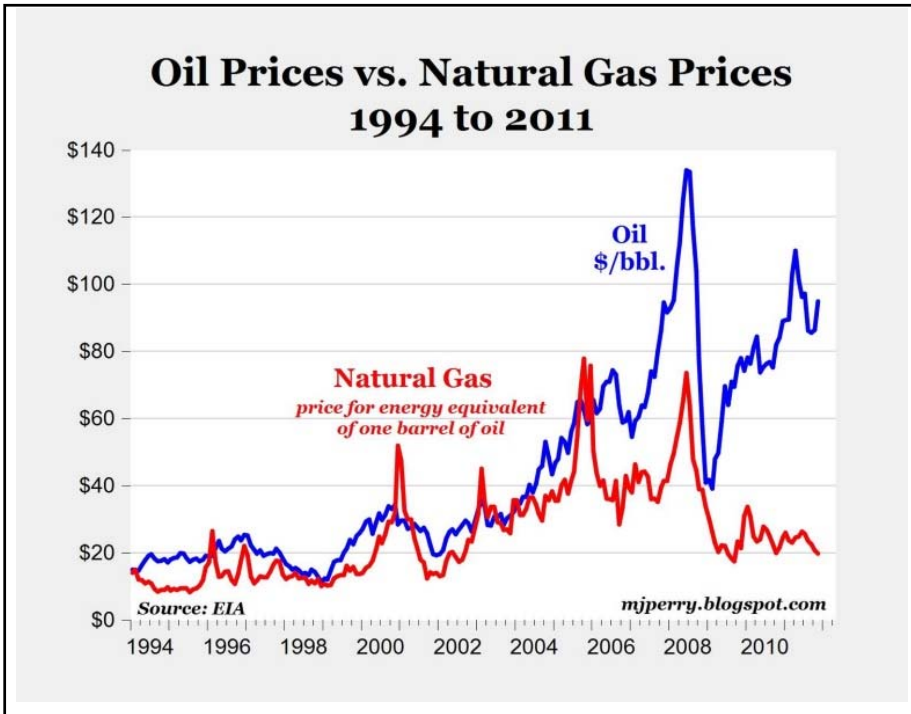
ADSZORPCIÓS GÁZTÁROLÁS

CONCEPT:
https://www.youtube.com/watch?v=qhlJgOFnvY0

Irodalom:
https://link.springer.com/content/pdf/10.1007%2F978-981-13-3504-4.pdf

2

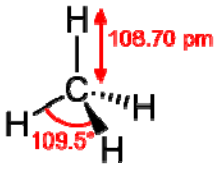


„Much Ado About Nothing”?

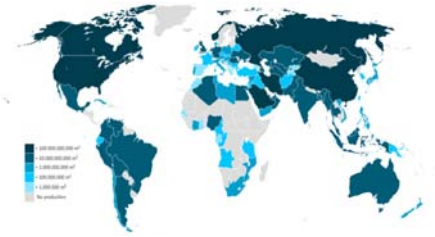
Natural gas (NG)

Composition

- **95% CH_4**
- 2,5% C_2H_6
- 0,3% C_3-C_{10}
- 1,6% N_2
- 0,7% CO_2
- ~ppm H_2S, H_2O



Exploitation in the world



1 800 000 000 m³/day (2013)

Properties

- $\rho_{NG} < \rho_{air}$
- Highly flammable
- Clean combustion
- Colourless, odourless
- Non-corrosive
- Explosive under pressure

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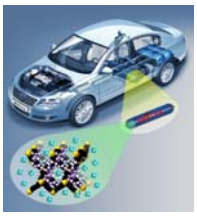
Gas storage technologies

