Effects of textural and surface characteristics of metal-organic frameworks on the methane adsorption for natural gas vehicular application

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Abstract

In this work, methane adsorption and textural and surface characteristics of selected 46 microporous metal-organic frameworks and 6 other adsorbents were measured experimentally. The objective of this work is to identify either the most relevant characteristics or a combination of multiple properties, which will qualify a given sample to be a good methane uptake material in a moderate pressure range (up to 70 bar) and at 298K. It is found that there is an overall linear tendency between maximum excess methane adsorption and BET specific surface area. The micropore volume correlates to the maximum excess methane adsorption as well, irrespective of the chemistry and functionalities of materials. In addition, micropore size distribution has an impact on methane uptake. When considering the total methane uptake, special attention should be paid to the effect from packing density. The

evaluation also focuses on the discussion of deliverable capacity and concludes that optimal adsorption enthalpy is desired to avoid large amount of methane retained at the minimum desorption pressure in practical vehicular applications.

Keywords

Natural gas/Methane adsorption, Metal-organic frameworks, Adsorption isotherms, Surface characteristics, Natural gas vehicles

1. Introduction

With rising oil prices and uncertainty about security of oil supplies, the diversification of energy resources for the automotive transportation sector has become of particular importance not only in North America, but in other countries around the world [1]. A promising alternative fuel is natural gas (NG). NG is a gaseous mixture of hydrocarbons, predominantly methane (about 70 to 90% CH₄). A typical NG composition from pipeline also contains carbon dioxide, nitrogen, oxygen and hydrogen sulphide [2,3]. Advantages of NG compared to gasoline are its relatively low price and wide availability. 80% to 90% of the natural gas used in US is domestically produced as it can be drawn from wells or extracted in conjunction with crude oil production. An extensive network of natural gas pipelines is already in place to deliver fuel directly to many sites including individual homes. In addition, NG is a clean-burning alternative fuel. However only ~0.1 % of NG in US is used for transportation fuel currently.

One of the challenges of using NG in automotive is the energy content of NG per unit volume of fuel (energy density) being low comparing to gasoline: 11 MJ.L⁻¹ for compressed natural gas (CNG) at

24.8 MPa (3,600 psi) vs 32 MJ.L⁻¹ for gasoline [4,5]. A CNG fuel tank would need to be approximately three times larger than a gasoline tank to allow a vehicle the same driving range. Currently, CNG is mainly stored in onboard tanks under high pressure at 250 bar service pressure in the United States and 200 bar service pressure in the rest of the world [6, 7]. The high pressure vessels for CNG storage are constrained in their geometry, typically cylindrical, and relatively heavy weight (about 1 kg per liter for steel tank). High pressure CNG also requires costly multi-stage compression [9].

These issues could be addressed by using the adsorbed natural gas (ANG) technology. With ANG technology, NG is reversibly adsorbed on the surface of sponge-like materials without any chemical bonding. Fuel can be stored at relatively low pressures, ~35 bar. The lower pressure design will allow the use of conformable and less expensive storage options containing advanced new material alternatives [2,7,9,10].

Considerable research and development are still required to move ANG to market. In-depth study of the adsorption fundamentals must be performed. The key component of the ANG technology is the adsorbent material. The adsorbents' evaluation and comparison are usually conducted by measuring the excess gravimetric gas adsorption at (P , T), that is, the difference between the amount of adsorbate stored in the adsorbed region and the amount that would be present in an identical volume in the absence of solid-gas interactions. The total volumetric adsorption, including all the gas molecules in the pores and defect voids, is then determined in order to compare to the CNG benchmark technology [4,10,11]. In addition, for vehicular NG storage system applications, the parameter known as "deliverable capacity" or "usable capacity" is most relevant for comparing the performances of different adsorbents. This "deliverable capacity" is defined as the amount of gas that is released from

the adsorbent when the pressure is reduced to a certain pressure from the service pressure [4]. 2 to 5 bar is a pressure range commonly cited as minimum desorption pressures, since the vehicle engine requires a minimum inlet NG pressure to operate [3,12,13]. Therefore, the deliverable capacity of an ANG system is always lower than the total storage capacity, usually by around 15% but sometimes by as much as 30% [4].

The porous adsorbent materials that have been reported in the literature for methane adsorption are essentially microporous: zeolites [14], activated carbons [8,15,16], porous organic polymer networks [3,11], and metal-organic frameworks (MOFs) [3,11]. Among these materials, MOFs are a relatively new family of microporous materials for gases sorption applications. For traditional carbons or zeolites materials, numerous works agree that methane adsorption uptake is favored by high surface areas, high micropore volumes, and average pore sizes within the range of 8-15 Å [5,15,19]. Considering MOF materials, more factors such as open metal sites, porosity, topologies and framework densities could be taken into account.

