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Monolayer Cuprous Chloride Dispersed on Pillared Clays for Olefin-Paraffin Separations by π-Complexation

LINDA S. CHENG AND RALPH T. YANG
Department of Chemical Engineering, State University of New York at Buffalo, Buffalo, NY 14260

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Abstract. New adsorbents containing cuprous chloride dispersed on pillared interlayered clays (PILC) have been prepared and studied for olefin-paraffin separations. High surface-area PILC's were synthesized with different metal oxide (Al_2O_3, Fe_2O_3, TiO_2 and ZrO_2) as the intercalating pillars. Cuprous chloride was dispersed in a submonolayer form on these PILC's. Pure-component isotherms were measured for C_2H_4, C_2H_6, C_3H_6 and C_3H_8 at 25°C and 60°C. All sorbents exhibited high C_2H_4/C_2H_6 and C_3H_6/C_3H_8 ratios with significantly high amounts of olefins adsorbed. The best sorbent was CuCl/TiO_2-PILC which showed a C_2H_4/C_2H_6 ratio of 5.3 and $C_3H_6/C_3H_8 = 2.9$ at 25°C. In all cases, olefins adsorbed by π-complexation with Cu(I) ion, reflected by heats of adsorption in the range 10.7–13.7 kcal/mol, as compared to 4.8–6.9 kcal/mol for the physical adsorption of the paraffins. The π-complexation was fully reversible, limited only by the rates of pore diffusion. Diffusion of C_2's was rapid while for C_3's the diffusion reached 60% completion in approximately 6 min. Comparing these results with those of CuCl/γ-Al_2O_3, the olefin/paraffin adsorption ratios were not as high as those of the later. However, the olefin isotherms on the PILC-supported CuCl displayed the desirable feature of having a steeper portion above the knee of the isotherm (the knee occurred at below 0.1 atm). This was a useful feature for separation because it yielded a larger working capacity. The steeper isotherm was attributed to a higher degree of energy heterogeneity as the PILC contained both surfaces of pillars and clay layers as opposed to only γ-Al_2O_3.

Keywords: π-complexation sorbents, pillared clays, olefin-paraffin separations

Introduction

Olefin-paraffin separations represent a class of most important and also most costly separations in the chemical and petrochemical industry. Cryogenic distillation has been used for over 60 years for these separations (Keller et al., 1992). They remain to be the most energy-intensive distillations because of the close relative volatilities (Humphery et al., 1991). For example, ethane-ethylene separation is carried out at about −25°C and 320 psig (2.306 MPa) in a column containing over 100 trays, and propane-propylene separation is performed by an equally energy-intensive distillation at about −30°C and 30 psig (0.308 MPa) (Keller et al., 1992). A number of alternatives have been investigated (Eldridge, 1993); the most promising one appears to be π-complexation.

Separation by π-complexation is a sub-group of chemical complexation where the mixture is contacted with a second phase containing a complexing agent (King, 1987). The advantage of chemical complexation is that the bonds formed are stronger than those by van der Waals forces alone, so it is possible to achieve high selectivity and high capacity for the component to be bound; at the same time, the bonds are still weak enough to be broken by using simple engineering operations such as raising the temperature or decreasing the pressure. This picture has been illustrated by the bond energy-bond type chart of G.E. Keller (King, 1987).

The π-complexation pertains to the main group (or *d*-block) transition metals, i.e., from Sc to Cu, Y to Ag and La to Au in the periodic table (Cotton and Wilkinson, 1966). These metals or their ions can form the normal σ bond to carbon and, in addition, the unique characteristics of the *d* orbitals in these metals or ions can form bonds with the unsaturated hydrocarbons (olefins) in a nonclassical manner. This type of bonding is broadly referred to as π-complexation. π-complexation has been seriously considered for olefin-paraffin separation and purification by employing liquid solutions containing silver (Ag^+) or cuprous (Cu^{+1})

ions (Quinn, 1971; Ho et al., 1988; Keller et al., 1992; Blytas, 1992; Eldridge, 1993). These involved gas-liquid operations. While gas-solid operations can be simpler as well as more efficient, particularly by pressure swing adsorption, the list of attempts for developing solid π-complexation sorbents is a short one. CuCl, which is insoluble in water, has been considered for olefin-paraffin separations (Gilliland, et al., 1941; Gilliland, 1945; Long, 1972). The only apparently successful solid sorbent of this nature is CuCl/γ-Al_2O_3 for binding with the π bond of CO (Xie and Tang, 1990; Kumar et al. 1993). Hirai et al. (1985a; 1985b) supported Ag^+ salts on anion exchange resins to obtain good C_2H_4/C_2H_6 selectivities. However, the salts apparently caused pore blockage which resulted in low diffusion rates (e.g., $D/R^2 = 9 \times 10^{-5}$ s^{-1} for C_2H_4 at 20°C, Hirai et al., 1985b). More recently, Yang and Kikkinides (1995) investigated two classes of π-complexation sorbents that yielded both high olefin/paraffin selectivities and high diffusion rates. The successful sorbents were: Ag^+ exchanged resins (starting from cation exchange resins) and CuCl/γ-Al_2O_3. It should also be noted that the commercially available sorbents do not have significant selectivities for olefins (over corresponding paraffins) and the use of these sorbents would require additional, substantial operations (Kulvaranon et al., 1990; Kumar et al., 1992; Jarvelin and Fair, 1993; Ghosh et al., 1993). Ion-exchanged zeolites containing Ag^+ and Cu^+ do not show high selectivities for olefins because the paraffins are also strongly adsorbed (due to their high polarizabilities) (Cen, 1991; Yang and Kikkinides, 1995).

Pillared interlayer clays (PILC) are a new class of aluminosilicate material which has attracted increasing interest for both adsorption (Yang and Baksh, 1991; Cheng and Yang, 1995) and catalysis (Burch, 1988). Because PILC has unique structural and chemical properties, it is examined in this work as the support for CuCl monolayer dispersion. This paper reports the results of a study on the equilibrium and kinetic adsorption properties of C_2H_4, C_2H_6, C_3H_6 and C_3H_8 on near-monolayer CuCl supported on several pillared clays.

Experimental

1. Preparation of Pillared Clays

The general procedure for preparation of pillared clays started from the preparation and aging of pillaring agents. At this step, the pillaring agent underwent hydrolysis, polymerization and complexation with anions in the solution. (Baes and Mesmer, 1976). The properties of the resulting pillaring agent can be controlled by varying hydrolysis temperature, solution pH, and aging time of the oligomer solution. The next step was to ion exchange the charge balancing cations (mainly Na^+ in Fisher Bentonite) between the clay layers with the oligomeric cations (prepared from the preceding step) by mixing the slurry of clay suspension and oligomer solution at a certain temperature, pH condition and length of time. Upon completion of the ion exchange step, the sample was washed and then separated from the liquid phase by vacuum filtration or centrifugation. The final step is drying and calcination, by which the intercalated oligomer cation is decomposed into metal oxides, H_2O and protons. The metal oxides serve as pillars propping open the silica layers of montmorillonite, while the protons serve to balance the charge originated from the substitution of Al^{3+} by Mg^{2+} in the octahedral sheets of montmorillonite.

Based upon the preparation methods from literature by Sterte (1986), Pinnavaia (1987) and Vaughan (1979), optimization of the methods were made in our lab, and detailed descriptions of individual pillared clay preparation are given as follows:

TiO_2-PILC Synthesis. The starting clay was a purified monomorillonite, as purified-grade bentonite powder from Fisher Company, which had a particle size of equal or less than 2 μm. The pillaring agent, a solution of partially hydrolyzed Ti-polycations, was prepared by first adding a predetermined amount of $TiCl_4$ into 1M HCl solution based on the suggestion of Sterte (1986). The mixture was then diluted by slowly adding distilled water while stirred to reach a final Ti concentration of 0.82 M, and HCl at an amount corresponding to the final concentration of 0.11 M was used in the preparation. Prior to its use, the solution was aged for 12 hrs at room temperature. A 4 g amount of bentonite was dispersed in 1 l of distilled water by prolonged stirring (5 hr.). The amount of pillaring agent required to obtain a Ti/Clay ratio of 10 (mmol Ti/g clay) was then added to the rigorously stirred suspension. The ion exchange step took 18 hrs. and subsequently the mixture was washed with distilled water several times until the liquid phase was free of chloride ions (by silver nitrate test) and separated from liquid by vacuum filtration. The final product was air dried at 120°C for 12 hrs. and calcined at a final temperature of 350°C for 12 hrs. The sample was then ground to 100–140 mesh.

