Enhancement of the Methane Storage on Activated Carbon by Preadsorbed Water

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The enhancement effect of preadsorbed water on methane storage on activated carbon was experimentally proven. Adsorption isotherms of methane on dry and wet activated carbon with different water content were measured at 275–283 K and pressures up to 11 MPa. A sudden change in the methane uptake mechanism that was indicated by the inflection point of isotherms was observed. The measured amount adsorbed always decreased with the increasing water content of carbon before the inflection point. However, a step rise in the isotherm to as much as 63.3% was observed when the pressure reached the inflexion point locating at 4–5 MPa. The significant enhancement of water on the methane-storage capacity of activated carbon is expected to considerably improve the adsorbed natural gas (ANG) technology.

Introduction

Studies on the adsorption of methane on activated carbon have been carried out in recent years because of the need for developing adsorbed natural gas (ANG) technology. Emission control calls for using clean fuels for vehicles. Although hydrogen is the cleanest fuel that can achieve zero emission through fuel cells, natural gas will play the major role for many years (Cannon, 1994) before hydrogen energy can be commercialized. Compared to compressed natural gas (CNG), ANG has the virtue of low storage pressure. As a consequence, savings in both investment and operation costs are expected. Activated carbon with high specific surface area was recognized as the best adsorbent for this purpose (Talu, 1992). For example, 16–17 wt % of methane can be adsorbed on activated carbon AX-21 at 298 K and 3.5 MPa (Zhou and Zhou, 2000). However, the activated carbon must be compressed to a bulk density of 0.6–0.7 g/cm^3 in order to enhance its volumetric storage capacity (Tan and Gubbins, 1990). However, the surface area and the amount adsorbed per gram of activated carbon decreased remarkably after compression. The best viable volumetric capacity was around 150 v/v of charging, and 140 v/v of delivery (Bose et al., 1991). The energy density as such is, however, considerably less than CNG, whose volumetric capacity is 200 V/V at 20 MPa (Parkyn and Quinn, 1995). In addition, pelleting the activated carbon is usually a time-consuming, and thus, inefficient process. In fact, ANG has no commercial application today. Therefore, efforts to improve the ANG technology have never ceased. It was reported (Miyawaki et al., 1998) that the presence of preadsorbed water noticeably enhanced methane adsorption at 303 K, even under subatmospheric pressure. To study the effect of moisture contained in activated carbon on the adsorption of methane, the authors ran the experiment twice (Zhou et al., 2001). In the first run, a dry carbon sample was exposed to a humid atmosphere for two weeks, and the water-to-carbon weight ratio reached 0.93. The sample was dried at 110°C and 6×10^{-2} Pa for different periods of time. The weight loss was recorded and the adsorption of methane was measured at 298.15 K. In the second run, the adsorption isotherm was first measured on a thoroughly dried sample. The sample was then placed in a desiccator without a desiccating agent together with a cup of water for a specified period, at a reduced adsorption temperature of 273 K. The isotherms were then measured for samples after 2, 4, 6, and 8 h of wetting. Although the negative effect of water on

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the adsorption of methane was always reported, we realized that the condition selected was too impervious to form methane hydrate. Therefore, we repeated the experiment a third time, increasing the temperature to 275–283 K. The observations of this run showed the increased storage of methane on wet activated carbon. More than 60% of the methane was superficially adsorbed per gram of activated carbon. In addition, making pellets is no longer necessary because the bulk density of the wet activated carbon can reach a high value simply by compression; even 1.0 g/cm^3 is possible if other considerations permit. It seems, instead of dry activated carbon, wet activated carbon is more suitable for storing natural gas, and unprecedented progress in ANG technology is expected.