Even though there have been several studies reporting on how each of those factors affects the methane storage uptake using either an experimental [12,20–22] or a simulation method [13,23–26], few reports have discussed the impact of the combination of the variable properties of MOFs on the material storage performances. A general comparison between MOF materials and other microporous adsorbents is yet to be established. Düren *et al.* performed a simulation study on the adsorption characteristics of methane in several isorecticular MOFs (IRMOF), molecular squares, zeolites, crystalline porous silica, and carbon nanotubes. They found a correlation between the methane adsorption at 35 bar and 298 K with the surface area and proposed new IRMOF structures as potential adsorbents [27].

Wang investigated the methane adsorption in nine MOF materials with different topologies using simulation methods as well. Similarly to Düren's work, the results showed that the specific surface area is more important than other properties of MOFs for methane adsorption at 298 K and moderate pressure [28]. Just recently, Long et. al. summarized total methane adsorption data reported in literature for MOFs and compared to experimental data obtained in their laboratory on the six most promising MOFs [3]. These reports and many other comparative studies rely on data from different sources and publications.

Herein, methane uptake and other physical properties, such as material porosity and density, of 52 microporous adsorbents including 4 carbons, 2 polymer materials, and 46 MOFs have been measured in our laboratory experimentally. The objective of this work is to identify either the most relevant characteristics or a combination of multiple properties, which will qualify a sample to deliver the required methane storage at 298K and pressures up to 70 bar. All adsorption data were collected from two identical PCT instruments, which minimized the effects of instrument and data analysis methodology differences on the adsorption results. This is a major difference from most reported comparative studies of MOFs based on data from public sources. The selected materials in this work cover a large range of surface functionalities, pore structures and BET surface areas. Comparing with the previous investigations mentioned above, our study also encompasses more potentially important factors. We also include the issue of "deliverable capacity" or "usable capacity" in our discussion and its relationship with open metal sites and pore sizes.

2. Experimental Methods

2.1 Materials

Various adsorbents have been explored as potential methane storage materials, among them are activated carbons, porous polymer networks (PPN), and metal-organic frameworks (MOFs). The adsorbents investigated in this study were either synthesized in house, obtained from numerous collaborations with Universities (Texas A&M University, University of Nottingham, University of California Berkeley, and University of Michigan), or bought from suppliers. All materials were provided along with their crystalline characterization.

2.2 Material characterizations

The air and moisture sensitive samples were handled, loaded, and weighed in an inert atmosphere (argon) on a precision balance (± 1 mg). The remaining samples were loaded and weighed in a room temperature atmosphere on a precision balance (± 0.1 mg). Additionally, all materials were outgassed in the sample holder at various temperatures and a 10^{-5} torr vacuum overnight prior to any sorption measurements. The analysis of the porous texture of the adsorbents was carried out using N_2 and Ar adsorption measurements at 77 K and 87 K, respectively, using a Quantachrome Autosorb-1 gas-sorption apparatus. The samples were degassed at 373 K under vacuum overnight. The specific surface area (SSA) was determined from N_2 at 77 K using the Brunauer-Emmett-Teller (BET) equation. It should be noted that the SSA was calculated over a range of P/P_0 of 5×10^{-2} - 1.0×10^{-1} , as these conditions can influence substantially the value of the resulting area. The pore size distribution was calculated from the Ar sorption data using a standard non-local density function theory (NLDFT) method for MOFs and PPNs. The total pore volume V_p was obtained from the saturation value of Ar adsorption isotherm ($0.995 P/P_0$) measured at 87 K using liquid Ar density. The micropore volume $V_{m,p}$ was calculated from the Ar sorption data or N_2 sorption data using Dubinin-Raduschkevich (DR) method

[29].

Volumetric methane adsorption measurements at ambient temperature were performed using an automated volumetric Sieverts' apparatus (PCT-Pro 2000 from Hy-Energy LLC) over the range of 0 to 70 bar. The excess methane adsorption isotherms were calculated from successive gas expansions. The dead space volumes were determined at 298K using helium gas as a negligibly adsorbing gas. Ultra-high purity methane and helium (99.999% purity) obtained from Airgas Inc. were used for all measurements.

2.3 Data analysis

The excess adsorption is the only quantity associated to the adsorbed phase readily accessible to measurements [4, 30]. Herein, the excess methane adsorption is measured on a gravimetric basis as the amount of excess methane per unit weight (gravimetric excess), namely G_{ex} . Using the volumetric method (*i.e.* Sieverts' method), G_{ex} can be calculated from successive gas expansions by summing the differences between the amounts of gas depleted from the reference cell and that occupying the sample cell after each expansion such as:

$$G_{ex} = \sum_j^k \Delta G_j - \rho_f^k V_d \quad (\text{Eq. 1})$$

Where ΔG is the amount of gas sent to a cell containing the adsorbent after an expansion, $\rho = P/ZRT$ is the gas density and V_d is the so-called dead-space volume of the sample cell. V_d is, in fact, directly measured with helium as a non-adsorbing gas and includes all the free volume accessible to the methane in the sample cell.

In order to accurately measure the excess adsorption, the selected material is tested at least two times to ensure the isotherm is reproducible and consistent.

