

Clathrate-Formation Mediated Adsorption of Methane on Cu-Complex Crystals

Hiroshi Noguchi,[†] Atsushi Kondoh,[†] Yoshiyuki Hattori,[§] Hirofumi Kanoh,[†]
Hiroshi Kajiro,[‡] and Katsumi Kaneko^{*,†}*Graduate School of Science and Technology, Chiba University, 1-33 Yayoi, Inage, Chiba, 263-8522 Japan, and Nippon Steel Corporation, 20-1 Shintomi, Futtsu, Chiba, 293-8511 Japan, and Institute of Research and Innovation, 12014 Takada, Chiba, 277-0861 Japan**Received: May 13, 2005; In Final Form: June 17, 2005*

We measured adsorption and desorption isotherms of methane on $[\text{Cu}(4, 4'\text{-bipyridine})_2(\text{BF}_4)_2]$ (LPC) at 258, 273, and 303 K. Adsorption proceeds almost vertically at a definite pressure, which is named gate pressure. The lower the measurement temperature, the smaller the gate pressure. The temperature dependence of the gate pressure is expressed by the Clapeyron–Clausius equation, giving a thermodynamic evidence on the clathrate formation between the Cu complex and methane.

1. Introduction

Gases are classified into vapors and supercritical gases according to the critical temperature (T_c). Gases below or above T_c are designated as vapors or supercritical gases, respectively. Although supercritical gases such as H_2 , N_2 , O_2 , and CH_4 occur in the atmosphere, storage of supercritical gases with porous solids is not easy because of the very weak interaction of the gas with the solid surface. Vapors can be physically adsorbed on solid surfaces, but physical adsorption is not effective for supercritical gases. As nanopores have an enhanced interaction potential for supercritical gases,¹ the design of optimum nanoporous materials for adsorption of supercritical gases has been actively studied for applications to storage of clean energy-source gases, such as hydrogen and methane. There are many reports on the adsorption of supercritical hydrogen and methane on traditional nanoporous materials, such as activated carbons and zeolites.^{2–6} Recently, nanocarbons and organic–inorganic hybrid complexes have gathered great attention owing to their hopeful potential applications.^{7–18} In particular, organic–inorganic hybrid complexes have an advantage in terms of structural design;^{19–22} organic chemistry can be applied to designing of the nanopore structure for gas storage.

We previously found a novel gate adsorption of CO_2 on Cu-complex crystals with no apparent open porosity.^{23,24} These crystals were called latent porous crystals (LPCs). The T_c of methane, which is the main constituent of natural gas and a potential clean energy source for vehicles, is 190.6 K, and researchers have thus been actively seeking a good adsorbent for supercritical methane.² This letter describes a predominant phenomenon of gate adsorption for supercritical methane and proposes a new adsorption mechanism.

2. Experimental Section

LPCs, consisting of $[\text{Cu}(\text{bpy})(\text{BF}_4)_2(\text{H}_2\text{O})_2(\text{bpy})]_n$ (bpy = 4,4'-bipyridine), were synthesized by the standard method described in the literature.^{23–25} The resulting blue crystals were examined by elemental analysis and X-ray diffraction with an angle-dispersive diffractometer and monochromated Mo K α radiation at 50 kV. The particle densities of the crystals were determined by the high-pressure helium buoyancy method²⁶ at 303 K before and after pretreating at 373 K under 1 mPa of pressure for 2 h. The high-pressure adsorption isotherms of methane were measured gravimetrically at 258, 273, and 303 K after the pretreating at the same conditions as the particle density measurement. The effect of temperature jump between 273 and 303 K on the methane adsorption was measured gravimetrically at 3.5 MPa. First, the adsorption isotherm was measured at 303 K up to 10 MPa. Second, the desorption isotherm was measured at 303 K down to 3.5 MPa. Third, the temperature was lowered to 273 K at the cooling rate of 5 K min^{-1} in the desorption at 3.5 MPa. Then the temperature was again elevated to 303 K at the heating rate of 5 K min^{-1} under 3.5 MPa. Finally, the desorption isotherm was measured down to the vacuum condition.