Experimental

The activated carbon used as the adsorbent in the experiments was manufactured in our laboratory. The raw material is carbonized coconut shells. A physical activation method was used to prepare the sample in a rotary kiln. The specific surface area of the sample was 1,800 m^2/g, which was estimated using the DRK plot of the CO_2 adsorption isotherm at 273 K (Gregg and Sing, 1982). The bulk density of the carbon was 0.33 g/cm^3, which was measured after the sample was dried at 393 K for 24 h in a vacuum. A definite amount of demineralized water was added to dry carbon by mechanical mixing to prepare the wet sample. Adsorption isotherms were measured on a typical volumetric setup, which was the same as that used for adsorption in previous studies (Zhou and Zhou, 2000). A diagram of the apparatus is shown in Figure 1. Two containers of known volume were connected by tubes via a valve C. One container, called the reference cell, with a volume of V_r, was kept at a constant temperature, T_r, which is usually close to room temperature. The value of V_r includes the volume of the tube between the reference cell and valve C. The other container, the adsorption cell, is where the adsorbent was located and the adsorption equilibrium temperature, T_d, was maintained. The volume of the tube connecting the adsorption cell and valve C was divided into two parts: one part of volume V_t was open to the room, and therefore had the same temperature as the reference cell; the other part, with temperature T_d, was immersed in the atmosphere of the cryostat and, thus, its volume was added to adsorption cell V_d. The amount adsorbed was calculated from the p-V-T readings before and after opening valve C. The precision and reliability of adsorption measurement rely on how accurately p, V, and T were measured and how reliably the compressibility factor was determined. A pressure transmitter model PAA-23/8465.1-200, manufactured by Keller Druckmesstechnik (Switzerland), was used to measure the pressure. The deviation from linearity in the whole range at 20 MPa was less than 0.05%. The volume of the reference cell was determined by the titration method. Volume V_d was determined by helium at temperature T_r. The amplitude of temperature variation was ± 0.1°C for both T_r and T_d. The purity of helium and methane used was higher than 99.995%. The condition of the experiments covered ranges of 275–283 K and 0–11 MPa. Since each isotherm starts at a pressure reading of zero, it is necessary to place the system in a vacuum. To minimize the vaporization loss of water, the wet sample was cooled to -20°C for every time the adsorption cell was put in a vacuum. The temperature was raised to the specified value after removal from the vacuum. The water loss during the experiment can be ignored, because the total weight of the sample before and after the isotherm measurement was almost unchanged.

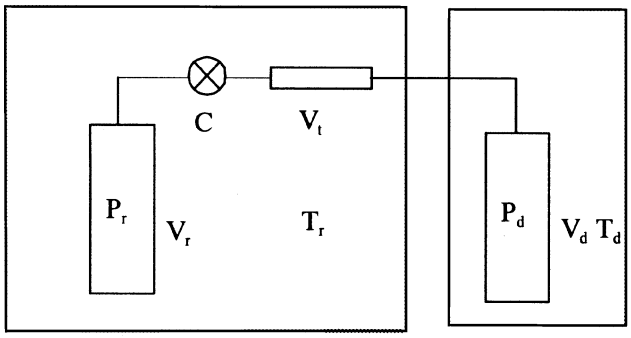

Figure 1. Experimental apparatus.

An ordinary adsorption isotherm of methane was measured first on a dry sample at 275 K. Two other sets of experiments were carried out with wet activated carbon afterward. Wet samples with different water/carbon ratios were used as adsorbents, and the adsorption isotherms were measured at 275 K in the first run. Next, the isotherms for 275–283 K at 2 K increments were measured while the water content was kept the same.

Results and Discussion

Mechanism transition in methane uptaking

The water content of the wet activated carbon is called the "water ratio, R_w," and is defined as the ratio of water weight to that of the dry activated carbon. Three wet samples were tested, the water ratios of which were 0.7, 1.4 and 3.0, respectively. The adsorption isotherms at 275 K for the dry and the wet samples are shown in Figure 2. The amount of methane sorbed or stored is expressed as the weight percent of methane on dry carbon, that is, a gram of methane sorbed or stored on 100 g of activated carbon. Curve *a* is the isotherm of dry carbon, which shows the feature of type I according to the IUPAC classification (IUPAC, 1985). The highest amount adsorbed per 100 g of dry carbon was 19.44 g, methane measured at pressure 7.46 MPa. A sharp increase was observed in isotherms *b* and *c*, the water ratios of which were 0.7 and 1.4, respectively. The amount adsorbed is considerably less than that recorded at dry carbon before the pressure reached the inflection point, and as more water was added to the carbon, the amount adsorbed greatly decreased. However, the recorded isotherm increased rapidly at pressure 4.6 MPa, and as more water was added to the carbon, the isotherm reached a higher level. The highest amounts of methane "adsorbed" per 100 g of dry carbon were 24.78 g for $R_w = 0.7$ at pressure 9.52 MPa and 31.74 g for $R_w = 1.4$ at pressure 9.26 MPa. The net gains relative to dry carbon were 27.5% and 63.3% for $R_w = 0.7$ and $R_w = 1.4$, respectively.