The total gravimetric methane adsorption (G_{tot}) differs from G_{ex} as it accounts for the total amount of adsorbate molecules present in the bulk volume of the material. G_{tot} is the convolution of all the methane stored in the adsorbing space (*i.e.* absolute adsorption) and in the non-adsorbing space (*i.e.* gas compressed in interparticular voids and macropores). G_{tot} can be calculated from G_{ex} according to the following equation:

$$G_{tot} = G_{ex} + \rho_g \times V_v$$

(Eq. 2)

Where ρ_g is the density of the bulk gas and V_v is the total void volume of the adsorbent. The void volume V_v is obtained from the bulk density (ρ_b) and the skeletal density (ρ_{ske}) of the adsorbent using:

$$V_v = (1/\rho_b) - (1/\rho_{ske}) \quad (\text{Eq. 3})$$

The total volumetric methane adsorption can then be expressed as follows:

$$V_{tot} = G_{tot} \times \rho_b$$

(Eq. 4)

Considering that the skeletal and bulk densities of an adsorbent can differ by up to an order of magnitude, it is clear that G_{tot} can be much higher than G_{ex} . Although the adsorbed excess amount is the quantity directly measureable, V_{tot} is the important quantity to take into account for engineering perspectives and technology comparison. The bulk density should be used for total adsorption calculations because it includes the contribution of the particle volume, the interparticle void volume, and internal pore volume. Contrary to the crystallographic density, the bulk density is not an intrinsic

property of the material and it can change depending on how the material is handled. However when the bulk density is not available, the crystallographic density, which excludes all voids that are not a fundamental part of the molecular arrangement, can be used. MOFs, offering a clear structural platform, allow for use of the crystallographic density. This leads to an ideal maximum estimate of a material's total adsorption capacity.

3. Results and Discussion

Table 1: Characterization properties and methane uptake for materials studied

Sample	type	BET SSA	V_p	$V_{m,p}$	$V_{m,p}/V_p$	d_p	ρ_{crys}	ρ_{ske}	Obs. $G_{max,ex}$	Corr $P_{max,ex}$	G_{ex} 50 bar	G_{tot} 50 bar	V_{tot} 50 bar	G_{ex} 4.5 bar	V_{tot} 4.5 bar	$V_{deliv.}$
Units		$m^2 \cdot g^{-1}$	$mL \cdot g^{-1}$	$cm^3 \cdot g^{-1}$		Å	$g \cdot mL^{-1}$	$g \cdot mL^{-1}$	$g \cdot g^{-1}$	bar	$g \cdot g^{-1}$	$g \cdot g^{-1}$	$g \cdot L^{-1}$	$g \cdot g^{-1}$	$g \cdot L^{-1}$	$g \cdot L^{-1}$
HKUST-1	Cu MOF	1577	0.750	0.232	0.309	7.18	0.880	1.92	0.125	65.0	0.100	0.122	107.1	0.038	35.0	72.1
UTSA-20	Cu MOF	1331	0.590	0.303	0.514	7.93	0.910	0.78	0.080	31.0	0.070	0.064	57.8	0.035	31.4	26.5
Co MOF-74	Co MOF	1013	0.421	0.435	1.033	5.22	1.169	2.20	0.085	32.4	0.076	0.089	104.4	0.055	65.7	38.8
Ni MOF-74	Ni MOF	760	0.540	0.430	0.796	5.22	1.206	1.12	0.037	22.0	0.030	0.028	33.5	0.020	23.9	9.6
PCN-224	Ni MOF	2541	1.081	0.431	0.399	9.13	0.559	1.78	0.140	66.0	0.140	0.183	102.5	0.032	19.9	82.6
PCN-223	Ni MOF	1335	1.400	0.208	0.149	36.74	0.529	1.84	0.060	33.0	0.050	0.098	51.6	0.017	11.1	40.5
PCN-14	Cu MOF	3370	0.710	0.666	0.939	10.03	0.871	2.10	0.137	38.0	0.136	0.160	139.1	0.052	47.0	92.1
NOTT-107	Cu MOF	1789	0.848	0.691	0.815	6.12	0.813	1.36	0.100	28.0	0.070	0.087	71.1	0.044	37.0	34.1
PCN-94	Zr MOF	1996	0.962	0.281	0.292	10.48	0.548	1.18	0.057	32.0	0.050	0.084	46.3	0.020	12.5	33.8
PCN-6'	Cu MOF	2976	1.106	0.746	0.675	10.48	0.292	1.86	0.182	60.0	0.170	0.272	79.4	0.030	11.2	68.1
PPN-13	P	2640	0.206	0.081	0.394	6.42	0.223	1.50	0.134	67.0	0.134			0.035		
PCN-306	Cu MOF	2336	0.992	0.487	0.491	7.90	0.720	2.59	0.160		0.150	0.185	133.5			
PCN-922	Cu MOF	2401	1.079	0.432	0.400	5.52	0.700	2.38	0.150		0.140	0.176	122.9			
PCN-307	Cu MOF	1264	1.012	0.639	0.631	7.93	0.721	1.80	0.170	52.0	0.170	0.199	143.7	0.055	41.4	102.3
PCN-56	Zr MOF	3117	1.240	0.768	0.619	13.03	0.523	1.93	0.150	65.0	0.150	0.179	93.7	0.025	15.2	78.5
PCN-57	Zr MOF	2502	1.180	0.605	0.513	10.48	0.555	2.10	0.129	56.0	0.130	0.177	98.1	0.030	18.8	79.3
PCN-563	Zr MOF	2672	1.153	0.712	0.618	9.13	0.600	1.54	0.151	60.0	0.140	0.176	105.5	0.022	15.0	90.5
PCN-124	Cu MOF	1835	0.845	0.767	0.908	5.52	0.881	1.40	0.134	44.0	0.130	0.145	127.6	0.047	42.5	85.1