Al_2O_3-PILC Synthesis. Hydroxy-aluminum oligomeric solution was prepared by slowly adding 0.1 M NaOH to 0.2 M $AlCl_3$ solution under constant stirring until a desired OH/Al ratio was reached. The oligomeric solution was then aged at room temperature for a day. A suspension containing 1% bentonite in deionized water was mixed with the oligometric solution at an Al/clay ratio of 10(mmol Al/g clay). The mixture was allowed to react at room temperature for 12 hrs. before being subjected to washing, filtration and final calcination at 350°C for 12 hrs.

ZrO_2-PILC Synthesis. The oligomeric solution was prepared from $ZrOCl_2 \cdot 8H_2O$ by dissolving the salt in deionized and distilled water to obtain a 0.1 M solution. The solution was aged at room temperature for three days. At a Zr/clay ratio of 5 mmol/g clay, the exchange was conducted at room temperature for three days. The mixture was then washed, filtered, dried and calcined up to 350°C for 12 hrs.

Fe_2O_3-PILC Synthesis. With vigorous mixing, sodium carbonate (Na_2CO_3) was slowly added to a 0.2 M ferric nitrate [$Fe(NO_3)_3$] solution until the OH/Fe ratio reached 2.0 and the pH value of the solution was 1.7. Hydrolysis of the solution was carried out at 25°C for 36 hrs. After slowly adding Fe-oligomeric solution to the clay suspension, the intercalation was conducted at room temperature for 24 hrs. before washing, filtration and calcination up to 350°C for 12 hrs.

2. Pillared Clay Characterization

a. X-Ray Diffraction. A Nicolet/Stoe transmission powder diffractometer with CuKα radiation was used to obtain X-ray diffraction patterns of the power samples.

b. Nitrogen Adsorption at 77 K. A Quantasorb Surface Area Analyzer (Quantachrome Corporation) was used to measure nitrogen adsorption isotherm at liquid nitrogen temperature (77 K). BET surface area was calculated from the isotherm.

3. Spontaneous Dispersion of CuCl on Pillared Clay Samples

The phenomenon of monolayer dispersion on the surface of certain metal oxides and zeolites has been reviewed by Xie and Tang (1990).

Our starting material, montmorillonite, was aluminosilicate. After the pillaring process, the internal surface area was greatly increased which gave rise to pillared clays with a wide variety of pore structures ranging from micropores to mesopores, depending on the starting clay, the pillaring agent and the pillaring conditions used.

CuCl crystals and pillared clays samples were first mixed thoroughly at a predetermined ratio, and then the mixture was calcined in an inert environment at 375°C for 24 hrs.

4. Equilibrium and Diffusion Rate Measurement

The sorption and diffusion experiments were carried out in a Thermogravimetric Analyzer (Cahn 2000 system 113, TGA), equipped with a programmed temperature control unit. High purity helium (Linde, minimum purity 99.945%) was used as the inert carrier gas and the gas for regeneration. The following hydrocarbons were used: ethane (CP grade, Linde, min. purity 99.0%), ethylene (CP grade, Matheson, min. purity 99.5%), propane (CP grade, Matheson, min. purity 99.0%) and propylene (CP grade, Matheson, min. purity 99.0%). Equilibrium isotherm and diffusion uptake rate measurement followed a similar method described in detail by Ackley and Yang (1991). Following each adsorption experiment, a desorption experiment was performed to check the reversibility of adsorption isotherm. In order to calculate the heats of desorption, measurements were conducted at two different temperatures (25°C and 60°C).

Results and Discussion

X-Ray Diffraction Analysis

Since montmorillonite clay contains only small cations (e.g., Na^+ and Ca^{2+}) as layer charge balancing cations and hydrate between layers, it has a d_{001} spacing of 9.76 Å, as shown by XRD in Figure 1. Upon pillaring with large oligometric cations and calcination, metal oxides resides in between the layers through covalence bonds to the adjacent silica tetrahedral surface layer. Therefore, the spacing between the layers depends on the size of the metal oxide pillars. The XRD patterns of the synthesized pillared clays are shown in Figure 1. The 2θ diffraction angle of (001) reflection of all the pillared clays decreased, or the d_{001}

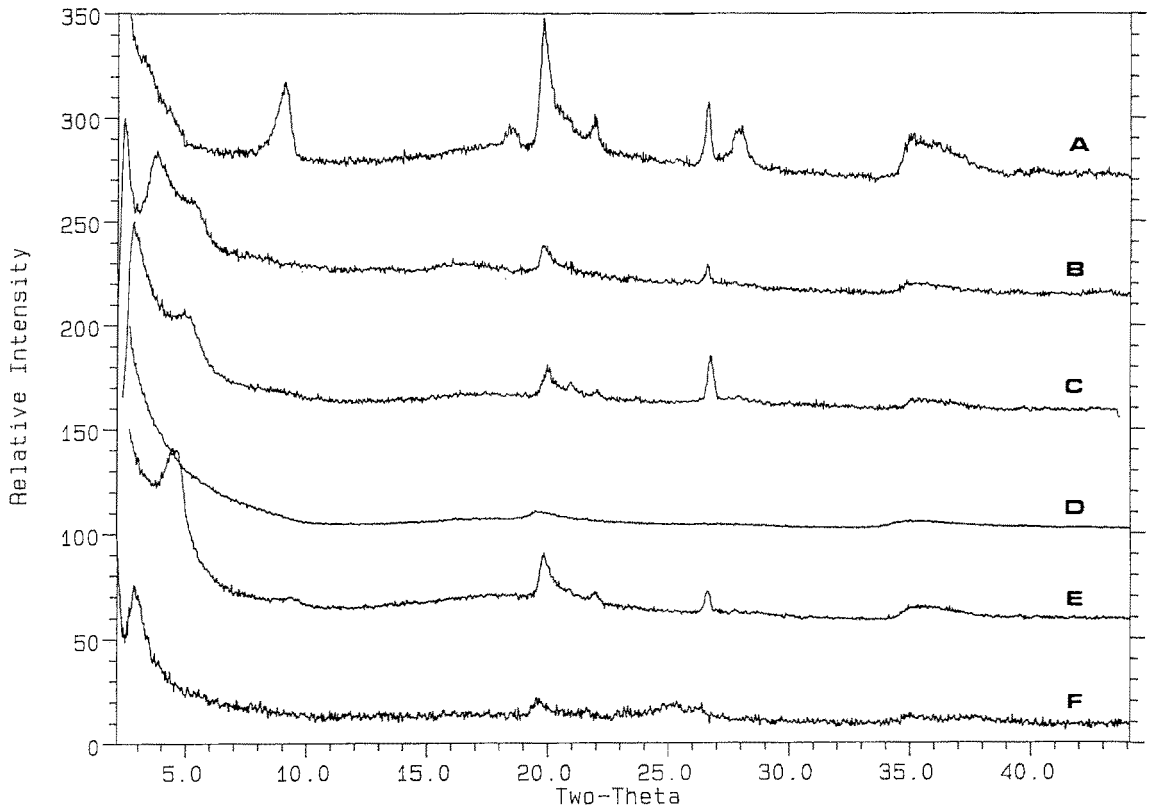

Fig. 1. X-raw powder diffraction patterns of clay and pillared clay samples. (A) Fisher Bentonite, (B) Fe_2O_3-PILC, (C) ZrO_2-PILC, (D) Al_2O_3-Laponite, (E) Al_2O_3-PILC, (F) TiO_2-PILC.

spacing increased, as compared to the original montomorillonite clay. The peak positions of the d_{001} reflection had the following values: 9.76 Å (bentonite), 20.1 Å (Al_2O_3-PILC), 23.5 Å (Fe_2O_3-PILC), 31.0 Å (TiO_2-PILC) and 18.0 Å (ZrO_2-PILC). The free interlayer spacings in these pillared clays were obtained by subtracting 9.6 Å, the thickness of the clay layer. The resulting free interlayer spacings for the pillared clays were: 10.5 Å (Al_2O_3-PILC), 13.9 Å (Fe_2O_3-PILC), 21.4 Å (TiO_2-PILC) and 8.4 Å (ZrO_2-PILC). These results indicated that the pillaring process was successful.

