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Principles of methane adsorption and natural gas storage

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Abstract The adsorption amount of methane on 16 different kinds of materials at 3.5 MPa and 298 K holds a linear relation with the specific surface area. The linear relationship implies that gases are adsorbed monolayerly on the surface of adsorbents at above-critical temperatures. Determination of surface area and calculation of storage capacity of a material are explicitly discussed. It is indicated that methane storage is different from natural gas storage and the difference affects the development of storage material. Natural gas is a mixture and all components other than methane cannot be desorbed when the tank pressure released to atmospheric at ambient temperature, therefore, a storage mechanism other than adsorption might be more suitable.

Keywords Principle · Adsorption · Storage · Methane · Natural gas

1 Introduction

The world faces two big challenges. Excessive consumption of fossil fuels induces climate change, and approach of fossil fuel to depletion induces petroleum price shooting up. The best policy facing these challenges is to use hydrogen energy. Unfortunately, the production technology of renewable hydrogen, the technology of on-board storage, and the technology of fuel cells are still far from commercialization. On the other hand, natural gas or other methane-based fuels are relatively practical alternative fuels. Utilization of alternative fuels will alleviate the pressure on environment and petroleum requirement. Therefore, following hydrogen storage, methane storage becomes a new motivation of developing novel materials such as MOF. However, different mechanism of gas storage calls for different kind of storage material, and a research conclusion may be misleading if the fundamental knowledge of adsorption and gas storage engineering are not correctly interpreted. Therefore, a systematic observation on methane adsorption is presented and a discussion on adsorption conceptions and fundamental rules in the calculation of gas storage capacity are presented.

2 Adsorption mechanism at above-critical temperatures

The adsorption mechanism of methane provides the basis of developing a storage material targeting at maximum storage capacity. A lesson might be learned from the experience with carbon nanotubes targeting at hydrogen storage. It was imagined that hydrogen fills in the tubes in a state of high density and, therefore, carbon nanotubes attracted world's attention without paying attention to the fundamental physics law that fluids cannot condense at above-critical temperatures. However, more and more reliable measurements showed that carbon nanotubes are not suitable for hydrogen storage. The hydrogen amount adsorbed on different materials holds a linear relation with the specific surface area (Nijkamp et al. 2001; Chu et al. 2006); therefore, the specific surface area of a material is the decisive factor of storage capacity. The linear relationship implies that hydrogen is adsorbed on the surface of materials in monomolec-

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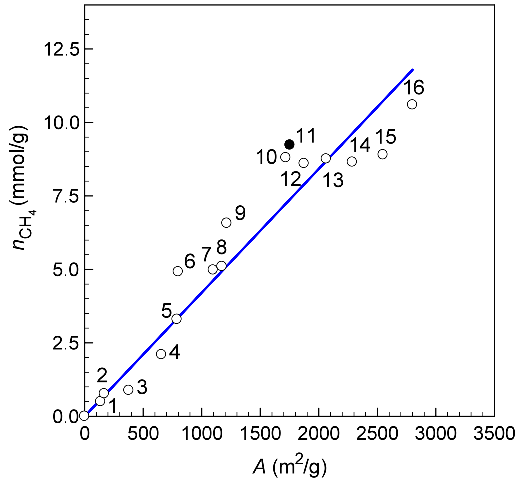

Fig. 1 Methane adsorption on different materials at 3.5 MPa and 298 K

ular layer. The monomolecular layer mechanism of adsorption holds for all adsorption at above-critical temperatures (Zhou 2002), and holds for the adsorption of methane either.