Liquefying (LNG)	Compression (CNG)	Adsorption (ANG)
• Volumetric energy density: ~72% (gasoline) • -160- (-196) °C K, 1 bar • Requires special handling	• Volumetric energy density: ~26% (gasoline) 8.8 MJ/L • High pressure: 20 MPa (tank!!!) • Special compressors	• Volumetric energy density: ~19% • High surface area, microporous adsorbents • ‚Low’ pressure, ambient temperature



5

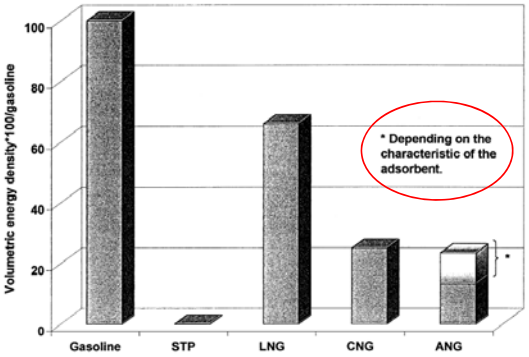
Natural gas as energy source

Advantages

- PRICE!
- High octane number (RON ~130)
- Low pollutant emission
- **Gravimetric energy density** compared to gasoline:
  NG: 50,0 MJ/kg
  vs.
  Gasoline: 44,5 MJ/kg

Challenges

- CO_2 emission
- Low **volumetric energy density**



Cél: a CNG 70-80 %-ának elérése

6

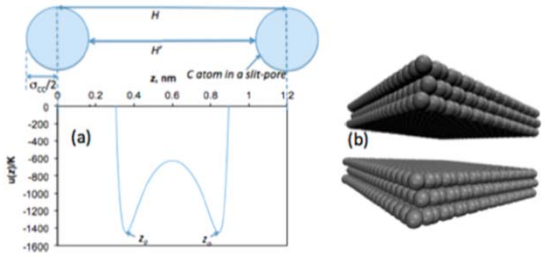


Figure 1. (a) Potential energy, $u(z)$, for a spherical methane Lennard-Jones (LJ) site interacting with the walls of a slit pore of width H = 1.2 nm. The LJ parameters for C and CH_4 were taken directly from the literature,[49] and z is a measure of the distance between the center of a carbon atom on the pore walls and the center of a methane molecule. (b) Carbon prototype of a slit-shaped pore that can be taken as a reasonable model representing the porosity of activated carbon.[29]

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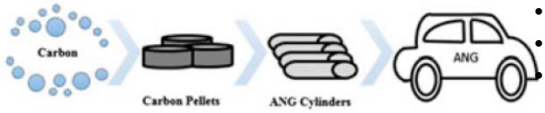
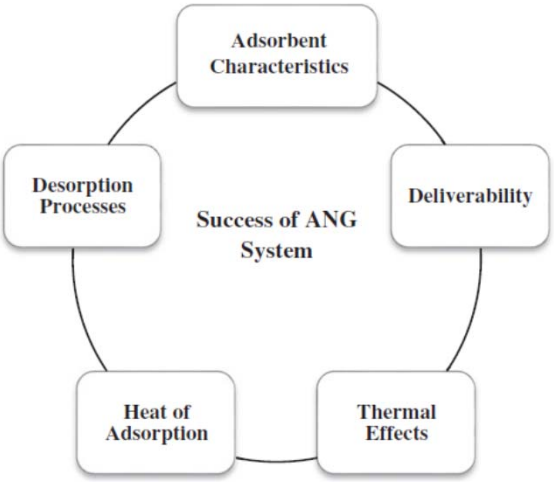
US Department of Energy (DOE):
500 mg/g MOF methane@35 bar
(2013)

Hogyan számolnánk ki?
Adszorbeált mennyiség/adszorbeált többlet



- CO2: 99 %
- Nox 30 %
- szénhidrogén 96 %
  -kal kevesebb, mint a benzin

ANG: legfontosabb tényezők



Key factors affecting success of an ANG storage system.

