

ADSORPTION MECHANISM OF SUPERCRITICAL METHANE

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INTRODUCTION

Methane is the main constituent of natural gas. Adsorption of methane at ambient temperature has been studied with a special relevance to methane storage. However, methane is a spherical molecule and the intermolecular interaction is quite weak. Furthermore, the bulk critical temperature is 191 K. It is quite difficult to adsorb methane sufficiently at ambient conditions. If we could find a good adsorbent for methane or elucidate the adsorption mechanism of supercritical methane, it should stimulate practical and fundamental research activities. The most hopeful applicant for methane storage is activated carbon. This is because the surface potentials from opposite micropore-walls are overlapped each other to induce an enhanced adsorption (micropore filling) even at a low pressure region for vapors and activated carbon has a great micropore volume. Even micropore filling is not so strong to adsorb supercritical methane at a subatmospheric pressure. Consequently, methane adsorption has been examined at high pressure region [1,2]. Molecular simulation studies predict the best pore width of the graphite slit-pore for the methane storage [3,4]. Kaneko et al proposed the chemisorption-assisted micropore filling for supercritical NO [5,6] and they showed that the dispersion of MgO improves the methane adsorptivity of activated carbon fiber (ACF) [7]. In this work, effect of dispersion of metal oxides on the adsorption properties of ACF for methane and the adsorption mechanism will be discussed.

EXPERIMENTAL

Pitch-based ACF and AX21 were used. ACF was modified with MgO , $\text{Mg}(\text{OH})_2$, CaO , Al_2O_3 , Cr_2O_3 , and NiO fine particles. The samples were designated ACF-Oxide. AX21 was modified with $\text{Mg}(\text{OH})_2$, which is expressed by AX21- $\text{Mg}(\text{OH})_2$. The micropore structures of carbon samples were determined by N_2 adsorption at 77 K [8]. The high pressure methane adsorption isotherm was gravimetrically measured at 303 K (at 273 K - 303 K in AX21- $\text{Mg}(\text{OH})_2$) in the methane pressure range up to 10 MPa.

RESULTS AND DISCUSSION

Microporosity. Dispersion of metal oxide particles changed slightly the micropore volume W_0 , specific surface area a_α , and pore width w of ACF. The changes were within 10 %. Therefore, the basic micropore structure of ACF is maintained even after the oxide-dispersion. On the other hand, the $\text{Mg}(\text{OH})_2$ dispersion changed the microporosity of AX21, as follows. AX21: W_0 ; 1.49 mlg^{-1} , a_α ; 2400 m^2g^{-1} , and w ; 1.30 nm. AX21- $\text{Mg}(\text{OH})_2$: W_0 ; 1.01 mlg^{-1} , a_α ; 1330 m^2g^{-1} , and w ; 1.56 nm.

Enhancement effect of methane adsorption by oxide-dispersion. Fig. 1 shows high pressure methane adsorption isotherms of metal oxide-dispersed ACF at 303 K. All the adsorption isotherms are Langmuirian, indicating the presence of micropores in which supercritical methane can be filled. The oxide dispersion

enhances remarkably the amount of methane adsorption. The dispersion of NiO fine particles is the most effective for improvement of methane adsorptivity. These high pressure adsorption isotherms were analyzed by the inherent micropore volume theory using the extended DR equation[9]: $[\ln(W_L/W_0)]^{1/2} = (RT/\beta E_0)(\ln P_{q_0} - \ln P)$. Here, W_L is the inherent micropore volume which can be determined by the Langmuir plot and P_{q_0} is the quasi saturated vapor pressure of methane in the micropore. All extended DR plots showed a good linearity, providing P_{q_0} and βE_0 values. The isosteric heat q_{st} of methane adsorption at fractional filling of $1/e$ was obtained from $\beta E_0 + 8.17$ (kJmol^{-1}). The metal oxide dispersion increases P_{q_0} , while q_{st} is almost constant regardless of the surface modification. The results on AX21 will be compared with those on ACF.

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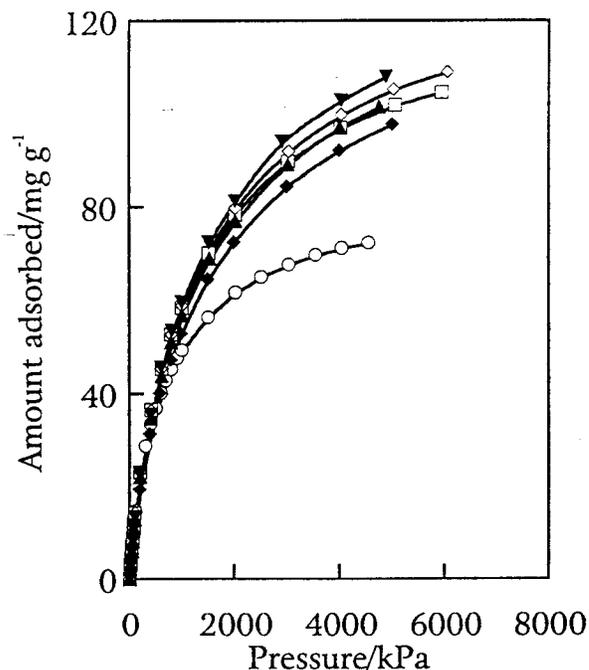


Fig. 1. High pressure methane adsorption isotherms at 303 K

ACF : ○ , ACF-MgO: ◇, ACF-CaO: □, ACF-Al₂O₃ : ◆, ACF-Cr₂O₃ : ▲, ACF-NiO: ▼

Table 1. Characteristic parameters of methane adsorption isotherms

| | W_L mgg^{-1} | q_{st} kJmol^{-1} | P_{q_0} MPa |
|------------------------------------|----------------------------|---------------------------------|------------------|
| ACF | 79.34 | 17.2 | 12.0 |
| ACF-Mg(OH) ₂ | 118.0 | 17.6 | 22.8 |
| ACF-MgO | 120.9 | 17.5 | 21.3 |
| ACF-CaO | 117.2 | 17.3 | 20.1 |
| ACF-Al ₂ O ₃ | 114.0 | 17.1 | 20.9 |
| ACF-Cr ₂ O ₃ | 116.8 | 17.2 | 19.7 |
| ACF-NiO | 125.4 | 17.1 | 20.4 |