This kind of increase in the isotherm has never been reported for the adsorption of methane on activated carbon. It does not have relevance to the adsorption of water either,

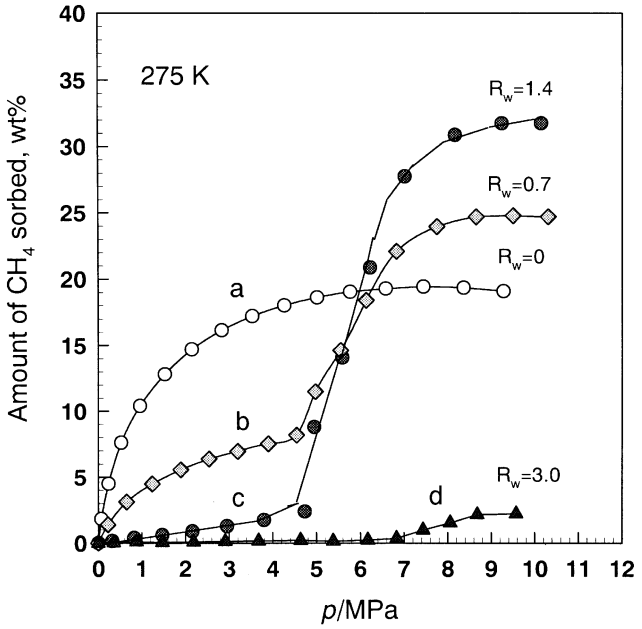

Figure 2. Effect of water content on the storage enhancement of methane.

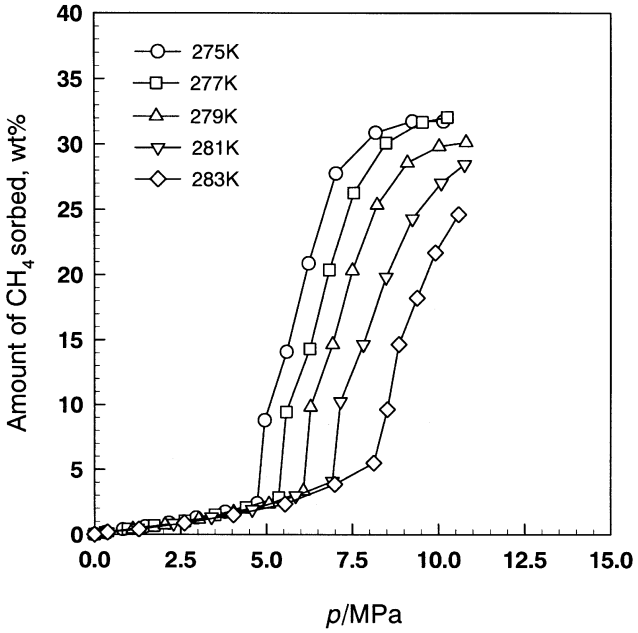

Figure 3. Effect of temperature on the storage enhancement.