PCN-66	Cu MOF	4037	1.710	0.365	0.213	18.71	0.470	2.66	0.133	40.5	0.130	0.193	89.0	0.032	17.1	71.8
NOTT-119	Cu MOF	2615	1.017				1.327	2.26	0.125	40.2	0.120	0.131	173.8	0.024	33.1	140.7
PCN-320	Zr MOF	2041	0.830	0.450	0.542	9.13	0.621	1.59	0.121	50.0	0.121	0.156	96.6	0.029	19.8	76.8
PCN-26	Cu MOF	1554	0.915	0.816	0.892	7.18	0.749	1.89	0.120	56.0	0.120	0.148	111.2	0.047	37.0	74.2
PCN-308	Cu MOF	2130	0.905	0.715	0.790	7.18	0.721	2.52	0.130		0.125	0.160	115.3			
PCN-11	Cu MOF	1446	0.260	0.180	0.692	7.55	0.749	0.97	0.100	28.0	0.080	0.091	68.0	0.047	35.9	32.1
AC Powder	C	1659	1.170	0.906	0.774	5.24		2.30	0.126	61.7	0.130			0.048		
IRMOF-1	Zn MOF	3249	1.320	0.492	0.373	11.98	0.610	3.13	0.154	68.0	0.150	0.167	101.6	0.020	14.6	87.0
PPN-4	P	3982	2.686	1.267	0.472	18.71	0.070*	1.58	0.263	68.0	0.260			0.035		
MIL-53	Al MOF	1184	0.446	0.351	0.787	16.50	0.721	2.76	0.080	70.0	0.065	0.080	57.7	0.001	1.5	56.2

* Experimentally measured bulk density in our lab.

3.1 Comparison of gravimetric maximum excess methane adsorptions at 298 K and pressure up to 70 bar

Excess methane adsorption uptake G_{ex} can be measured directly and is the most important characterization parameter for adsorbents. The presence of a maximum is a typical feature of excess adsorption isotherms. At higher pressures, the adsorbed phase density inside the material's pores starts to saturate while the bulk gas density keeps increasing. The maximum and following rollover in the isotherm occur when the density of the coexistent bulk phase increases faster than the adsorbed phase.

From the reported adsorption data in literatures the following properties influence the excess adsorption uptakes: accessible surface area, pore volume, pore size, and adsorbent/guest affinity (adsorption energy). In this study, almost all the materials have an average pore width in the range of 8-15 Å. Table 1 summarizes our experimental characterizations including the maximum excess CH₄ uptakes, total CH₄ uptakes calculated from crystallographic density at 4.5 and 50 bar, the resulting deliverable CH₄ capacities, and textural characteristics (BET SSA, total pore volume V_p , micropore volume $V_{m,p}$, average pore width d_p , crystal density ρ_{crys} , and skeletal density ρ_{ske}). The metal ions used in MOF structures are also listed here in order to evaluate their potential influence on the methane sorption performance of the material. Note also that for most of the studied MOFs materials the porosity activation was conducted in the laboratory and could lead to some discrepancy in final results compared to already published data. In addition, it comes to our attention that in a number of instances, there was no indication whether published methane adsorption data were given in terms of excess, total, or absolute adsorption. This could also lead to potential disagreement when comparing our results with

published data [3,14].

The relations between the physical properties of the adsorbents in Table 1 and the maximum excess methane adsorptions have been examined. Our methane sorption measurements are performed over the entire pressure range, from vacuum to saturation, to more fully characterize these promising high surface area materials. As shown in Fig. 1(a) the maximum excess methane uptake, $G_{max.ex}$, and the BET specific surface area have a linear correlation (red dash line in Fig. 1(a)). We also set up the “tolerance band” as shown between two orange dash lines. Most of the plots fall in the band (blue diamonds). This occurs regardless of the adsorbents’ chemistry or functionality. The maximum excess methane uptake correlates more strongly with the micropore volume $V_{m,p}$ than it does with the total pore volume V_p , as shown in Fig. 1 (b) and Fig. S1. This is consistent because any pores of a larger dimension will not contribute significantly to the overall methane adsorption performances of a predominantly microporous adsorbent. The greatest variation of $G_{max.ex}$ vs. V_p is shown for materials which are most likely to have broader pore size distribution. This can explain the greater overall scatter presented in the pore volume data.