3. Results and Discussion

3.1. Particle Densities of LPC before and after Pretreating.

The weight of the sample decreases linearly with the He pressure due to the buoyancy, and the slope of the linear relation gives the particle density.²⁶ The particle densities before and after the pretreating were 1.72 and 1.70 g mL^{-1} , respectively. As the preevacuation removes lattice water molecules of 6.45 wt %, the chemical formula changes into $[\text{Cu}(\text{bpy})_2(\text{BF}_4)_2]_n$ by elemental analysis. The measured particle density of 1.72 g mL^{-1} before the preheating agrees with the true density (1.71 g mL^{-1}) from X-ray diffraction. As the particle density takes into account the closed pore volume, the good agreement between the particle and true densities indicates that pores are open for He.

* Corresponding author. E-mail: kaneko@pchem2.s.chiba-u.ac.jp. Tel: +81-43-290-2779. Fax: +81-43-290-2788.

[†] Chiba University.

[‡] Nippon Steel Corporation.

[§] Institute of Research and Innovation.

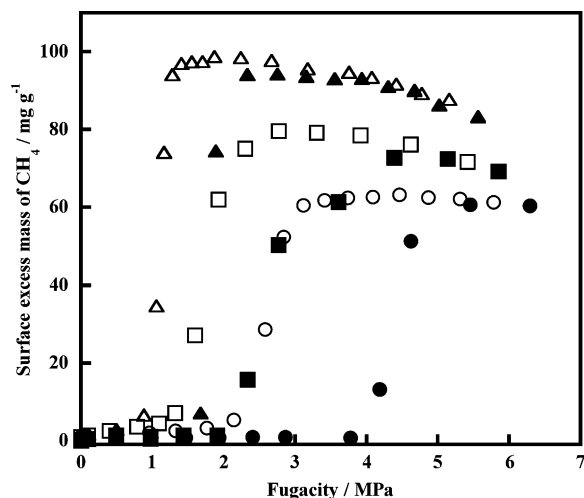


Figure 1. High-pressure adsorption isotherms of CH₄ on LPCs: (●) 303 K, (■) 273 K, and (▲) 258 K. Closed symbol, adsorption; open symbol, desorption.

Accordingly, He can access the voids in the LPC lattices, even though they are closed to methane molecules, as shown later. Although the lattice water molecules are removed, the particle density does not change. The preliminary X-ray diffraction analysis of the pretreated crystals suggests an elongation of the inter-sheet distance. Hence, He molecules can have a better accessibility to the intersheet spaces in the pretreated crystals, which does not contradict with the unchanged particle density of the pretreated crystals. Thus, the particle density data of the crystals before and after pretreating indicate a changeable stacking structure.

3.2. Clathrate-Formation Mediated Adsorption. Figure 1 shows the high-pressure adsorption isotherms of supercritical methane on LPCs at 258, 273, and 303 K. Adsorption begins almost vertically at a definite pressure, which is designated the gate adsorption pressure; the adsorption amount below the gate adsorption pressure is nil. In a similar way, a predominant desorption occurs at the pressure lower than the adsorption gate pressure, which is named the gate desorption pressure. Lowering the measurement temperature decreases both gate pressures but increases adsorption amount above the gate pressure. If we assume that this gate adsorption stems from a clathrate formation reaction, the following chemical equilibrium should hold



Here, [LPC:CH₄](s) is a new clathrate compound of LPC and CH₄. van der Waals and Platteeuw showed that the Clapeyron–Clausius equation can be applied to binary systems.²⁷ The gate pressure should be the vapor pressure of the clathrate compound [LPC:CH₄](s). Also, the volume change ΔV can be approximated by $\Delta V = V(\text{CH}_4) (=zRT/P)$, where z is the compression factor). Therefore, the following Clapeyron–Clausius equation

$$\frac{d \ln P}{d(1/T)} = \frac{\Delta H}{zR} \quad (2)$$

can be applied to the temperature dependence of the gate pressure, giving the enthalpy change ΔH_f of the clathrate formation equilibrium. This relation can be applied to the gate pressures for both adsorption and desorption.