The Al_2O_3 pillared Laponite sample (Courtesy of Laporte Ltd.) was synthesized from Laponite (a synthetic hectorite). Since the clay crystal has a relatively small layer aspect ratio, the platelets tend to have edge-to-edge and edge-to-face aggregates, resulting in a house-of-cards structure. The lack of long-range stacking order causes XRD pattern amorphous as shown in Fig. 1 and the sample be termed as delaminated pillared clay.

Surface Areas and Pore Structures

According to the BDDT classification (Gregg and Sing, 1982), the N_2 adsorption isotherms at 77 K for TiO_2-PILC, Al_2O_3-Laponite and Fe_2O_3-PILC showed type II isotherm shape, indicating the presence of both micropores and mesopores, whereas Al_2O_3-PILC and ZrO_2-PILC showed typical type I isotherms indicating micropores only. The d_{001} spacings, the free interlayer spacings, the BET surface areas and pore volumes of all samples are summarized in Table 1. The large surface areas and pore volumes were again the results of successful pillaring, which prompted us to investigate the use of these pillared clay samples as supports for CuCl monolayer dispersion for the purpose of olefin and paraffin separations.

Monolayer Dispersion

The phenomenon of spontaneous dispersion of oxides and salts in monolayer or submonolayer forms onto the

Table 1. Interlayer spacings, BET surface areas and pore volumes of pillared clays including Al_2O_3-Laponite (LP).

Sample	d_{001} Å	Free Interlayer Spacing, Å	BET S.A., m^2/g	Pore Volume, cm^3/g
Al_2O_3-LP	–	–	453.8	0.39
Al_2O_3-PILC	20.1	10.5	346.5	0.18
Fe_2O_3-PILC	23.5	13.9	267.4	0.16
TiO_2-PILC	31.0	21.4	387.8	0.25
ZiO_2-PILC	18.0	8.4	331.9	0.20
Bentonite	9.8	–	35.1	0.06

surfaces of inorganic supports with high surface areas has been studied extensively by Xie and Tang (1990). If the interactions between the overlayer and substrate are strong enough, monolayer or submonolayer dispersion is a thermodynamically favorable process.

In order to determine the monolayer dispersion capacity of CuCl on TiO_2-PILC, the adsorption isotherms of C_2H_4 were measured with these samples. Figure 2 shows the C_2H_4 adsorption capacities on CuCl/TiO_2-PILC and C_2H_4/CuCl molar ratios as functions of the ratio of CuCl/TiO_2-PILC. The C_2H_4 amount adsorbed at first increased with increasing amount of CuCl content on TiO_2-PILC support. After reaching a maximum at 0.3 of the weight ratio of CuCl/TiO_2-PILC, the C_2H_4 adsorption capacity gradually decreased with further increase in CuCl content. As is known, pillared clay has a relatively wide distribution of pore sizes (Yang and Baksh, 1991), the decrease of C_2H_4 adsorption capacity with increasing CuCl/TiO_2-PILC ratio was probably caused by the blocking of small pores in the support. Compared to the monolayer CuCl/γ-Al_2O_3 of 0.5 used by Yang and Kikkinides (1995), the optimum CuCl/TiO_2-PILC ratio of 0.3 on pillared clay was lower. This result can be attributed to the difference between the surfaces of the two supports. Unlike γ-Al_2O_3, pillared clays contain two kinds of oxides that are exposed on the surface. One is the surface of the tetrahedral clay layer of SiO_2; the other is the surface of the metal oxide pillars (e.g., TiO_2 and Al_2O_3) inserted between the silica layers. The monolayer dispersion capacity has been shown to depend on the support surface properties (Xie and Tang, 1990). While the monolayer capacities for CuCl on γ-Al_2O_3 and TiO_2 are approximately the same, it is lower for SiO_2. This difference can only account partially for the different coverage capacities observed for Al_2O_3 and pillared clays. The lower ratio of 0.3 for CuCl/TiO_2-PILC indicated that the CuCl on the PILC was below a full monolayer coverage. Therefore, the dispersion should be termed more precisely as submonolayer dispersion (Xie and Tang, 1990). As shown also in Figure 2, C_2H_4/CuCl molar ratio decreased monotonously with increasing CuCl/TiO_2-PILC ratio, which was due to both energetic and steric factors. Upon dispersion, Cu^+ filled the vacancy on oxide surface to be 4-, 5-, or 6-coordinated with O^{2-}. However, only 4-coordinated Cu^+ ions can form π-complex with olefins, and their relative amount decreases with increasing Cu^+ ions occupying 5-, or 6-coordinated sites. As the CuCl content becomes high enough, the mismatch of Cl^- ions (1.81 Å) and O^{2-} ions (1.32 Å) on the surface causes the congregation of CuCl and hence less available Cu^+ ions (Gui, et al 1984).

Equilibrium Isotherms

The equilibrium isotherms of C_2H_4 and C_2H_6 on CuCl/TiO_2-PILC at 25°C and 60°C are are shown in Figure 3. Also shown are the C_2H_4 and C_2H_6 isotherms on the original TiO_2-PILC sample at 25°C. Due to the slightly higher polarizability of C_2H_4 (than C_2H_6), the amount adsorbed of C_2H_4 on the uncovered pillared clay was also slightly higher. With CuCl dispersion, the C_2H_6 adsorption was significantly enhanced, whereas the C_2H_6 adsorption was suppressed. The strong C_2H_4 adsorption was caused by π-complexation of the unsaturated π bond with the Cu(I) cation. The suppression of C_2H_6 adsorption by CuCl dispersion was indicative of weaker interaction on CuCl than pillared clay surface. A similar suppression behavior for C_2H_6 adsorption was observed by Hirai et al. (1985b) on an adsorbent by doping copper (I) chloride on polystyrene resin having amino groups. Ion exchange of Na^+ by Cu^+ on *Y* zeolite also resulted in suppression of C_2H_6 adsorption (Cen, 1991). The net result of the C_2H_6 suppression and the π-complexation with C_2H_4 was the significant increase