As a proof of the above-mentioned argument, the linear relationship between the adsorption amount of methane and the specific surface area of adsorbents is shown in Fig. 1, where the adsorption amount of methane at 3.5 MPa and 298 K is presented against the specific surface area of 16 different materials that listed in Table 1. All but PCN-114 were measured in the author's lab, and that of PCN-114 was extrapolated from literature. The adsorption amount was measured using a volumetric setup, details of which were previously described (Zhou et al. 2003a, 2003b). Purity of methane used in measurements was 99.995%. The adsorption amount of methane on PCN-14 at 3.5 MPa and 298 K, 180 v(STP)/v, was obtained by extrapolation of the data presented in literature (Ma et al. 2008). This value is converted to the adsorption amount per unit mass of adsorbent in terms of "bulk density" of 0.871 g cm^{-3}:

$$180/0.871 = 206.7\ \text{cm}^3/\text{g}$$

$$206.7/22.4 \Rightarrow 9.23\ \text{mmol/g} \Rightarrow 14.8\ \text{wt\%}$$

PCN-14 is one of MOF material and was claimed of abnormal sorption capacity for methane (Ma et al. 2008). However, the adsorption amount of methane on PCN-14 is quite normal if the result is given on unit mass basis as usually does in adsorption studies. Although with scattered points, the linear relationship is clearly shown in Fig. 1, no mater how differently these materials are made of. The linearity of the plot states that how much methane to be adsorbed is determined basically by the specific surface area of materials, and the other material property plays a minor role in the adsorption. PCN-14 or other novel materials cannot get around the rule either.

The data scatter of Fig. 1 originates largely in the values of the specific surface area of materials. Quite a many researchers use commercial instruments to measure the adsorption isotherm of nitrogen at 77 K, and treat the experimental data by the software provided with the instrument for the calculation of so-called BET surface area or Langmuir surface area. However, evaluation of the specific surface area of porous solids has not reached a universally accepted procedure. The BET equation (Brunauer et al. 1938) is applicable for Type-II or Type-IV isotherms, but not for Type-I isotherms that usually yielded on microporous solids (Gregg and Sing 1982). The space dimension in the crystallographic structure of most MOF materials falls in the range of micropores (Sing 1985); therefore, the BET equation may not be an appropriate choice. Instead of nitrogen adsorption isotherm at 77 K, the adsorption isotherm of CO_2 at 298 K was proposed to use for microporous materials as the basis of surface evaluation because the latter could detect smaller pores (Cazorla-Amoros et al. 1996). The CO_2 adsorption data are treated with the Dubinin-Radushkevich-Kaganer (DRK) equation with assumption of monolayer surface coverage (Gregg and Sing 1982). Therefore, the reported specific surface area of different materials can hardly have a common comparison basis due to difference in the microscopic structure and the imperfect adsorption theory.

3 Calculation of storage capacity

It might be helpful to keep in mind that it is not possible to directly measure the absolute adsorption even for systems with known crystal structure as those of MOF. The definition of absolute adsorption is (Everett 1971):

$$n = n^s - \rho_g V_a = V_a(\rho_a - \rho_g) \tag{1}$$

where n_s is the absolute adsorption and represents the total mass confined in the adsorbed phase; n is the surface excess quantity of adsorption (briefly excess adsorption or usually adsorption); ρ_a and ρ_g is the density of adsorbed phase and bulk gas phase, respectively. V_a is the volume of adsorbed phase, which is a variant during adsorption irrespective of the structure of adsorbent. The so-called absolute adsorption defined in literature (Ma et al. 2008) and related works is only an expression of storage quantity, but not a scientific definition of adsorption because some gas existing in pore spaces but outside the adsorbed phase was also included in "what adsorbed". The experimental techniques applied in the literature cannot determine the boundary between the adsorbed phase and the bulk gas phase, therefore, cannot directly measure the quantity of absolute adsorption either.