Taking a closer look at the textural characteristics of these potential natural gas adsorbents, we found that samples outside (red diamonds) or on the edge (green diamonds) of the tolerance band in Fig. 1(a), by having lower methane uptakes than that predicted from the linear correlation with BET SSA, display relatively low micropore volume $V_{m,p}$ (pore width $< 20 \text{ \AA}$), compared with other samples with similar surface areas. From Table 1, it is also shown that samples with low ratios of $V_{m,p}$ to V_p have relatively low methane uptakes. For instance, PCN-94, PCN-61, and PCN-66 whose maximum excess

adsorption uptakes are lower than expected have ratios of 0.292, 0.300, and 0.213, respectively. On the contrary, samples with higher methane uptakes than that predicted from the linear correlation with BET SSA usually display relatively high ratios of $V_{m,p}$ to V_p (> 0.5).

Besides of having the large proportion of micropores, samples showing higher uptakes than that predicted from the correlation also show a narrow micropore size distribution. These samples contain a large proportion of micropores with pore sizes which are believed to be with the optimum pore size range for methane adsorption, around 8 Å [1]. On contrast, those with a broad pore size distribution or relatively large average pore width have lower methane uptakes than those read from the line in Fig. 1(a). As shown in Fig. 1(a), PCN-307 (red diamond) has higher methane uptake than that predicted from the linear correlation between the maximum excess uptakes and BET SSA data. PCN-70 (blue diamond) falls right on the line. UMCM-3 (red diamond) and UMCM-300 (green diamond) are below the line, having lower methane uptake than that expected from the linear correlation.

Fig. 2 depicts the comparison of the cited materials' micropore size distributions. PCN-307 has mainly a narrow single peak with the average pore width of 7.93 Å. PCN-70 with the average pore width of 9.13 Å has one major peak centered at about 8 Å, but several small peaks with pore width between 15 and 20 Å, indicating the existence of some larger micropores. The pore size distribution plot of UMCM-3 present two large narrow peaks centered at around 16 and 27 Å, respectively, thus the average pore width is 16.86 Å, much larger than the theoretical optimum pore size of 8 Å for methane adsorption. UMCM -300 has an average pore width of 7.9 Å, but also a broad distribution of pore sizes between 8 and 27 Å. The results of these four samples clearly indicate that although surface area and micropore

volume are the two major factors to affect the $G_{max.ex}$, average pore widths and pore size distributions should also be considered, while the adsorbents chemistry and functionalities are not showing a great impact under these test conditions.

In fact, even for the samples in the tolerance band (blue diamonds), ones having similar values of BET SSA can differ by 50 – 100% in $G_{max.ex}$ in Fig. 1(a). In most cases, that can be explained by comparing to the data of micropore volume $V_{m,p}$ (Table 1 and Fig. 1(b)). Samples with low $V_{m,p}$ have low $G_{max.ex}$ generally. For example, PCN-223 (Ni) with SSA of $1335 \text{ m}^2.\text{g}^{-1}$ has much lower $V_{m,p}$ of PCN-223 (Ni), 0.149 mL.g^{-1} comparing to PCN-250 Ca with SSA of $1387 \text{ m}^2.\text{g}^{-1}$ ($V_{m,p} = 0.795 \text{ mL.g}^{-1}$). We can see that the $G_{max.ex}$ of PCN-223 (Ni), 0.050 g/g , is also much lower than that of PCN-250 Ca, 0.11 g/g , though the adsorption enthalpy of MOFs with Ni should be higher than that of MOFs with Ca. The metal effect is not significant here. In some complicated cases, other factors like the portion of micropores, and pore size have to be considered as described above. MD6-128 ($1681 \text{ m}^2.\text{g}^{-1}$), AC powder ($1659 \text{ m}^2.\text{g}^{-1}$), PCN-250 Co ($1630 \text{ m}^2.\text{g}^{-1}$), and PCN-250 Mg ($1561 \text{ m}^2.\text{g}^{-1}$) with similar BET SSA have $G_{max.ex}$ of 0.063 , 0.126 , 0.13 , and 0.15 g/g , respectively. The $G_{max.ex}$ of AC powder and PCN-250 Co are twice of that of MD6-128. PCN-250 Mg has even better performance. As shown in Table 2, MD 6-128 with the lowest methane uptake has the lowest $V_{m,p}$, 0.369 mL.g^{-1} , and the lowest $V_{m,p}$ to V_p ratio, 0.492 . AC powder has the highest $V_{m,p}$, 0.906 mL.g^{-1} , but its average pore size is only $5.24 \text{ \AA}$, too small for methane uptake. PCN-250 Co and PCN-250 Mg are isostructural with different metal centers. Herein, again metal effect is not obvious. Even though PCN-250 Co should have higher methane adsorption enthalpy than PCN-250 Mg, PCN-250 Mg with higher $V_{m,p}$ displays higher $G_{max.ex}$.