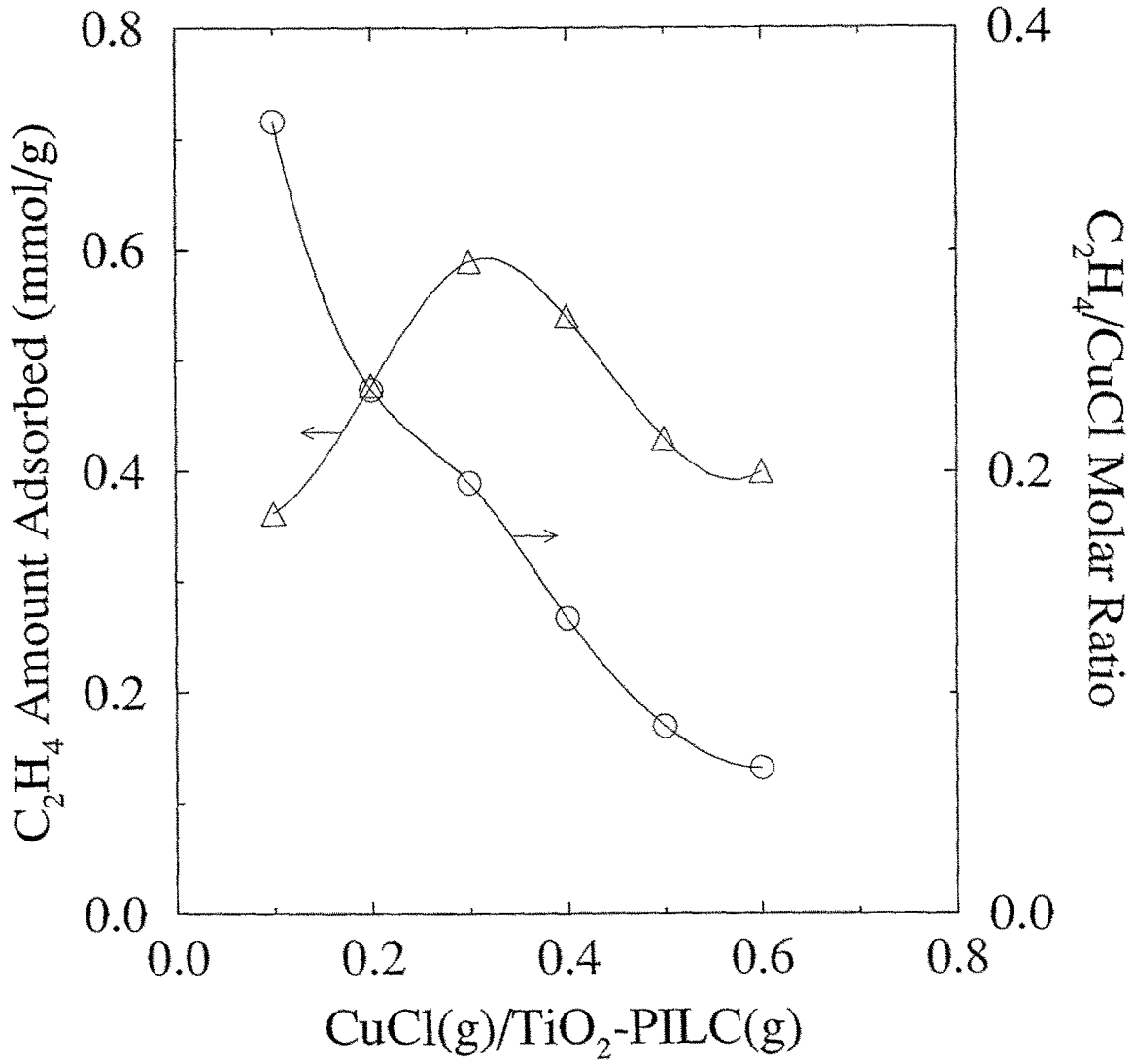

Fig. 2. Ethylene adsorption and ethylene to CuCl molar ratio as a function of CuCl content in CuCl/TiO_2-PILC at 1 atm and 25°C.

of the pure-component selectivity ratio of C_2H_4/C_2H_6 from 1.2 to 5.3 (at 1 atm and 25°C) by CuCl dispersion. A comparison of this result with the CuCl/γ-Al_2O_3 result of Yang and Kikkinides (1995) shows that the C_2H_4 capacity on CuCl/TiO_2-PILC is about 15% lower. Considering the close surface areas of the two supports, the lower C_2H_4 adsorption again reflects the submonolayer coverage by CuCl on the pillared clay.

The equilibrium adsorption isotherms of C_3H_6 and C_3H_8 on CuCl/TiO_2-PILC at 25°C and 60°C are shown in Figure 4, with the pure-component selectivity ratio of C_3H_6/C_3H_8 being 2.9 at 1 atm and 25°C. Although the C_3H_6/C_3H_8 ratio was modest, the differential in the amounts adsorbed of C_3H_6 between $p = 1.0$ and $P = 0.1$ atm was 0.45 mmol, which was much higher than the corresponding value for CuCl/γ-Al_2O_3. Further discussion on this aspect will follow in a later section. The equilibrium adsorption isotherms of C_2H_4 and C_2H_6 on Al_2O_3-LP (Laponite), Al_2O_3-PILC, ZrO_2-PILC and Fe_2O_3-PILC samples (without CuCl dispersion) are shown in Figure 5. Again, the surfaces on these samples exhibited only a small preference for C_2H_4 due to its higher polarizability (than C_2H_6). The differences among different samples were caused mainly by the differences in surface areas and pore volumes, and only to a small extent by the surface

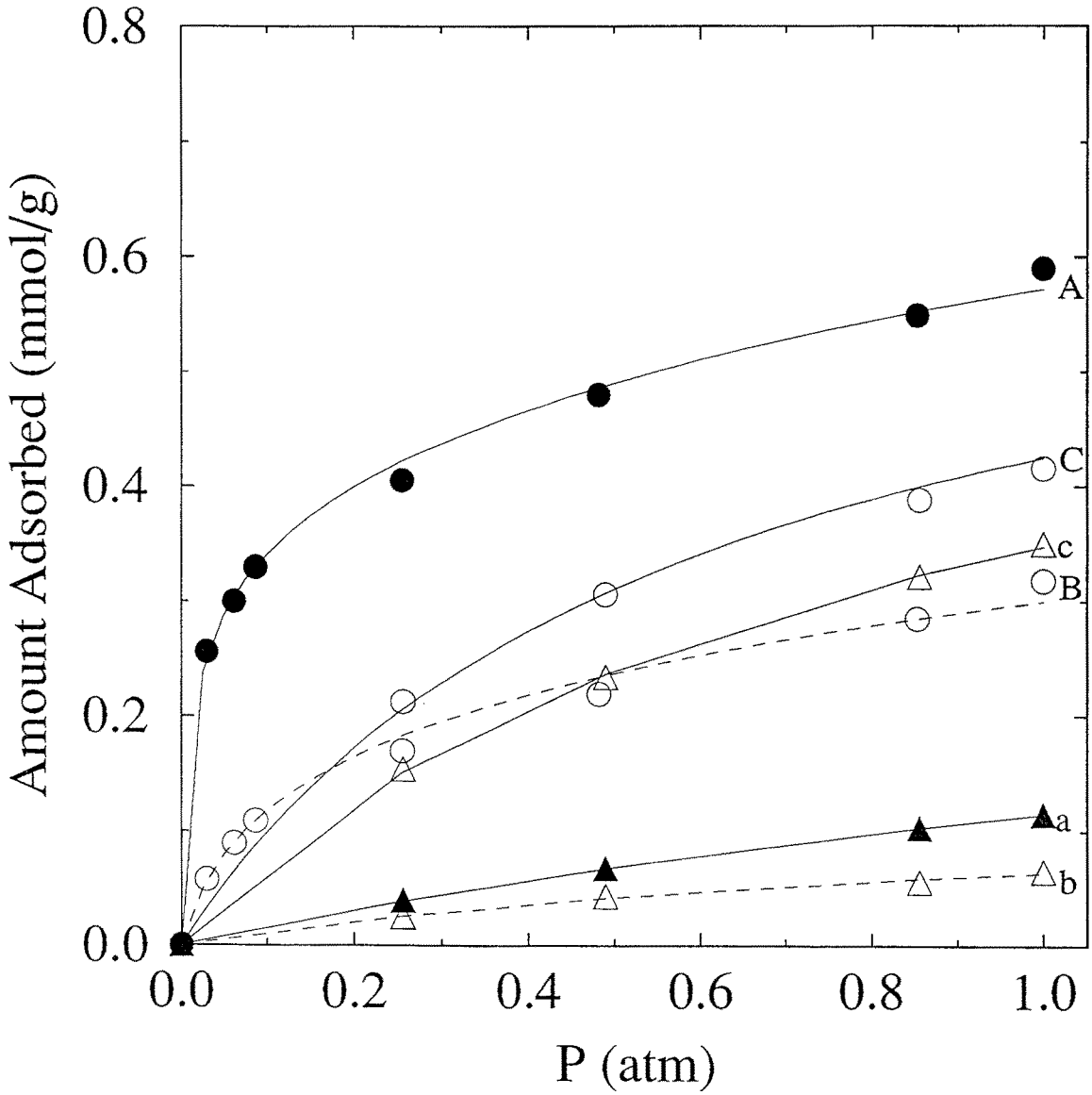

Fig. 3. Equilibrium isotherms of C_2H_4 and C_2H_6 on TiO_2-PILC and $CuCl/TiO_2$-PILC. (A) C_2H_4 on $CuCl/TiO_2$-PILC at 25°C, (B) C_2H_4 on $CuCl/TiO_2$-PILC at 60°C, (C) C_2H_4 on TiO_2-PILC at 25°C, (a) C_2H_6 on $CuCl/TiO_2$-PILC at 25°C, (b) C_2H_6 on $CuCl/TiO_2$-PILC at 60°C, (c) C_2H_6 on TiO_2-PILC at 25°C.

composition. Figures 6 and 7 display, respectively, the pure-component C_2H_4/C_2H_6 and C_3H_6/C_3H_8 equilibrium adsorption isotherms on CuCl dispersed samples, including Al_2O_3-LP, Al_2O_3-PILC, ZrO_2-PILC and Fe_2O_3-PILC. The ratios of C_2H_4/C_2H_6 and C_3H_6/C_3H_8 on all CuCl dispersed samples are listed in Table 2.

