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 298 K. 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.

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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 70–90% CH_4). 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%–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 (3600 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

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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]. 2–5 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 [17,18], 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 isoreticular 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 298 K 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 $P.P_0^{-1}$ 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 $P.P_0^{-1}$) 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 0–70 bar. The excess methane adsorption isotherms were calculated from successive gas expansions. The dead space volumes were determined at 298 K 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