Table 2: Characterization properties and methane uptakes for MD6-128, AC Powder, PCN-250 Co, and PCN-250 Mg

Sample	type	BET SSA	$V_{m,p}$	$V_{m,p}/V_p$	d_p	Obs. $G_{max.}$ ex
Units		$m^2 \cdot g^{-1}$	$cm^3 \cdot g^{-1}$		$\text{\AA}$	$g \cdot g^{-1}$
MD6-128	Cu MOF	1681	0.369	0.492	9.13	0.063
AC Powder	C	1659	0.906	0.774	5.24	0.126
PCN-250 Co	Co MOF	1631	0.415	0.916	8.7	0.13
PCN-250 Mg	Mg MOF	1561	0.604	0.724	10.03	0.15

Another way to ponder the excess methane uptakes vs. the textural properties of the materials, is to consider the pressure at which the material reaches its maximum adsorption value, $P_{max.ex}$. Experimental excess adsorption data clearly exhibit maxima. As mentioned earlier this is a typical feature of excess adsorption isotherms. At low pressures, the adsorbed phase density is much higher than the bulk density of methane. Both densities increase with pressure but the bulk density increases more rapidly than the adsorbed phase density and eventually at the maximum, both densities are increasing at the same rate so that pressure has no effect on the excess amount adsorbed. At even higher pressure the bulk density continues to increase with pressure while the adsorbed phase density approaches a saturation condition where no more molecules can fit into the pores. The excess adsorption is zero at the pressure where the bulk and adsorbed phase densities are equal. Therefore, we can expect that the pressure at which the material reach its maximum excess adsorption directly relates to its pore volume.

Additionally, $P_{max,ex}$ also reflects the interaction potential between the adsorbate molecules and the walls of the pores, also described as the adsorption energy. A strong adsorption energy results in a steep initial slope of the isotherm curve at low pressure, in accordance with Henry's Law adsorption. If the adsorption energy is weaker the slope of the isotherm does not look as steep and the $P_{max,ex}$ moves to higher pressures. The pore size and pore size distributions, surface functionalities, and open metal sites for MOFs, as the common factors affecting adsorption energy have been discussed extensively in the literature.

Fig. 3 shows that for most of our samples (blue diamonds), there is a linear trend between the total pore volume V_p and the $P_{max,ex}$. This is consistent with the expectation described above, and suggest that those samples feature similar adsorption enthalpies. No obvious trends between either the BET surface area and $P_{max,ex}$ or $V_{m,p}$ and $P_{max,ex}$ are observed in Fig. S2 (a) and (b), respectively. Specifically for MOFs, since metal centers have been identified as the primary methane adsorption sites, the adsorption energy is expected to vary depending on the constitutive metal center ions. However, the fact that most MOFs with different metal ions fall on the line in Fig. 3 indicates the low impact from the metals on adsorption energy, under the experimental conditions, *i.e.* up to 70 bar. We conclude that metal centers have a strong influence on the adsorption energy at low coverage but do not strongly affect the adsorption energy at the maximum adsorbate uptake. That is consistent with the previous conclusion from the discussion of the $G_{max,ex}$.

The few samples (red diamonds) not falling on the line in Fig. 3, such as PPN-4, MSC-30, and Polymer display lower maximum pressure than predicted from the linear correlation. They all feature

broad pore size distributions with relatively small portion of micropores. The MOF samples displaying lower than expected maximum pressure, UMCM-3 (Zn) and UMCM-152 (Cu), exhibit average pore widths of 16.86 Å and 9.13 Å, respectively. UMCM-152 features a broad pore size distribution as well as a V_p of 2.77 mL.g⁻¹ and a $V_{m,p}$ of 1.216 mL.g⁻¹ (ratio of $V_{m,p}$ to V_p is 0.439). The influence from the adsorption energy to the $P_{max,ex}$ is observed here, since large pores cause weaker interactions between the adsorbate molecules and the pore walls.

3.2 Comparison of total methane adsorptions at 298 K and 50 bar

35 bar is a typical benchmark for the maximum achievable pressure of common single-stage compressors and is often used in the evaluation of total methane adsorptions at room temperature in literature [3,11,14]. Nevertheless, herein most of the adsorption isotherms measured for our samples do not achieve the maximum methane adsorption uptake at 35 bar. We therefore use 50 bar as our reference maximum pressure to discuss and compare total methane uptakes.

The gravimetric and volumetric total adsorption, G_{tot} and V_{tot} respectively, were converted from experimentally measured excess methane adsorption using Eq. 2-4. The void volume and volumetric adsorption were both calculated using the samples' crystallographic density with the known implications we discussed earlier in the manuscript. Therefore, only MOF samples with known crystallographic densities are discussed here. The bulk density was measured for carbons based materials and polymers as they do not share the same crystalline platform as MOFs.