The results show that, after CuCl dispersion on the Al_2O_3-LP, Al_2O_3-PILC, ZrO_2-PILC samples, the C_2H_4 adsorption increased, while the adsorption of C_2H_6 decreased. CuCl dispersion had the same effect on

Table 2. Pure-component selectivity ratios for C_2H_4/C_2H_6 and C_3H_6/C_3H_8.

Sample	Selectivity Ratio	
	C_2H_4/C_2H_6	C_3H_6/C_3H_8
$CuCl/TiO_2$-PILC	5.3	2.9
$CuCl/Al_2O_3$-LP	4.2	2.0
$CuCl/Al_2O_3$-PILC	2.4	1.6
$CuCl/ZrO_2$-PILC	2.6	1.7
$CuCl/Fe_2O_3$-PILC	2.1	1.4

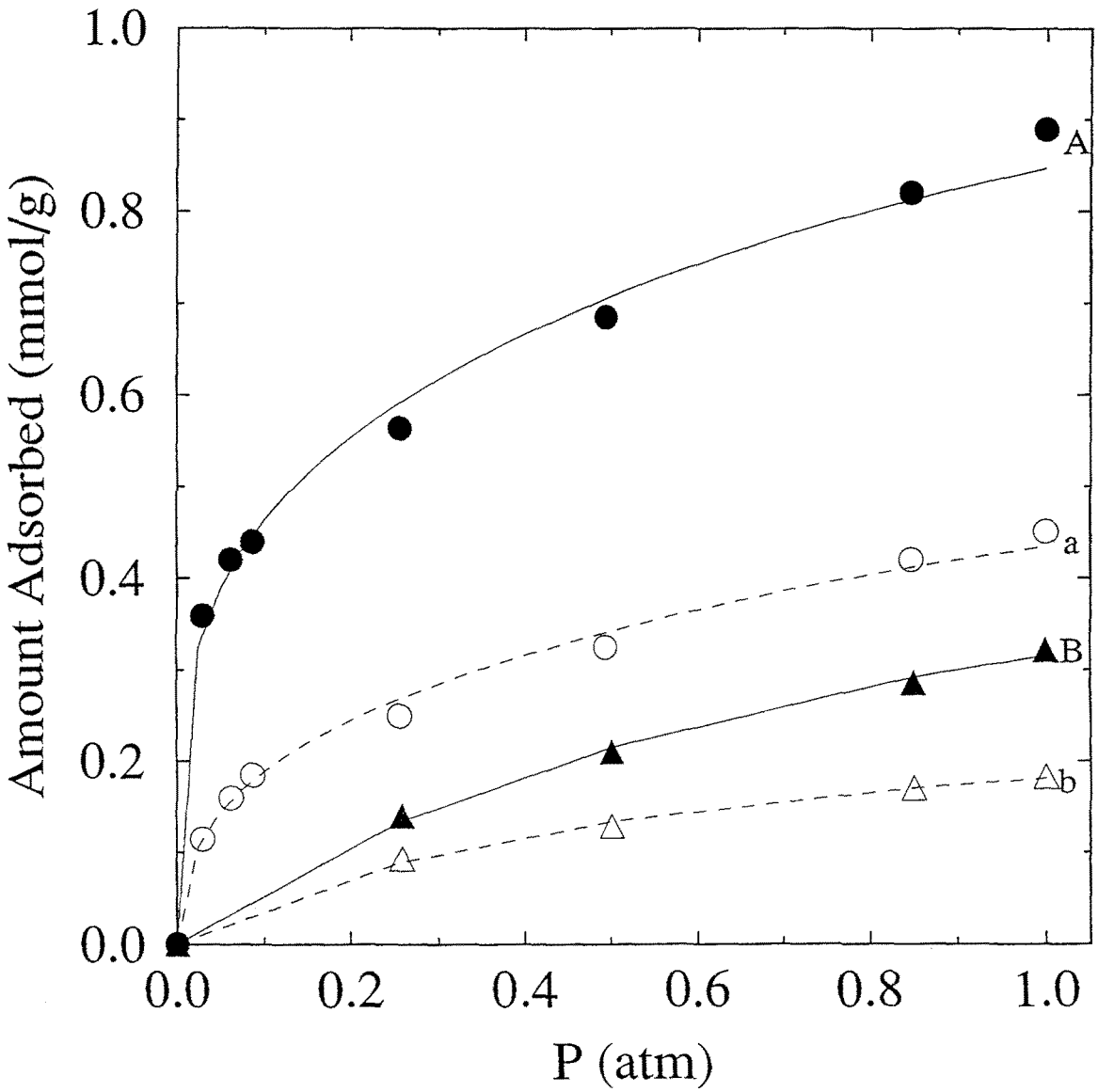

Fig. 4. Equilibrium isotherms of C_3H_6 and C_3H_8 on $CuCl/TiO_2$-PILC. (A) C_3H_6 on $CuCl/TiO_2$-PILC at 25°C, (B) C_3H_8 on $CuCl/TiO_2$-PILC at 25°C, (a) C_3H_6 on $CuCl/TiO_2$-PILC at 60°C, (b) C_3H_8 on $CuCl/TiO_2$-PILC at 60°C.

these samples as on TiO_2-PILC, but to a smaller extent. Unlike the other pillared clays, Fe_2O_3-PILC adsorbed less amount of C_2H_4 upon CuCl dispersion. The fact that Fe_2O_3-PILC contains quite a fraction of mesopores seems to preclude the pore blocking mechanism. However, the actual monolayer capacity for CuCl on Fe_2O_3-PILC is possibly much less then on other pillared clays due to the incompatibility of Fe_2O_3 with CuCl in lattice matching, and thus the excess CuCl may have formed conglomerate blocking the pores.

Isosteric Heats of Adsorption

From the adsorption isotherms at two temperatures, 25°C and 60°C, isosteric heats of adsorption were calculated for different systems and are given in Table 3.

The adsorption of olefins (C_2H_4 and C_3H_6) involves π-complexation which is a weak chemical bond, as reflected by the heats of adsorption in the range 10.7 to 13.7 kcal/mol. The isosteric heats of adsorption for the olefins were, however, substantially higher than