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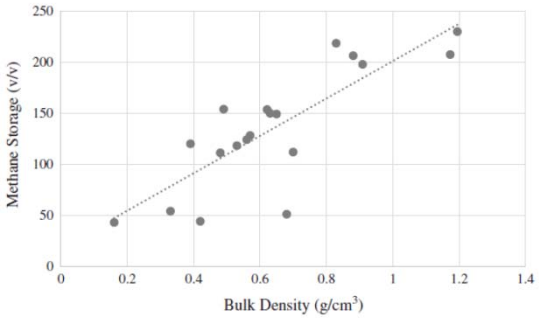
ADSZORBENS

Sample	Bulk Density (g/cm^3)	Micropore Volume (cm^3/g)	Methane Storage v/v (cm^3/cm^3)	Area BET (m^2/g)	Type
SMS-30	0.39	0.98	120	2860	Adsorbent Carbon Monolith
HSAC Sample 19	–	0.62	145.5	1619.29	HSAC
HSAC Sample 23	–	0.58	146.4	1784.36	HSAC
HSAC Sample 23B	–	0.37	108	841.14	HSAC
HSAC Sample 29	–	0.45	120.3	1087.46	HSAC
HSAC Sample 30	–	0.15	77.1	346.86	HSAC
HSAC Sample 21	–	0.83	147.2	1465.67	HSAC
Ni_2 (dobdc)	1.195	0.56	230	1218	MOF
$Cu3(btc)_2$	0.881	0.73	206.3	1642.5	MOF
Co_2(dobdc)	1.173	0.495	207.5	1056	MOF
Cu_2(adip)	0.829	0.85	218.5	1868.5	MOF
Mg_2(dobde)	0.909	0.643	197.75	1542.3	MOF
Zn_{4O}(bdc)	0.621	1.3875	153.67	3800	MOF
AX-21 activated carbon	0.49	1.64	154	–	AC
Maxsorb	–	1.088	174.4	–	AC
KF-1500	–	0.601	149.4	–	AC
CMS	–	0.303	103	–	AC

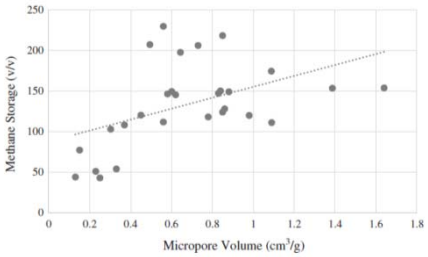
Alhasan 2016

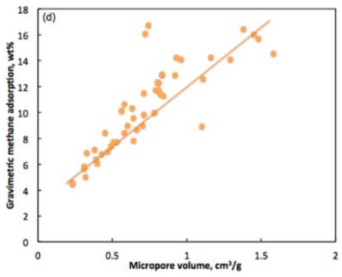
35 bar, RT

Látszólagos sűrűség



Mikropórustérfogat





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Kumar 2017

Fajlagos felület

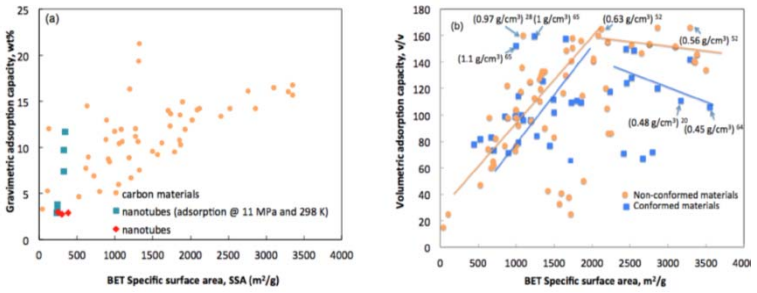
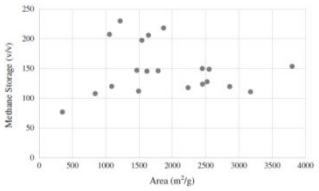
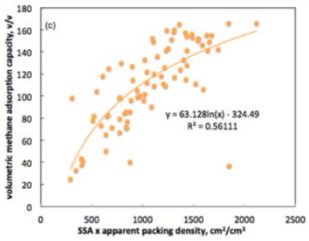


