions provides polar sites for strong guest-host interactions in close proximity. It revealed the energy favorable binding sites for methane molecules are located in the middle of the cavity decorated with CrO_4^{2-} anion, where inducing C-H···O hydrogen bond with the distance of 2.52 Å. Simultaneously, each adsorbed CH_4 molecule is surrounded by eight pyridyl rings, among which one forms dominant cooperative supramolecular interactions

between C(δ^-) of CH_4 and H(δ^+) from the pyridyl ring (C···H = 3.43 Å) and moderate-to-weak σ···π stacking interactions between the electrons in the π orbitals of the pyridyl ring and the electrons in H of CH_4 (H···pyridyl ring = 3.47 Å). Furthermore, the weak intermolecular electrostatic dipole interactions between the H(δ^+) of CH_4 and S (δ^-) (H···S = 3.82 Å) are also observed. Such an angular inorganic anion provides a cooperative effect conferred by polar sites and multiple guest-host interactions in close proximity, affording tight binding affinity.

Dynamic breakthrough experiments were carried in a stainless-steel column manually packed with $Ni(4\text{-}DPDS)_2CrO_4$. The outlet gas passing through the column was analyzed using a **Hiden HPR-20 EGA mass spectrometer** for continuous sampling gas analysis. It certified N_2 was eluted almost immediately and then quickly approached a pure grade while no detectable CH_4, whereas CH_4 was retained in the packed column for a remarkable time (~15 min) until reaching the saturated uptake and breakthrough. After the concentration of eluting gas remained unchanged, the amount of CH_4 adsorbed into the column reached 0.94 mmol/g, with a selectivity of 4.7 to N_2 (0.2 mmo/g), which suggest it is a promising material in natural gas purification by further regenerability tests. It is a thriving exploration in two-dimensional MOFs that will emerge the development of various materials for CH_4 trap in the future.

Project summary by:

Zongbi Bao
Key Laboratory of Biomass Chemical Engineering of the Ministry of Education,
College of Chemical and Biological Engineering,
Zhejiang University,
38 Zheda Road,
Hangzhou 310027
P. R. China.

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