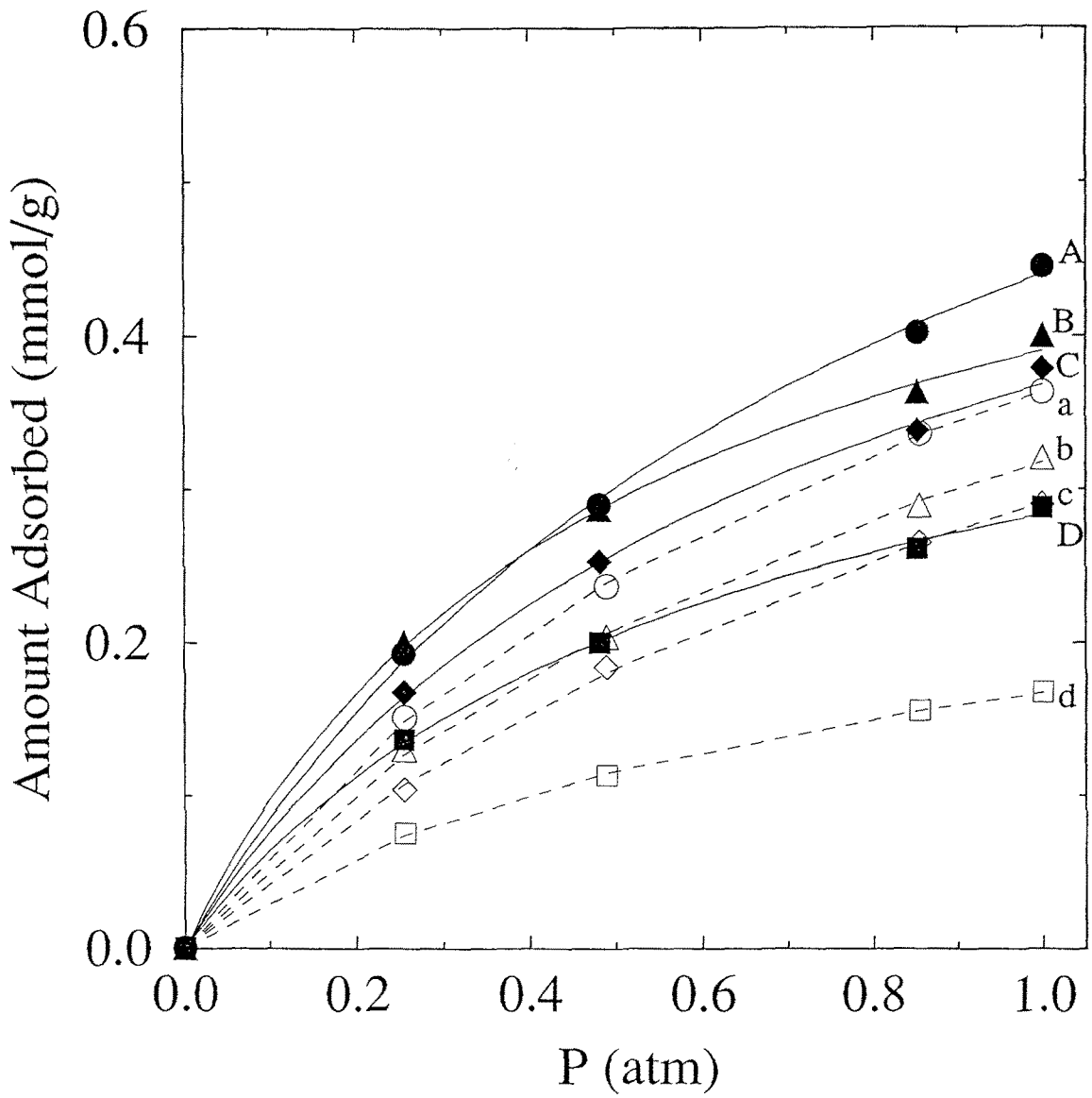

Fig. 5. Equilibrium isotherms of C_2H_4 and C_2H_6 on pillared clay samples at 25°C. (LP = Laponite). (A) C_2H_4 on Al_2O_3-LP, (B) C_2H_4 on Al_2O_3-PILC, (C) C_2H_4 on ZrO_2-PILC, (D) C_2H_4 on Fe_2O_3-PILC, (a) C_2H_6 on Al_2O_3-LP, (b) C_2H_6 on Al_2O_3-PILC, (c) C_2H_6 on ZrO_2-PILC, (d) C_2H_6 on Fe_2O_3-PILC.

Table 3. Isosteric heats of adsorption (ΔH).

Sample	$-\Delta H$, kcal/mol			
	C_2H_4	C_2H_6	C_3H_6	C_3H_8
CuCl/TiO_2-PILC	13.7	4.8	13.0	5.2
CuCl/Al_2O_3-LP	12.2	5.4	11.9	6.3
CuCl/Al_2O_3-PILC	11.4	5.5	11.2	6.4
CuCl/ZrO_2-PILC	11.0	5.7	10.7	6.9
CuCl/Fe_2O_3-PILC	11.2	5.5	10.8	6.6

those of paraffins which involved only van der Waals forces.

An interesting result on Table 3 is the comparison between C_2H_4 and C_3H_6. The heats of adsorption of C_2H_4 were slightly, but consistently, higher than those of C_3H_6. This result indicates that the π-complexation between C_2H_4 and CuCl/PILC is stronger than that with C_3H_6. This result is different from the comparison with CuCl/γ-Al_2O_3 (Yang and Kikkinides, 1995), where the heats of adsorption

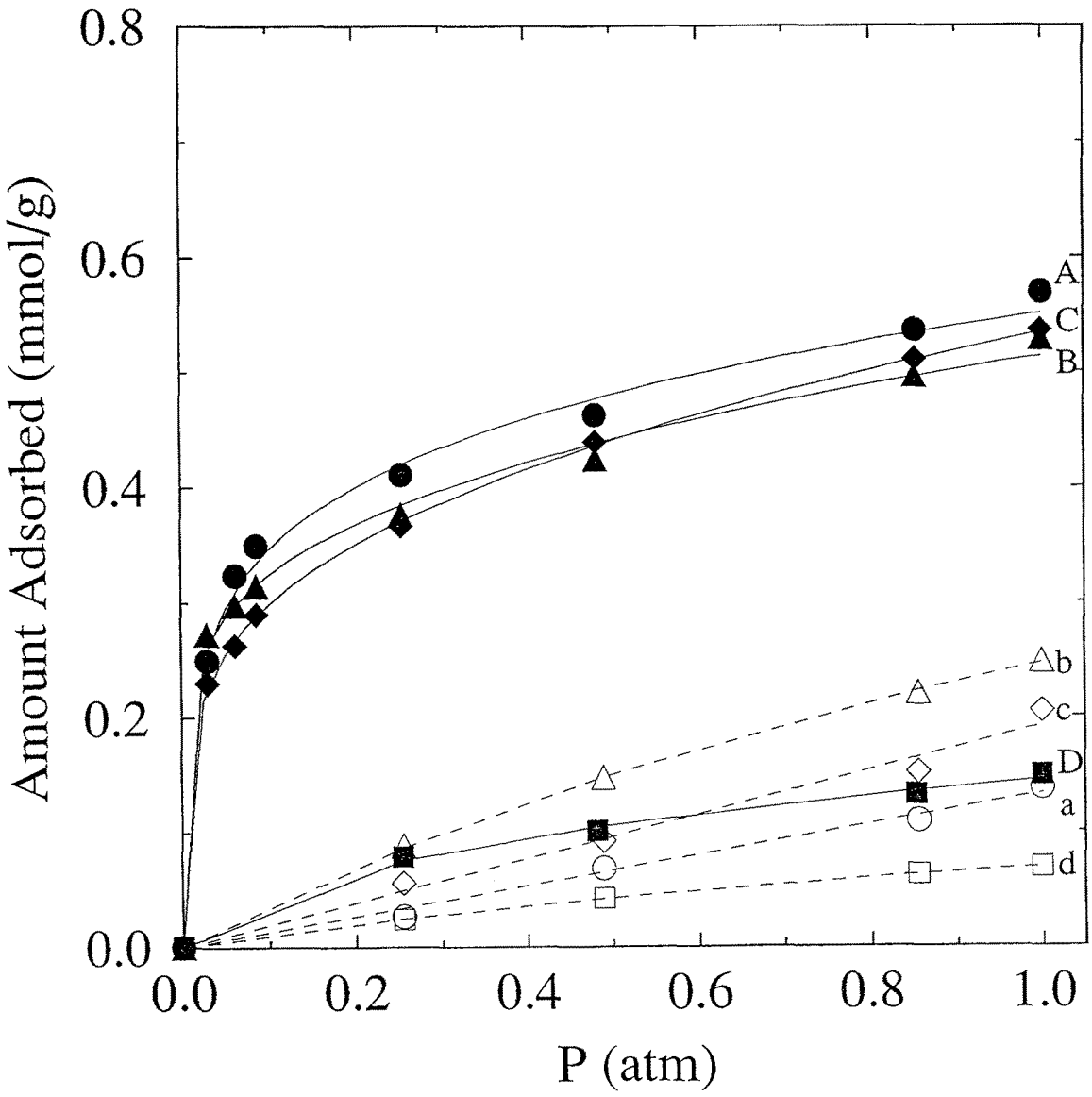

Fig. 6. Equilibrium isotherms of C_2H_4 and C_2H_6 on CuCl dispersed on pillared clay samples at 25°C. (A) C_2H_4 on $CuCl/Al_2O_3$-LP, (B) C_2H_4 on $CuCl/Al_2O_3$-PILC, (C) C_2H_4 on $CuCl/ZrO_2$-PILC, (D) C_2H_4 on $CuCl/Fe_2O_3$-PILC, (a) C_2H_6 on $CuCl/Al_2O_3$-LP, (b) C_2H_6 on $CuCl/Al_2O_3$-PILC, (c) C_2H_6 on $CuCl/ZrO_2$-PILC, (d) C_2H_6 on $CuCl/Fe_2O_3$-PILC.

for C_3H_6 were higher. In view of the molecular orbital (MO) calculations (Chen and Yang, 1995), this result is not surprising. The MO results showed that the π-complexation bond depends strongly on the local chemical environment of the cation (in this case, Cu^+). In fact, the MO calculations predicted (Chen and Yang, 1995) that the π-complexation bond of C_2H_4 on $Ag^+SO_3C_6H_5$ (a model compound used for Ag^+ ion exchanged resin) is higher than that of C_3H_6 on the same sorbent.