because what is expressed by the isotherm is only *the quantity of methane* that "fixed" on the adsorbent. The preadsorbed water occupied some surface (or pore volume) of activated carbon, and hence the amount of methane adsorbed is remarkably less than that on dry carbon until the "inflection pressure" is reached. Because the inflection pressure—4.6 MPa at 275 K—is a little higher than the formation pressure of methane hydrate (3.23 MPa; Sloan and Parrish, 1981), hydrate formation is a reasonable mechanism for the sudden increase in the isotherm. However, too much water does not help hydrate formation as shown by curve *d*, whose $R_w = 3.0$, and the isotherm is very low, even at pressure 10 MPa. The water content seems more than enough for filling the pore volume of activated carbon at $R_w = 3.0$, and methane can only touch the surface water. It is argued, therefore, that the formation of methane hydrate was catalyzed only in the "pore space" of activated carbon. It is believed that the inner diffusion resistance in pores and the related percolation within the pore structure causes the difference between the inflection pressure and the genuine formation pressure of hydrate. It is clear that excessive water is absolutely negative for the storage of methane on activated carbon, but an appropriate quantity of water preadded to activated carbon greatly enhances (more than 60%) the storage of methane on activated carbon, as long as the pressure is no less than the value of the inflection point of the isotherm.

Effect of temperature on the inflection pressure

For practical application, the storage of natural gas is hopefully not sensitive to temperature. Therefore, the equilibrium between methane and wet activated carbon was measured at 275–283 K for 2 K increments while keeping the water ratio of the sample constant ($R_w = 1.4$). The isotherms obtained are presented in Figure 3. As mentioned earlier, the pressure of methane hydrate formation at 275 K is only 3.23 MPa, but the inflection pressure observed was higher (4.6 MPa) due to the inner diffusion resistance or the transport-related effects in the porous space. The inflection pressure of the isotherm increases rapidly as the temperature increases, while the gain in storage capacity of methane decreases. Therefore, higher temperatures are not favorable for purposes of storage.

Charging/discharging property on wet activated carbon

In order to study the discharge property of methane from the wet activated carbon, desorption isotherms were measured at 275 K and 281 K for the sample with $R_w = 1.4$, as shown in Figures 4 and 5. Although no hysteresis was observed on the dry activated carbon (Zhou and Zhou, 2000), a remarkable hysteresis was recorded on the wet carbons. This hysteresis was caused by the decomposition of methane hydrate, just as was observed on decomposing hydride and the release of hydrogen from alloy (Schlapbach, 1992). The "isotherm loop" shown in Figure 4 is composed of four sections. Section A is a piece of normal adsorption isotherm. Section B shows the formation of hydrate. Section C depicts the process of hydrate decomposition due to pressure decrease, plus the decomposition of all the hydrates down to point *j*. Section D appears to be a piece of normal desorption isotherm, but it can disappear if the formation pressure of hydrates becomes quite low, as was the case at 275 K shown in Figure 5.

The isotherm loop shown in Figure 5 represents the favorable condition of the charging/discharging state of a fuel tank. The quantity of methane uptaken increases rapidly at a relatively low (less than 5 MPa) pressure in the charging process. The flow rate remained almost constant at the highest level at quite a wide range of pressures on discharging. The quantity of gas released dropped rapidly when the pressure

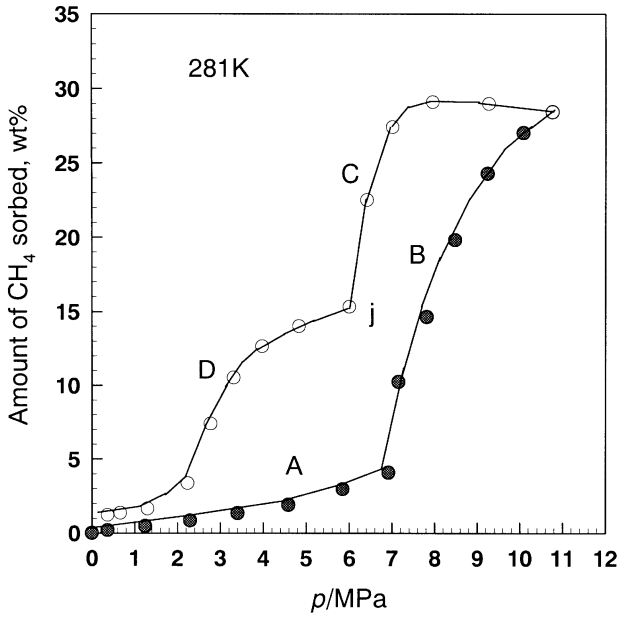

Figure 4. Hysteresis measured for wet carbon with R_w = 1.4 at 281 K.

dropped to 3.5 MPa. If the tank is used to supply fuel for vehicles, full power could be guaranteed for a wide range of fuel pressures above 3.5 MPa.