Figure 2. (a) Gravimetric adsorption capacity of methane (in weight percentage) versus the BET specific surface area of carbon structures. (Orange circles represent carbon materials corresponding to materials with slit-shaped pores, including activated carbons and carbon fibers.) (b) Volumetric adsorption capacity (v/v) versus the product of the BET specific surface area (SSA) and packing density. (For the case of conformed materials such





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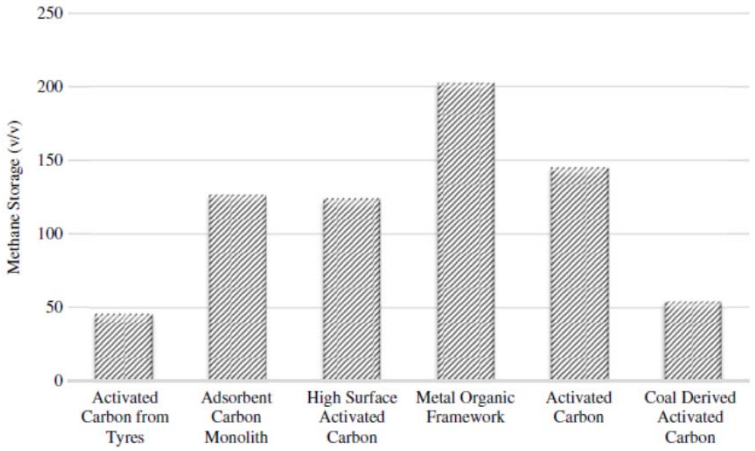
Kumar 2017

Nagy térfogatra fajlagosított felület a cél

12



3. Methane storage performance of various materials tested in the literature.

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TERMIKUS VISELKEDÉS

Kinetika (adsz gyors/desz lassú)

Adsz/desz hő!!!!

KINYERHETŐ GÁZ MENNYISÉGE

Adszorbeált mennyiség/adszorbeált többlet

TOVÁBBI SZEMPONTOK

Stabilitás (szerkezeti, kémiai,…)
Irreverzibilitás (kontamináció, ciklikus használat)
Költségek

14

Ideal adsorption storage system

- High adsorption capacity
- Reversible ad/desorption
- Narrow pore size distribution
- Optimal pore size:
  - For maximum capacity: 7.6 Å
  - For maximum delivery: 11.4 Å
- **Low heat of adsorption!!!**
- Hydrophobic pore
- „Cheap”

Commercial adsorbents

I. Carbonaceous

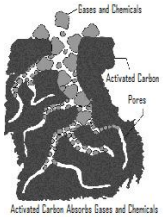
ADVANTAGE:
Cheap
Fundamental capacity: 220 V(STP)/V

