Metal Organic Frameworks and Methane Storage for Greener Vehicles

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Abstract

Methane (CH_4), a component of natural gas, could be used as a replacement for gasoline and a transition to zero emission vehicles. It is both readily accessible and produces far less carbon monoxide and carbon dioxide.

While it emits less greenhouse gases than gasoline, it is a much smaller molecule, and being a gas, it has low energy density. More methane is needed for a vehicle to go the same distance than it does on gasoline. This translates to larger vehicle fuel tanks, limited trunk space and increased manufacturing cost.

Metal Organic Frameworks(MOFs) are a way to minimize both tank size and cost by maximizing the amount of methane that can be held in a tank. MOFs are nano-porous materials that allow gas to be adsorbed, increasing the volume of methane a tank can hold.

MOFs are predominantly rigid structures but a new study on flexible MOFs with intrinsic thermal management is showing potential. Following is a review of MOFs and their viability for methane fuel storage.

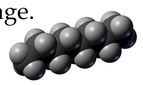

Figure 1[9]: Octane molecule

Figure 2[11]: Methane

Figure 3[10]

The Story of Metal Organic Frameworks

Metal Organic Frameworks are made of transition metal ions and organic ligands (benzene derivatives). Together they form porous 3D nano-structures. The number and size (3.8 to 28.8Å) of the pores, where methane is absorbed, can be changed allowing for various modifications.

Normally in order to increase the amount of gas contained in a tank, it has to be compressed under high pressure. This is not only costly, but also not safe for the everyday user. MOFs adsorb gases at a much lower pressure, mitigating the cost for high pressure equipment, decreasing the space needed for such a system and making it overall safer to keep a natural gas tank in a vehicle.

MOFs are a nascent field and as such data is not reported across labs in a uniform manner, making direct comparisons difficult. Most experiments are done using pure methane, rather than natural gas. While methane is the largest component of natural gas, how the other molecules interact with MOFs is unknown. It is possible that heavier impurities would corrode bonding sites, decreasing the amount of methane that can held.

Methane

- Non-polar molecule
- Smallest hydrocarbons
- Highest hydrogen to carbon ratio among fossil fuels
- Possible transition fuel
- Tetrahedral structure
- Diameter of 3.988 Å

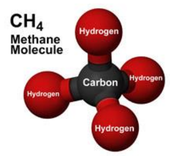

Figure 4: Methane[8]

Rigid MOFs

HKUST-1[5] and IRMOF-6[1] are examples of the first generation of MOFs. They have shown potential in meeting the US Department of Energy (DOE) target for Absorbed Natural Gas (ANG) of $263\,{}^{cm^3_{STP}}/_{cm^3}$ assuming a 25% loss of volume capacity because of packing.

HKUST-1

It is the most well know of the MOFs and deemed a benchmark for other MOFs. The Structure of HKUST-1 is characterized by 3D copper paddlewheels. The copper cations (Cu^{2+}) act as strong binding sites for methane and combined with weaker secondary sites, they lead to its high gravimetric uptake. HKUST-1 has several pore sizes because it is made up of several different cage sizes ranging from 5-13.5 Å.

66% of the adsorbed methane on HKUST-1 can use for combustion, as not all the methane desorbs when the pressure drops from 35bar to 5 bar. Uptake volume can be increased by lowering the temperature at which methane is adsorbed.

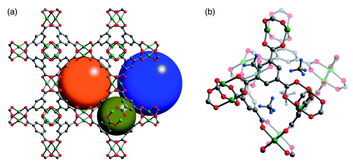

Figure 5[5]: HKUST-1 model: Green pore 5 Å, Orange pore 11 Å, Blue pore 13.5 Å

IRMOFs consist of Zn-O-C clusters with benzene linkers and various functional groups. These functional groups create cage structures that vary in size. Some of these structures have interpenetrating linkers with functional groups that stick into the pore. Methane fills the structure but incomplete desorption results in a lower useable methane compared to actual volume.