Table 1 Materials presented in Fig. 1

Point	Material	A, m^2 g^{-1}	n, mmol g^{-1}
1	MWCNT	137	0.50
2	Zeolite 13X	168	0.77
3	Silica gel	377	0.88
4	MCM41	657	2.10
5	H103[a]	789	3.30
6	ACF1[b]	800	4.92
7	CMK-3[c]	1098	4.98
8	ACF2	1173	5.10
9	ML-L[d]	1215	6.57
10	AC-BY0	1718	8.80
11	PCN-14[e]	1753	9.23
12	AC-LM1[f]	1874	8.60
13	AC-BY1	2063	8.76
14	AC-Paper	2286	8.65
15	AC-LM3	2548	8.90
16	AC-BY2	2800	10.60

[a] Adsorption resin made in the Resin Factory of Nankai University, Tianjin, China

[b] ACF = activated carbon fiber

[c] A carbon mesoporous molecular sieve, refer to Liu et al. (2006) for details of structure

[d] A hypercrosslinked polymer network, refer to Wood et al. (2008) for details of structure

[e] A MOF material, refer to Ma et al. (2008) for details of structure

[f] AC = activated carbon, either purchased or made in the author's lab

A fuzzy usage of "material bulk density" often leads to a misleading conclusion. For example, the amount adsorbed was not provided on unit mass basis, but "converted directly into v(STP)/v by using the *crystallographic density* (0.871 g cm^{-3}), and as large a storage capacity as 230 v(STP)/v was reached (Ma et al. 2008). Underneath the conversion is, however, an unreal assumption that the PCN-14 material filling in a fuel tank has a uniform crystal structure. However, any MOF as synthesized are powder materials, though the material has an ordered microscopic structure. It can hardly imagine that a MOF material filling in a fuel tank is a single block of crystal. The "material bulk density (ρ)" should rather be package density than crystal density. The former is much less than the latter due to existence of void spaces in between particles. As consequence, the real v/v value of the MOF material must be much smaller than that reported.

Even if a huge block of MOF crystal is available, it cannot be applied for gas storage because the time for gas to charge in the crystal and occupy all adsorption sites will be awfully long. It is well known in the research community of natural gas storage that an activated carbon used for storage cannot only have micropores, but also have some meso- even macro-pores to decrease the transportation resistance of gas. Charging and discharging time is an important concern of users. Therefore, the constraint on charging and discharging dynamics must be taken into account in developing a material suitable for gas storage.

The storage capacity of a material must be calculated on the basis of experimentally measured excess adsorption, the data of skeleton density, and the package density of material. The storage capacity in a given volume is the sum of adsorption capacity on material surface and the compression capacity in the void space. The volume of void space before adsorption, V_{he}, is the sum of pore volume inside an adsorbent particle and the volume in between particles. This volume is experimentally determined with helium expansion provided helium does not adsorb. However, the volume of void space decreased to V_g when adsorption takes place since a space of V_a was occupied by the adsorbed phase and

$$V_{he} = V_a + V_g \tag{2}$$

Multiplying both sides of (2) by the gas phase density, ρ_g, we get:

$$\rho_g V_{he} = \rho_g V_a + \rho_g V_g \tag{3}$$

Adding the excess adsorption, n, to both sides of (2), we have

$$\begin{aligned} n + \rho_g V_{he} &= (n + \rho_g V_a) + \rho_g V_g \\ &= n^s + \rho_g V_g \\ &= C_{tot} \end{aligned} \tag{4}$$

Apparently, (1) was applied for the above deduction. C_{tot} is the total storage capacity and can be calculated based on the values of n, V_{he} and ρ_g. Suppose the package density and skeleton density of the material is ρ_b and ρ_s, then the volume fraction occupied by "solid" or "skeleton" is $V_s = \rho_b/\rho_s$, and that of void space $V_{he} = 1 - \rho_b/\rho_s$. Determination of ρ_b is a common practice of laboratory, however, the package density of a powder material must not be same as that calculated from the crystal structure of the material. The skeleton density ρ_s should be evaluated from the experimentally determined skeleton volume, which is the difference between the volume of adsorption cell before and after loading adsorbent.