DRAWBACK:
Broad pore size distribution
Difficult to control

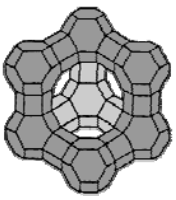
II. Zeolites

ADVANTAGE:
Easy to control the structure

DRAWBACK:
Low microporosity
Hydrophilic pores



Activated carbon



Faujasite

15

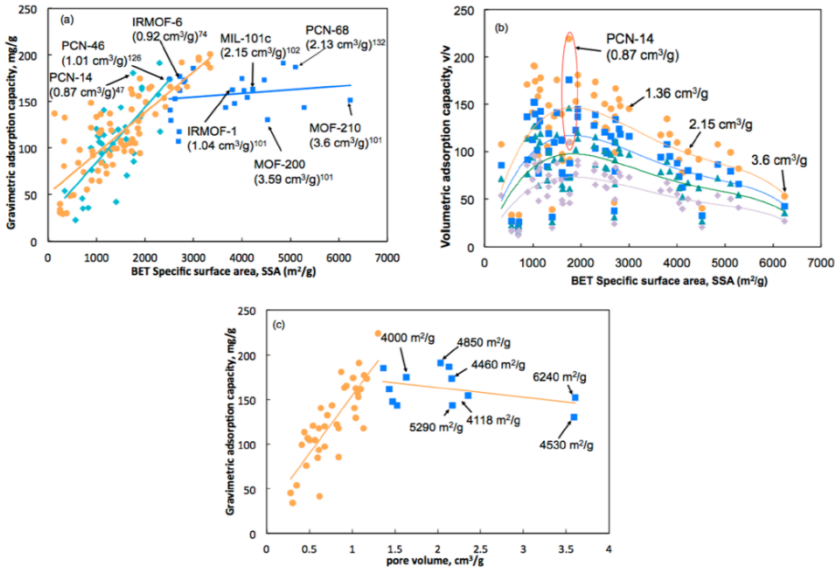


Figure 3. (a) Gravimetric methane adsorption capacity at 3.5 MPa and 298 K versus BET surface area (teal diamonds, MOF structures with specific surface areas of ≤2500 m^2/g; blue squares, MOF structures with specific surface areas of ≥2500 m^2/g; orange circles, carbon-based materials). (b) Volumetric methane adsorption capacity at 3.5 MPa and 298 K versus BET surface area for different assumed values of packing efficiency, where X_d represents the packing density/crystal density (orange circles, X_d = 1; blue squares, X_d = 1.25; teal triangles, X_d = 1.5; lilac diamonds, X_d = 2). (c) Volumetric methane storage capacity at 3.5 MPa and 298 K versus pore volume (orange circles, MOFs with pore volumes of ≤0.92 cm^3/g; blue squares, MOFs with pore volumes of ≥0.92 cm^3/g).[47,48,84,87,90,95,97−137] All of the adsorption values correspond to adsorption excess. All of the adsorption values correspond to adsorption excess (except PCN-14, all the adsorption values correspond to the experiments performed at 298 K; adsorption value in PCN-14 was performed at 290 K).

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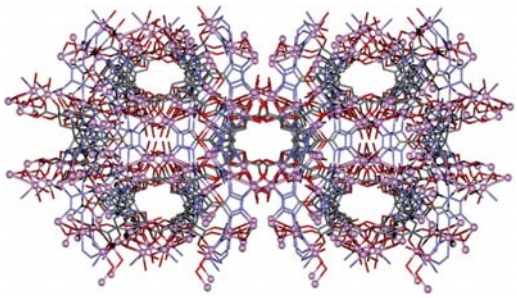
Metal-Organic Frameworks

A new class of highly porous materials



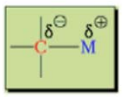
YAGHI:
https://www.youtube.com/watch?v=wPXfWLOj_ZU

17

Bevezetés

Metal-Organic ≠ **Organo-Metallic**

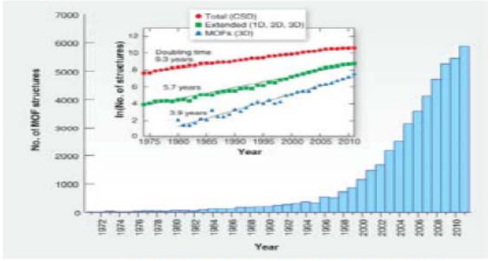
Magyarul mindkettő FÉMORGANIKUS!



Másodlagos kölcsönhatások!!!