Diffusion Rates of Paraffins and Olefins

Since pillared clays consist of platelet crystals, the diffusion process was two dimensional, and the diffusion equation in cylindrical coordinates was used. The diffusion time constant, D/R^2, was calculated by nonlinear regression by fitting the experimental data with the solution of the diffusion equation:

$$\frac{M_t}{M_\infty} = 1 - 4\sum_{n=1}^{\infty} \frac{1}{\beta_n^2} \exp\left(-\frac{\beta_n^2 t D}{R^2}\right) \qquad (1)$$

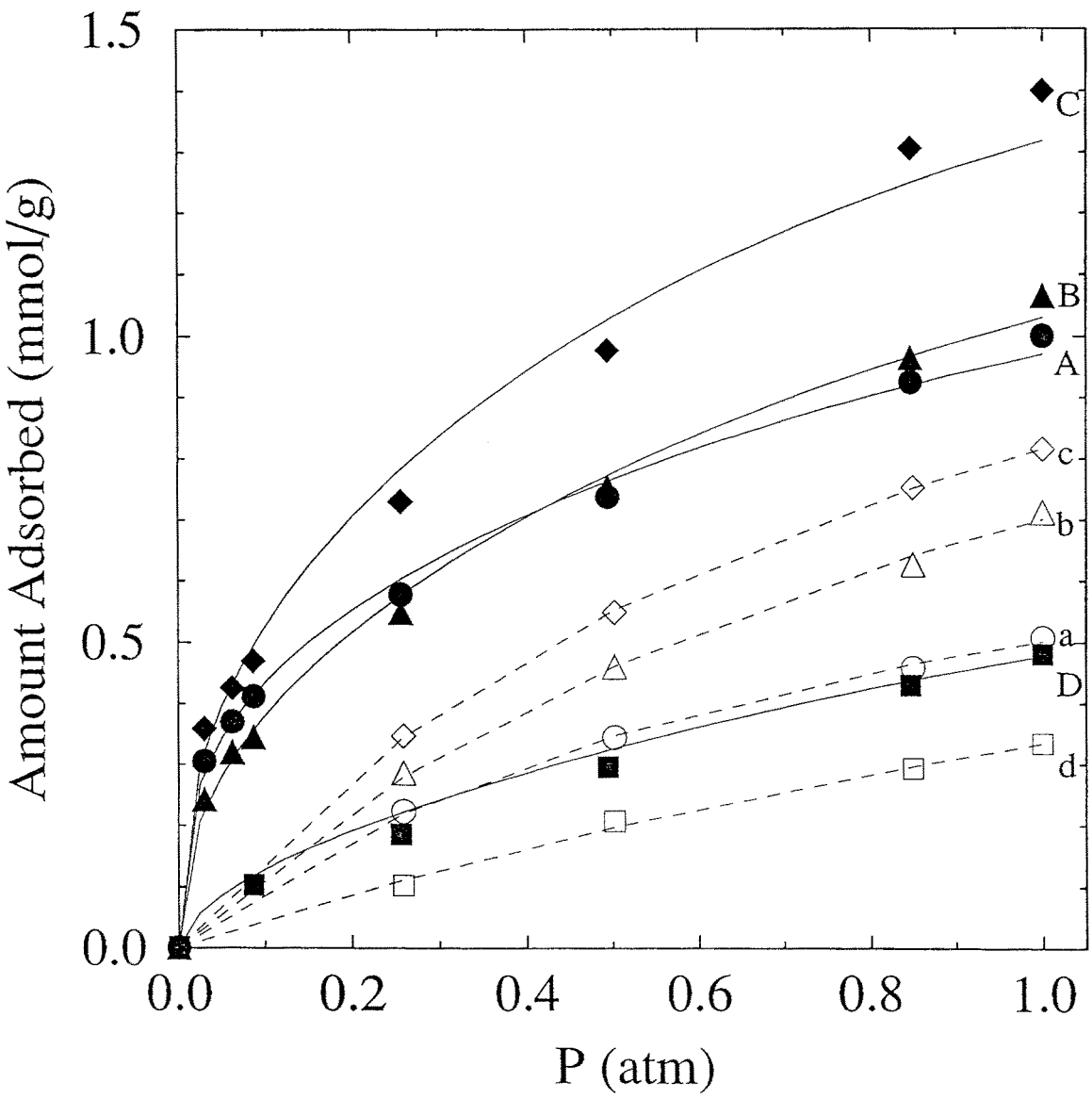

Fig. 7. Equilibrium isotherms of C_3H_6 and C_2H_6 on CuCl monolayer dispersed pillared clay samples at 25°C. (A) C_3H_6 on $CuCl/Al_2O_3$-LP, (B) C_3H_6 on $CuCl/Al_2O_3$-PILC, (C) C_3H_6 on $CuCl/ZrO_2$-PILC, (D) C_3H_6 on $CuCl/Fe_2O_3$-PILC, (a) C_3H_8 on $CuCl/Al_2O_3$-LP, (b) C_3H_8 on $CuCl/Al_2O_3$-PILC, (c) C_3H_8 on $CuCl/ZrO_2$-PILC, (d) C_3H_8 on $CuCl/Fe_2O_3$-PILC.

where β_n are the roots of the Bessel function of the first kind of zero order:

$$J_0(\beta_b) = 0 \tag{2}$$

As shown in Figure 8, diffusion of C_2H_4 and C_2H_6 in $CuCl/TiO_2$-PILC was rapid, and completed in about two minutes. Whereas C_3H_8 and C_3H_6 diffusion rates were relatively slow with over 50% completion achieved in six minutes at 25°C and 0.26 atm. The diffusion time constants (D/R^2) of different adsorbate-systems are listed in Table 4. These data showed a correlation between the pore structure of the original pillared clays and the diffusion rates. The house-of-cards structure of the delaminated Al_2O_3 pillared Laponite resulted in a large portion of mesopores and consequently high diffusion rates. The ZrO_2-PILC sample, on the other hand, contained mainly micropores hence yielded slow diffusion rates.