The gravimetric total amount of methane adsorbed increases with increasing surface area and

micropore volume as shown in Fig. 4 (a) and Fig. S3, similarly to the plots for the $G_{max.ex}$ in Fig. 1(a) and (b). Among all of the MOFs measured, PCN-6' with the highest $G_{max.ex}$ of 0.182 g.g^{-1} also reaches the highest G_{tot} of 0.272 g.g^{-1} at 50 bar. Some data points change their relative positions significantly in Fig. 4 (a) and Fig. S3 comparing to those in Fig. 1(a) and (b), due to the addition of other parameters in the calculation. For example, UMCM-3 has the fifth highest G_{tot} of 0.199 g.g^{-1} , with only an average $G_{max.ex}$ of 0.126 g.g^{-1} . The reasons could be: (1) some MOFs with higher $G_{max.ex}$ have lower G_{ex} at 50 bar; and (2) the ρ_{crys} of some MOFs can be very low.

The free volume, which could be the total pore volume V_p obtained experimentally using Ar as the adsorbate or the void volume calculated by Eq. 3, and the crystallographic density are related properties of an adsorbent. Adsorbents with lower crystallographic density have higher free volume. There are obvious linear trends in the plots of G_{tot} at 50 bar versus V_p and ρ_{crys} shown in Fig. 4 (b) and (c), respectively. Materials with low ρ_{crys} and high V_p , show high G_{tot} at 50 bar. In the case of UMCM-3 discussed above, it has the second highest V_p and the second lowest ρ_{crys} among the MOFs measured. The combination of these two lead to high gravimetric total methane uptake. That indicates the important influence of crystallographic density (total pore volume) to the gravimetric total methane uptake.

Volumetric total adsorption capacity has to be determined when considering these materials as potential adsorbents for adsorbed methane technology. Pressure vessels defined by their water volume are used for compressed natural gas and ultimately the adsorbents performances will be compared to the current benchmark system. In Fig. S4 (a) and (b), the volumetric total methane uptakes V_{tot} at 50 bar

of studied MOFs are plotted against the BET specific surface area and micropore volume $V_{m,p}$, respectively. At that stage, there is no clear relationship between the textural characteristics of the adsorbents and their V_{tot} unlike what was observed for G_{tot} . The trends in capacity differ significantly, comparing to the G_{tot} at 50 bar plots. In Fig. 5(a) and (b), materials with low V_p and high ρ_{crys} have high V_{tot} at 50 bar generally. NOTT-119 with the highest V_{tot} at 50 bar of 173.8 g.L⁻¹ has the highest ρ_{crys} , 1.327 mL.g⁻¹. While PCN-6' with the highest G_{tot} of 0.272 g.g⁻¹ has relatively low V_{tot} (79.4 g.L⁻¹, lower than the average value) because of its low ρ_{crys} (0.292 mL.g⁻¹). These plots highlight that the crystallographic density (or bulk density) of an adsorbent, comparing to surface area and micropore volume, is the most critical factor to reach significant volumetric total methane uptake capacity. In fact, in real applications, bulk density, which is related to but cannot be directly reflected from crystallographic density, mainly affects the volumetric total capacity. The actual volumetric capacities based on packing densities of the MOFs may be very different from our current results, in term of both numbers and trends in those plots. One must keep in mind that using crystallographic densities lead to overestimated V_{tot} , as ideal case scenarios.

3.3 Comparison of deliverable methane capacity (50-4.5 bar)

The deliverable methane capacity is defined as the amount of methane that is desorbed from the adsorption service pressure to a specific desorption pressure. This is actually the most essential parameter in the evaluation of adsorbents for the adsorbed natural gas technology vehicular applications. The methane uptake at low pressure shall be considered in addition to the previous discussions. 5 bar is usually cited as a minimum desorption pressure in order to maintain a sufficient

inlet pressure to fuel the engine. However, a lower minimum desorption pressure would allow for a higher deliverable capacity and longer vehicle driving range. 50 – 4.5 bar was selected as the usable pressures range in this section.

The plots of G_{ex} at 4.5 bar versus BET surface area are presented in Fig. S5(a). Interestingly, most of samples with relatively high methane uptake at 4.5 bar (higher than 0.04 g.g⁻¹) are copper centered MOFs, regardless their surface areas. This is consistent with the statement established previously in the literature; copper centers (normally Cu (II)) are strong primary adsorption sites [12,22,31]. Under the experimental conditions, methane molecules occupy open copper sites first, and distribute unevenly in the adsorbent [31]. Comparing with MOFs having no strong adsorption sites, such as IRMOF-1 with Zn metal centers, the Cu centered MOFs generally have isotherms with steep initial slopes. Fig. 6(a) depicts the isotherms of IRMOF-1 (Zn), PCN-61 (Cu), PCN-11 (Cu) and PCN-307 (Cu). The maximum excess methane adsorptions of PCN-307 is comparable to that of IRMOF-1. Both PCN-61 and PCN-11 have lower $G_{max.ex}$. On the other hand, all the Cu centered MOFs have higher G_{ex} at low pressures (up to about 20 bar) than IRMOF-1 (Zn) does, suggesting that they have a higher adsorption energy.