~ 68.000 találat
[ScienceDirect]

625.000 különféle szerkezet (2012)
[Cambridge Structural Database]



[H. Furukawa et al. Science 2013;341:1230444]

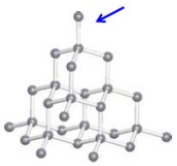
Történelem

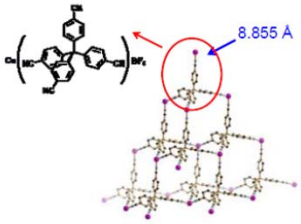
1897 Hofmann: Cianid zárványvegyület $Ni(CN)_2 \cdot NH_3 \cdot C_6H_6$ [1]

1966 Walker és Hawthrone: *n*-alkilamin Hofmann-komplex [2]

1989 Robert: Első szerves koordinációs háló (OCN) [3]

Gyémánt 1,545 Å

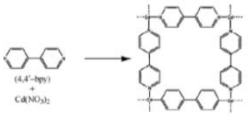




Cu
C
N

[1] Anorg. Chem. 1897.15.204.
[2] Trans. Faraday Soc. 1967.63.166.
[3] J.Am.Chem.Soc. 1989.111.5962

1990 Robert: Makrociklusos polimer komplexek [4]

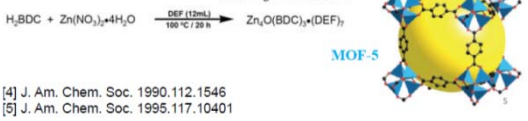


1,4-benzodicarboxylate és Zn

1995 Yaghi: „MOF" [5]

Hydrothermal Synthesis of a Metal–Organic Framework Containing Large Rectangular Channels

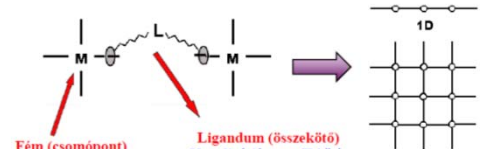
O. M. Yaghi* and Hailian Li



[4] J. Am. Chem. Soc. 1990.112.1546
[5] J. Am. Chem. Soc. 1995.117.10401

BDC: 1,4-benzodikarboxilát

Szerkezet, topológia



Fém (csomópont)
Különböző koordinációjú és tulajdonságú fémionok

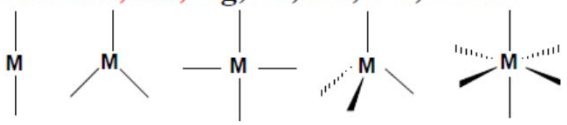
Ligandum (összekötő)
Koordinációs vagy H-kötés vagy gyengébb kölcsönhatások

Különböző szerkezetű hálózatok hozhatóak létre a csomópont (fém) koordinációjától függően és a ligandum szerkezetétől függően!

Szabályozható szerkezet és pórusméret!

A szerkezet típusa elsődlegesen a fém koordinációs geometriájától és a fém-ligandum kötés orientációjától függ!

Fém ionok: Cu, Zn, Ag, Ni, Co, Cd, Mo…



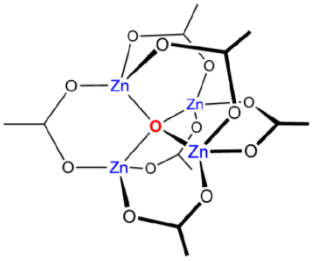
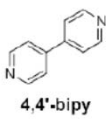
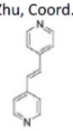


Fig. 2. Examples of organic linkers.

S. Qiu, G. Zhu, Coord. Chem. Rev. (2009), doi:10.1016/j.ccr.2009.07.020



4,4'-bipy
4,4'-bipyridine



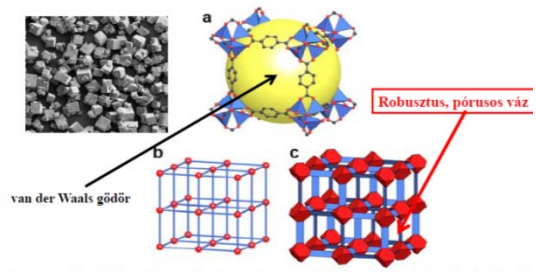
4,4'-bpe
4,4'-trans-bis(4-pyridyl)-ethylene

dabco
1,4-diazabicyclo[2.2.2]octane

pyz
pyrazine

8

Az elsők: izoretikuláris szerkezetű MOFok (IRMOF)



A vázat alkotó elemek meghatározott, egyenlő távolságra helyezkednek el egymástól, közöttük úgynevezett van der Waals gödör helyezkedik el.