4 Methane storage vs. natural gas storage

The engineering background of gas storage has to be taken into account for the study of methane storage materials. Methane as a pure material existing in nature may be found only in flammable ice, though the technology to explore flammable ice has not been matured. However, most available methane fuels such as natural gas and coalmine methane are mixtures. Methane storage is different from natural gas storage, though methane is the major component of natural gas. Most components of natural gas other than methane cannot totally be desorbed on discharging a storage tank, and the storage capacity will gradually disappear (Fu and Zhou 2000a, 2000b). It is not practical to screen all components other than methane out before charging a fuel tank, not mention the other technical drawbacks of the ANG method (Zhou et al. 2002). This method, indeed, has not been applied for on-board storage of natural gas so far. Instead of adsorption, formation of hydrates in porous media is another mechanism to enhance the storage of methane as well as methane-based fuels, and as high as 41.2 wt% of storage capacity (compared to 14.8 wt% in PCN-14) is achieved on carbon mesoporous molecular sieve CMK-3 with loading an appropriate amount of water as shown in Fig. 2 (Liu et al. 2006).

The storage method basing on hydrate formation in porous solids is referred to "wet storage method" due to the pre-adsorption of water in adsorbents. Advantage of the wet storage method of natural gas over the conventional "dry storage method", i.e. ANG was proved by static (Zhou et al. 2002; Liu et al. 2006) and dynamic (Zhou et al. 2005) experiments. The thermal effect on charging gas was less than one tenth of that in ANG, and the thermal effect on discharging didn't affect the process. All gas charged in was released out on discharging, therefore, charging and discharging were shown reversible. Making solid pellets of activated carbon with high specific surface area was an annoying job of ANG. However, such a job may not be necessary for the wet storage method because the wet carbon powder is quite plastic. However, the packing density has to be optimally tailored (Zhou et al. 2004). Although the storage material should have as high a specific surface area as possible in ANG as required by the monolayer adsorption mechanism, such materials may not be suitable for the wet storage method. Curves 1 and 3 of Fig. 2 represent the performance of activated carbons possessing partial micropore and partial mesopore. Curve 2 represents the performance of activated carbon possessing only micropores. Curves 4 and 5 represent the performance of carbon materials possessing only mesopores. It is concluded from the Figure that microporous materials are not suitable for the wet storage method. The pore dimension must be larger than the size of a hydrate clathrate, but it cannot be too large to retard the formation rate of hydrates. To our present experience, a mesoporous carbon material with pore size 2–5 nm may show satisfactory performance for the wet storage method of natural gas.

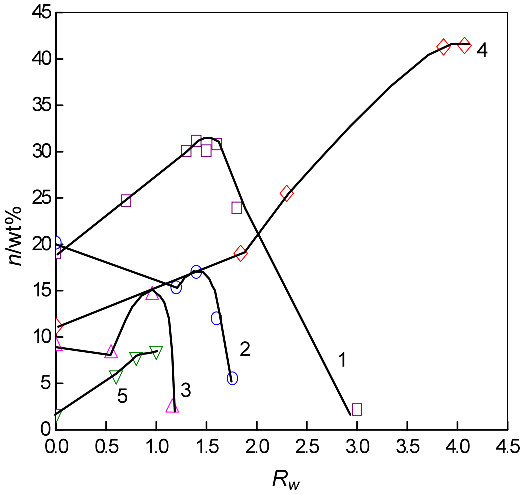

Fig. 2 Methane storage capacity in wet carbons. The capacity is in weight percentage basing on dry carbon. R_w is the weight ratio of water to carbon. 1: Activated carbon BY-1; 2: Activated carbon AX-21; 3: Activated carbon JX-406; 4: Mesoporous carbon molecular sieve CMK-3; 5: Multi-walled carbon nanotubes

5 Conclusion

The mechanism of gas storage is an inevitable factor to consider in the studies of storage materials, and different mechanism calls for different type of materials. The storage capacity must be based on the experimentally measured excess amount of adsorption, and the difference between the crystallographic and package densities must not be confused. In addition, the engineering background of gas storage must also be considered in material development. The difference between methane storage and natural gas storage suggests that a new mechanism other than adsorption might be promising to enhance the storage of natural gas.

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