Besides the effects from the Cu adsorption sites, other factors, such as the micropore shapes, pore size, and pore size distributions, could contribute to the adsorption energy. In term of pore size and pore size distributions, PCN-61 has similar average pore width (10.48 Å) to IRMOF-1 (11.98 Å), the isotherms shape differences are mainly due to the primary methane adsorption sites. However, both PCN-307 and PCN-11 have smaller average pore width, 7.93 and 7.55 Å, respectively. The micropore size distribution of PCN-307 is extremely narrow as described above. From the studies of carbon adsorbents, it has been

established that highly microporous carbons have steep initial slopes to their uptakes, and therefore retain a larger proportion of the gas on delivery [32].

The methane adsorption at 4.5 bar causes the changes in the relative positions of the materials in volumetric deliverable capacities versus crystallographic densities plots (Fig. S5(b)), compared to what is observed in the V_{tot} at 50 bar plots (Fig. 5 (b)). Taking the comparison of Co MOF-74 and Zr-mBTB as an example, despite the fact that Co MOF-74 has much higher V_{tot} at 50 bar than Zr-mBTB does, Zr-mBTB has a higher deliverable methane uptake. Their isotherms are illustrated in Fig. 6(b). At 4.5 bar, the higher adsorption energy of Co MOF-75 results in much higher V_{tot} , comparing to that of Zr-mBTB. The volumetric deliverable capacity of Co MOF-75 is 38.8 g.L^{-1} , only 37.1% of its 50 bar total capacity (104.4 g.L^{-1}). In contrast Zr-mBTB has 65.6 g.L^{-1} deliverable capacity, 83% of its 50 bar total capacity (79 g.L^{-1}).

The discussion in this section illustrates the importance of optimizing the methane adsorption energy when designing adsorbents, specifically MOFs. Optimal micropore size, narrow micropore size distribution, and strong methane adsorption sites can help increase the adsorption energy and ultimately the material's overall performance. However, to achieve a good deliverable capacity, those parameters all have to be optimized to avoid retaining too much methane at low desorption pressure.

4. Conclusion

With detailed comparisons of the methane adsorption capacity and physical properties of 52 adsorbents, we have shown that the BET SSA and micropore volume of an adsorbent basically determine its maximum gravimetric excess methane adsorption capacity at 298K and up to 70 bar, irrespective of

the chemistry and functionalities of materials. In addition, the capacity also depends on the pore size distributions. Narrow pore size distribution with optimum pore width improves the gravimetric maximum excess methane adsorption. The pressure at which the material reaches its maximum excess methane adsorption relates to the total pore volume, also irrespective of the various materials or metal centers. The impacts from different metal centers are relatively low on adsorption enthalpy and capacity at moderate pressures (20- 70 bar). Both the gravimetric and volumetric total methane capacities at 50 bar closely relate to the packing density of the adsorbents. For the volumetric capacity, which can be directly linked to the driving range of a vehicle, packing density is the major factor among all the physical properties. In this paper and most of published studies, crystallographic density is used instead of actual packing density of MOF sample for the volumetric total gas uptake determination. The total volumetric capacities calculated this way end up being much higher than those in reality. The capacity change due to different open metal centers as primary methane adsorption sites of different materials can be observed obviously at relatively low pressure (< 5 bar). However, the methane adsorption energy has to be thought of carefully, since it may decrease the deliverable capacity, which is actually most directly related to NG vehicular applications.

In this study, PCN -307, PCN-70, PCN-305, and NOTT-119 all display deliverable storage uptakes higher than 100 g.L^{-1} , with NOTT-119 having the highest uptake of 140.7 g.L^{-1} . Interestingly, these MOFs are all Cu based MOFs which are in general moisture sensitive, adding difficulties to practical use. The current achieved deliverable capacity would still require improvement as well. To design MOFs as better NG adsorbents, we conclude that large surface area and micropore volume with optimum pore size

distributions are desired. Many studies have been focusing on those parameters, however, more work has to be done to understand the influence and to improve the packing density of adsorbents.

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Figures

Fig. 1 Plots of maximum excess methane uptake versus BET Specific surface area (a), micropore volume (b) for all materials. Error bars equivalent to 10% for X and 5% for y, as represented on PPN-4 in (a), and UMCM-152 in (b), respectively.

Fig. 2 Measured pore size distributions for PCN-307, PCN-70, UCMC-300, and UCMC-3.

Fig. 3 Plots of $P_{\text{max, ex}}$ versus total pore volume for all materials. Error bars equivalent to 10% for X and 5% for y, as represented on PPN-4.

Fig. 4 Plots of gravimetric total methane uptake at 50 bar versus BET specific surface area (a), total pore volume (b), and crystallographic density (c) for all materials. Error bars equivalent to 10% for X and 5% for y, as represented on UMCN-4 in (a), UMCN-152 in (b), and NOTT-119 in (c), respectively.

Fig. 5 Plots of volumetric total methane uptake at 50 bar versus total pore volume (a), and crystallographic density (b) for all materials. Error bars equivalent to 10% for X and 5% for y, as represented on UCMC-152 in (a), and NOTT-119 in (b), respectively.

Fig. 6 (a) excess methane adsorption at 298K on PCN-61, PCN-307, PCN-11, and IRMOF-1, and (b) volumetric total methane adsorption at 298 K on Co MOF-74 and Zr-mBTB.