Állandó porozitás, szabályos pórusméreteloszlás,
nagy látszólagos fajlagos felület

11

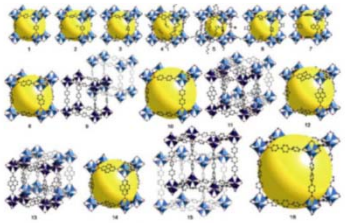
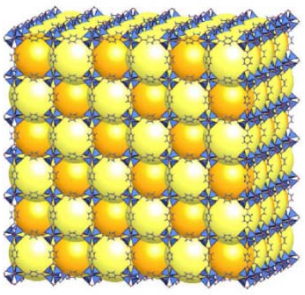
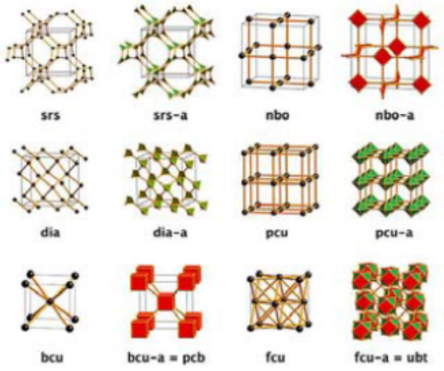


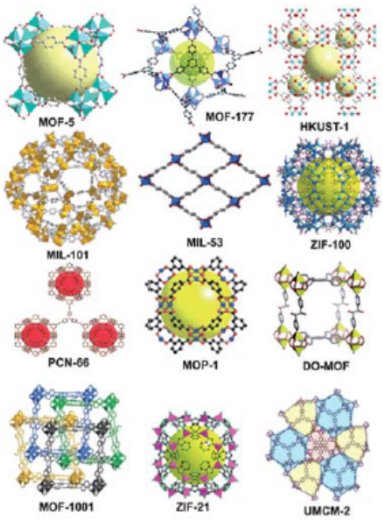
Fig. 2. A large series of isoreticular metal–organic frameworks (IRMOFs) has been produced in which each member shares the same cubic topology. Each compound is synthesized by employing the corresponding organic link in the solvothermal conditions established for formation of the octahedral secondary building unit (SBU). The links differ both in functionality of the pendant groups (IRMOF-1 to -7) and in length (IRMOF-8 to -16). While expansion of the links increases the internal void space (represented by yellow spheres), it also allows the formation of catenated phases (IRMOF-9, -11, -13 and -15) [83].



Szerkezetek…



Elnevezések…



Default 3D szerkezetek

srs: $SrSi_2$ net-like
dia: diamond like
bcu: body-centred
nbo: NbO like
pcu: primitive cubic
fcu: face-centred

példák

S. Qiu, G. Zhu, Coord. Chem. Rev. (2009), doi:10.1016/j.ccr.2009.07.020

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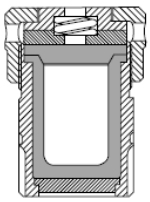
Synthesis methods

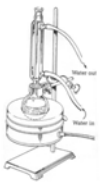
1. **Thermal methods (high temperature, autoclaves)**
   a) **Solvothermal:** dilute precursor sol of ligand+metal (DEF, DMF, alcohol)
   b) **Ionothermal:** ionic liquids as solvent and template
   c) **Urothermal:** carbamide derivative as solvent
   → **IN SITU ligand**



2. **Electrochemical methods:** the desired metal (eg. Cu) used as anode and catode, the ligand is dissolved in electrolyte, constant voltage (12 – 19 V)

3. **Diffusion techniques:** the most simple way, but not suitable for single crystal growing

4. **Reflux:** high temperature (~100 °C) continuous stirring, reflux of the solvent



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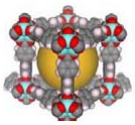
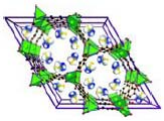
Characterization

What do we want to characterize?