IRMOF-6

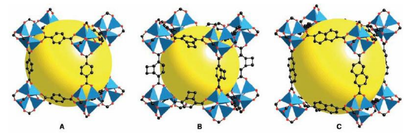

Figure 6[1]: From left to right Rigid IRMOF-5, -6, -8

IRMOF-6 is one of the Isoreticular Metal Organic Frameworks, that is suitable for methane storage. It has a cage size of 5.9 Å.

It can hold $155\,{}^{cm^3}/_{cm^3}$ methane at 36 bar and 25°C.

Of the total volume of a condensed methane tank, IRMOF-6 can hold 70% of the total volume at 35bar, a much safer pressure compared to 208 bar.

Flexible Metal Organic Frameworks

Co(bdp) (bdp^{2-} = 1, 4- benezenedipyrazolate) (and Fe(bdp)) forms flexible framework that features 1D chains of tetrahedral Co^{2+} cations bridged by μ^2 - pyazolate to form a structure with square channels with edge length of 13 Å. The pores open and close based on pressurized gas bonding to the cobalt cation (Co^{2+}) active sites.[4] Above 15 bar the previously collapsed non-porous Co(bdp) transitions to an expanded, porous framework, allowing additional methane to be adsorbed. Conversely, when the pressure drops between 10 bar and 5 bar, the pore collapses pushing out methane. This CH_4 pressure responsive gate opening and closing gives Co(bdp) the highest usable CH_4 capacity reported to date for any adsorbent under similar conditions.

The exothermic nature of methane adsorption and endothermic nature of methane desorption cause temperature changes of as much as 80°C resulting in reductions in usable CH_4 capacity. The expansion-collapse structural phase transition of Fe(bdp) and Co(bdp) provide intrinsic heat management by reducing the amount of heat released during adsorption and the impact of cooling during desorption.

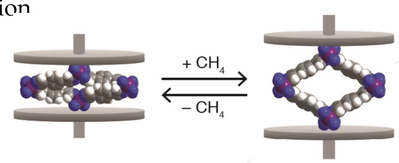

Figure 7[4]: Phase transition of Co(bdp). Purple, grey, blue, and white represent Co, C, N, and H atoms respectively.

Fe(bdp) which is similar in structure to Co(bdp) afforded greater intrinsic thermal management making it more effective for methane storage and desorption at temperature as low as -25°C. This would find application in methane-powered vehicles in cold weather climates. Heat dissipation during methane adsorption has also been mitigated by increasing energy of phase transition by applying moderate external mechanical pressure to flexible MOFs.

As the next generation of MOFs, Flexible MOFs are superior to rigid MOFs with higher usable methane capacities and better intrinsic heat management.

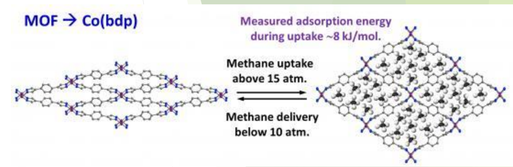

Figure 6[4]: MOF with Cobalt metal, demonstrating the open and close gate nature of flexible MOFs.

Conclusion

Table 1: Usable Methane Capacity Comparison[4]

Adsorbent	35 Bar(v/v)	65 Bar(v/v)
HKUST-1	145	
USTA-76a (Cu paddlewheel structure, similar to KHUST-1)		189
Co(bdp)	155	197
Average of 65,000 Adsorbents		196
DOE Target		263

While increasing usable methane capacity is a formidable challenge it is not the only challenge. Long-term performance, tolerance to impurities, cost to scale-up organic ligands, packing strategies and optimizations of system performance also need to be addressed before MOFs can find practical use in the transportation industry. With volumetric methane uptake capacity of flexible MOFs approaching the DOE target of 263v/v, these new materials show much promise and avenues for tuning methane storage and delivery.

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