Flexible plasticity and the volumetric capacity of wet activated carbon

Making activated carbon pellets hinders the application of ANG technology. Whether or not a binder is used, making pellets is a time-consuming and inefficient process. Using compression, the bulk density of the wet activated carbon can be increased to a high of 1.0 g/cm^3, and it will stay there when pressure is released. Compressing the wet powder of activated carbon too tightly may not be effective because of the inner diffusion resistance in the charging/discharging process. However, the optimum density, commonly considered to be 0.6–0.7 g/cm^3, could be guaranteed. Based on a bulk density of 0.7 g/cm^3, about 200 v/v of volumetric capacity was reached on the wet activated carbon tested. The storage pressure must be as high as 20 MPa for CNG to reach the same capacity. A higher capacity is possible because the activated carbon used in the experiments did not have the best surface area and pore structure for this purpose, so there is still room for improving the storage condition.

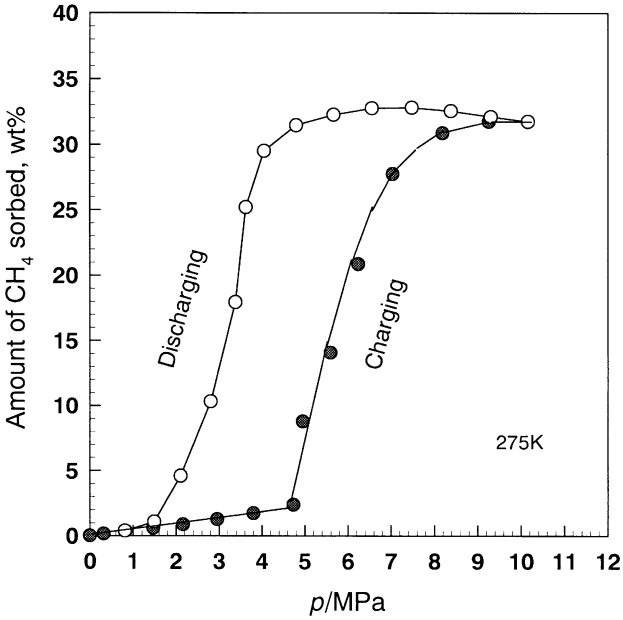

Figure 5. Hysteresis measured for wet carbon with R_w = 1.4 at 275 K.

Reusability of the wet activated carbon

The wet activated carbon can be used repeatedly. The five isotherms shown in Figure 3 are measured on the same wet carbon sample. Creating a vacuum is a necessary step in any isotherm measurement; therefore, an isotherm means a charging/discharging process. As physical adsorption, all the methane adsorbed on activated carbon can be desorbed thoroughly as the pressure drops to zero. As seen in Figures 4 and 5, methane hydrate decomposes as pressure becomes lower than its formation pressure. Therefore, the wet activated carbon can be applied repeatedly as a methane carrier.

Conclusion

1. A transition mechanism in the equilibrium between methane and wet activated carbon was observed for the temperature range 275–283 K. This process was considered a transition from methane adsorption to methane hydrate formation that was catalyzed by the pore space of activated carbon.

2. The transition mechanism results in a significant improvement in ANG technology. The methane storage capacity was increased by more than 60% based on the weight of the dry carbon, and over 200 v/v is possible at pressures less than 10 MPa. Because methane is the major component of natural gas, and the formation pressure of heavier paraffin (C_2^+) hydrates is lower than that of methane, the storage technology for wet activated carbon is suitable for natural gas.

3. Because the feasible storage pressure increased rapidly with increasing temperature, storing natural gas at ambient temperature is not feasible. Fortunately, it is not a difficult job to maintain the temperature in the 2–8°C range using current refrigeration technology.

Acknowledgment

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