- Morphology ('texture')
- Structure
- Functionality (e.g. adsorption sites)
- Adsorption properties





How do we want to characterize?

- Microscopy (optical, SEM, TEM)
- Diffraction (X-ray, neutron)
- Thermal analysis (DTA, DSC)
- Spectroscopy (Raman, FTIR)
- Adsorption techniques
  - N_2, H_2O (characterization)
  - CH_4, H_2 (application)

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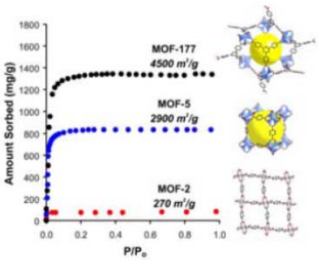
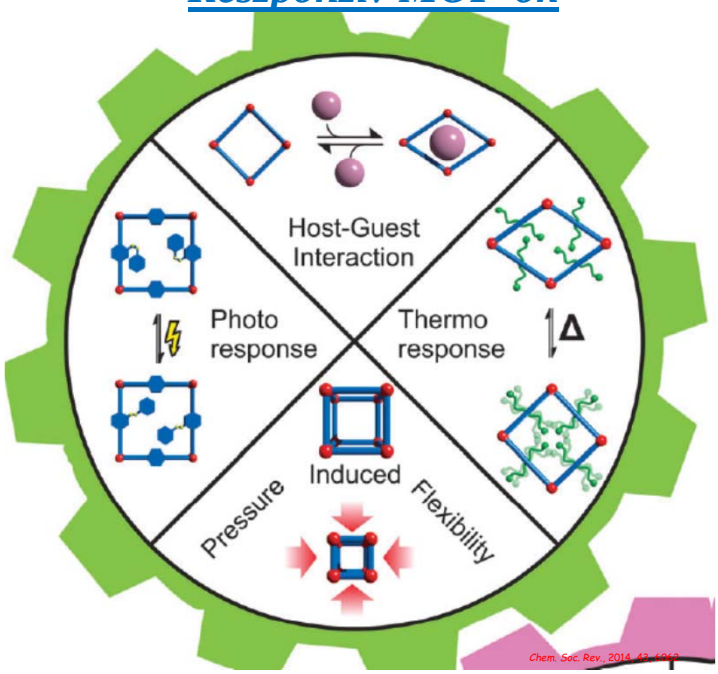
Adszorpciós tulajdonságok:

gyors kinetika
fiziszorpció (gyenge kölcsönhatás)
exoterm
méretkizárás



Reszponzív MOF-ok



Megoldandó…

The available adsorbent materials present different limitations especially for on-board storage applications: slow desorption/absorption rates, unstable structures, heavy weight, irreversibility on cycling and expensive production costs. MOFs have the highest performance and have a great potential to lead in the vehicular application of ANG systems compared to other types of adsorbents. A roughly linear relationship is found between methane adsorption capacity, and the surface area, bulk density, and micropore size.

The central region of the adsorbent bed suffers from the greatest thermal fluctuations because of poor thermal conductivity. The thermal profiles during discharge are highly dependent on several parameters including adsorbent characteristics, properties and composition, flow rate, vessel design and geometry, material of construction, and room temperature.

The heat of adsorption has a great effect on the overall performance of an ANG storage system. There is a major temperature drop during discharge. The temperature change can

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