Figure 2 shows the linear relationship between the logarithm of the gate pressure and the reciprocal of the measurement

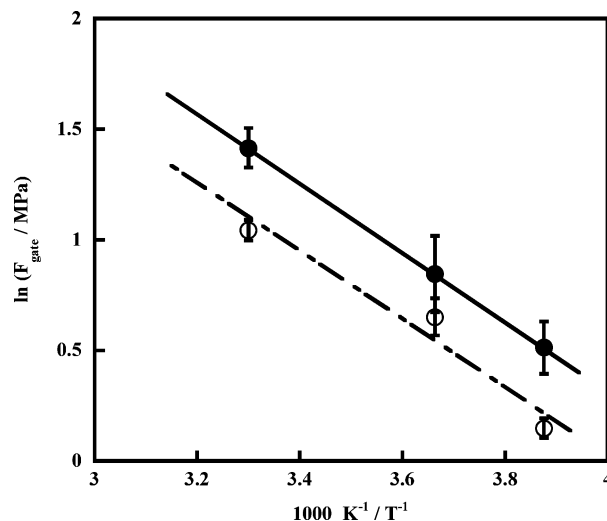


Figure 2. The temperature dependence of gate pressure: Closed symbol, adsorption; open symbol, desorption.

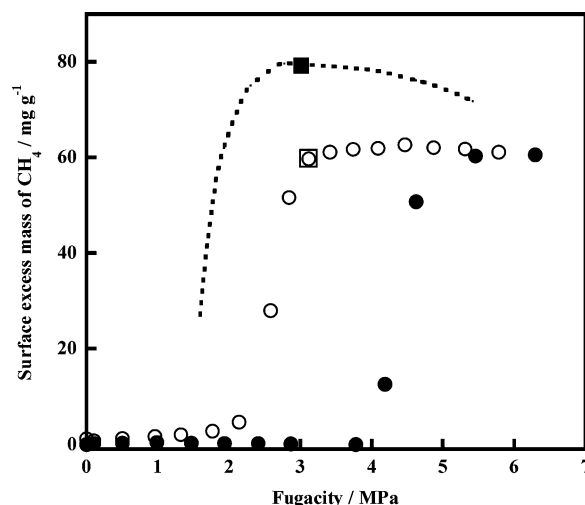


Figure 3. Effect of temperature jump on methane adsorption: (●) Adsorption at 303 K, (○) desorption at 303 K, (■) temperature drop from 303 to 273 K, (□) elevation temperature from 273 to 303 K, (...) desorption isotherm at 273 K.

temperature. The formation enthalpy of the clathrate from adsorption is $13.0 \pm 1.2 \text{ kJ mol}^{-1}$ and the corresponding dissociation enthalpy of the clathrate is $12.5 \pm 1.5 \text{ kJ mol}^{-1}$.

3.3. Change in Adsorption Isotherm of Methane on Temperature Jump. Figure 3 shows the effect of a measurement temperature jump on the adsorption behavior. When the sample used for the desorption branch at 2.5 MPa is cooled to 273 K, an explicit increase is observed, as shown in Figure 3. This point at 273 K coincides with the desorption branch at 273 K, which is shown by a broken line. That point then dropped again after elevating the temperature to 303 K, matching the desorption branch at 303 K. Consequently, this gate adsorption is in a thermal equilibrium that supports the clathrate formation mechanism. Finally, we must note the difference between the gate adsorption and adsorption in the subcritical range. It is well-known that vapor–liquid transition on the solid surface in the subcritical region induces a sharp uptake in the isotherm.²⁸ However, the gate adsorption of methane is observed above the critical temperature of the bulk methane. Furthermore, the measurement temperature is much higher than the two-dimensional critical temperature. Then, this gate adsorption cannot be ascribed to the vapor–liquid-phase transition. We

need to evidence this clathrate-formation mediated adsorption mechanism with in situ X-ray diffraction in future.

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