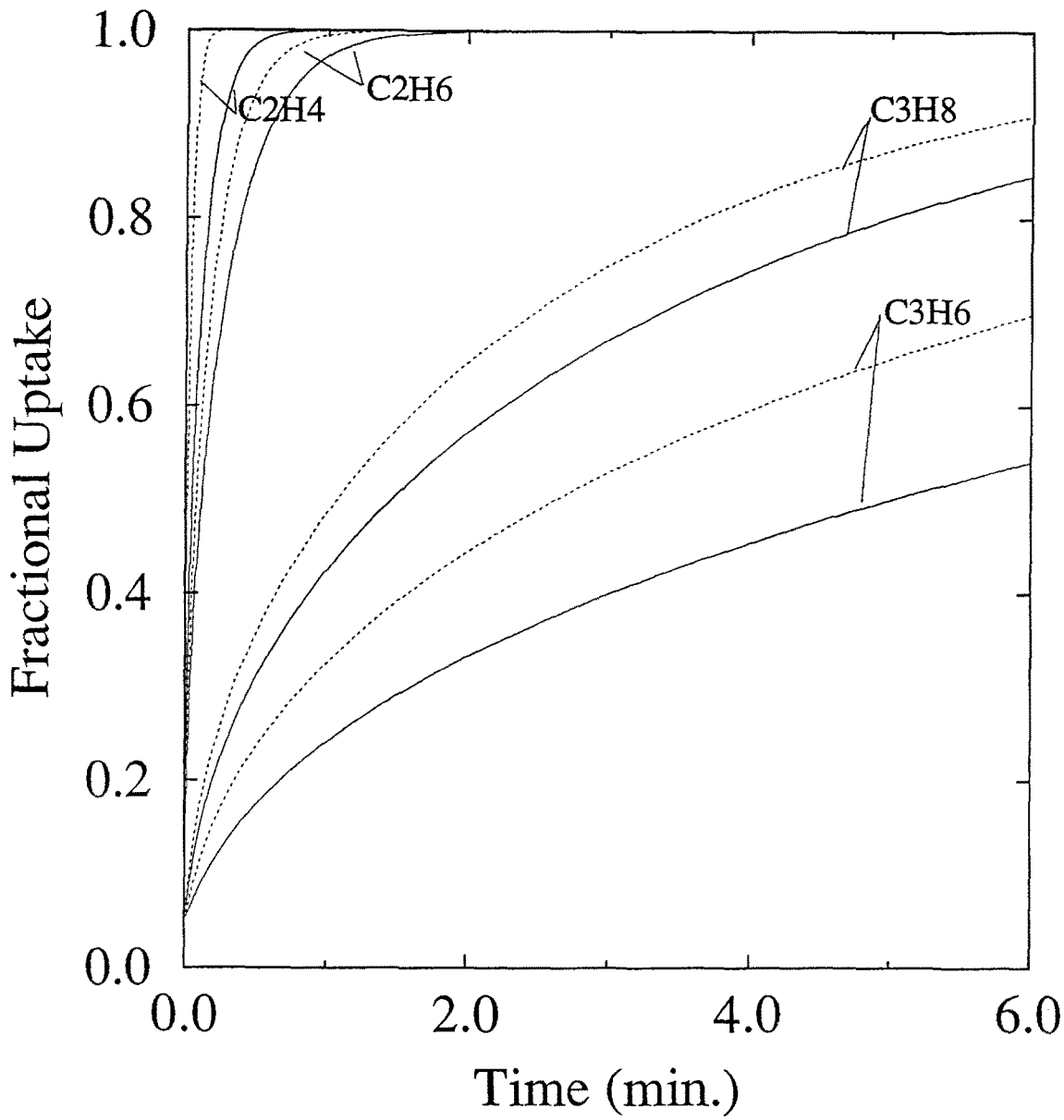

Fig. 8. Uptake rates (at $p = 0.26$ atm) on CuCl/TiO_2-PILC at 25°C (solid curves) and 60°C (dashed curves).

Mechanism of Adsorption, Isotherm Equation and Relevance for Separation

The basic concept for π-complexation was described in a qualitative theory by Dewar (1951). The outer shell orbital for Cu(I) consists of an empty s orbital and filled d orbitals (by 10 electrons). The π-complexation is formed by a σ-bond from the overlap of the empty s orbital of the metal with a filled $2p\pi$ orbital of the olefin (i.e., donation of π electrons from olefin to the metal), and by the overlap of filled d-orbitals of the metal with a vacant $2p\pi^*$ antibonding orbital of the olefin (i.e., back donation of electrons to the empty olefin antibonding orbital). The recent molecular orbital calculations performed in our laboratory (Chen and Yang, 1995) showed that the π-σ dona-

Table 4. Diffusion time constants (D/R^2)

	$D/R^2(\text{sec}^{-1})$							
	25°C		60°C		25°C		60°C	
Sample	C_2H_4	C_2H_6	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_3H_6	C_3H_8
$CuCl/Al_2O_3$-LP	1.8×10^{-2}	1.0×10^{-2}	4.8×10^{-2}	2.5×10^{-2}	1.2×10^{-3}	1.5×10^{-3}	2.2×10^{-3}	3.0×10^{-3}
$CuCl/TiO_2$-PILC	2.3×10^{-2}	9.3×10^{-3}	8.1×10^{-2}	1.4×10^{-2}	2.2×10^{-4}	6.9×10^{-4}	4.1×10^{-4}	9.2×10^{-4}
$CuCl/Al_2O_3$-PILC	5.4×10^{-3}	3.7×10^{-3}	6.0×10^{-3}	4.2×10^{-3}	6.0×10^{-5}	7.2×10^{-5}	7.1×10^{-5}	9.0×10^{-5}
$CuCl/ZrO_2$-PILC	3.9×10^{-3}	1.3×10^{-3}	4.9×10^{-3}	3.5×10^{-3}	5.5×10^{-5}	6.2×10^{-5}	5.8×10^{-5}	8.4×10^{-5}
$CuCl/Fe_2O_3$-PILC	5.5×10^{-3}	4.0×10^{-3}	6.4×10^{-3}	6.0×10^{-3}	5.2×10^{-5}	7.0×10^{-5}	8.3×10^{-5}	9.1×10^{-5}

tion is the major contribution to the π-complexation whereas the back donation of the d-orbital electrons from the metal makes only a minor contribution. For the example of C_2H_4 on $AgSO_3C_6H_5$ (a model compound used for Ag^+ exchanged resin), the σ donation accounts for 84% of the bond whereas the d-π^* back donation accounts for only 16% (Chen and Yang, 1995).

An equilibrium isotherm equation has been derived (Yang and Kikkinides, 1995) by considering the adsorption of olefin molecules as the sum of physical adsorption and π-complexation. The physical adsorption can be represented by the Langmuir isotherm. Chemisorption is the result of a reversible reaction which, for energetically homogeneous surfaces, also leads to the Langmuir isotherm. Using the uniform energy distribution (Valenzuela and Myers, 1989) for the chemisorption, the following overall isotherm equation was derived by Yang and Kikkinides (1995):

$$q = \frac{q_{mp} b_p P}{1 + b_p P} + \frac{q_{mc}}{2s} \ln \frac{1 + b_c P e^{s}}{1 + b_c P e^{-s}} \qquad (3)$$

where subscripts p and c indicate, respectively, physical adsorption and chemisorption, q_m is the saturated amount absorbed, b is the Langmuir constant, P is pressure, and s is the heterogeneity parameter which indicates the spread of the energy. When $s \to 0$, the chemisorption term in Eq. 3 (i.e., the second term on the RHS) reduces to the Langmuir isotherm.

Equation 3 was used to fit all equilibrium data by regression. The fitted curves are plotted on Figures 3–7. Of particular interest for separations are the data on C_2H_6, C_2H_4, C_3H_8 and C_3H_6 on $CuCl/TiO_2$-PILC. The isotherm fitting parameters for these systems at 25°C are given in Table 5. As noted earlier by Yang and Kikkinides (1995), there were only two fitting parameters for the paraffins, while these two parameters were

Table 5. Equilibrium (eq. 3) parameters for $CuCl/TiO_2$-PILC at 25°C

	q_{mp}, mmol/g	b_p, atm^{-1}	q_{mc}, mmol/g	b_c, atm^{-1}	s
C_2H_6	0.348	0.51			
C_2H_4	0.260	0.49	0.76	4.75	5.8
C_3H_8	0.592	1.17			
C_3H_6	0.480	1.15	1.05	2.00	8.5

to be used as the upper bounds for the corresponding olefins. Thus there were only three fitting parameters for the olefins.

The fitted isotherm parameters shown on Table 5 are reasonable values. Of particular significance are the values of s, the heterogeneity parameter. For C_2H_4 on Ag^+ exchanged resin, $s = 3.5$, and for C_3H_6 on the same sorbent, $s = 5.0$ (Yang and Kikkinides, 1995). The respective values from Table 5 are 5.8 and 8.5. A higher value of s indicates a higher degree of heterogeneity and the direct consequence is the larger differential of the absorbed amount between two partial pressures.

The C_2H_4 and C_3H_6 isotherms (on $CuCl/TiO_2$-PILC) are compared with those on $CuCl/\gamma$-Al_2O_3, shown in Figure 9. The height of the knee on the isotherm is determined by the π-complexation, and it is not useful for separation. The value of Δq between two practical partial pressures (e.g., 0.1 and 1 atm) is of direct use for separation. This Δq, or working capacity, is determined by the steepness of the isotherm above the knee. As mentioned, the steepness in this portion of the isotherm depends on the heterogeneity. The higher s values for $CuCl/TiO_2$-PILC are therefore of use to separations.

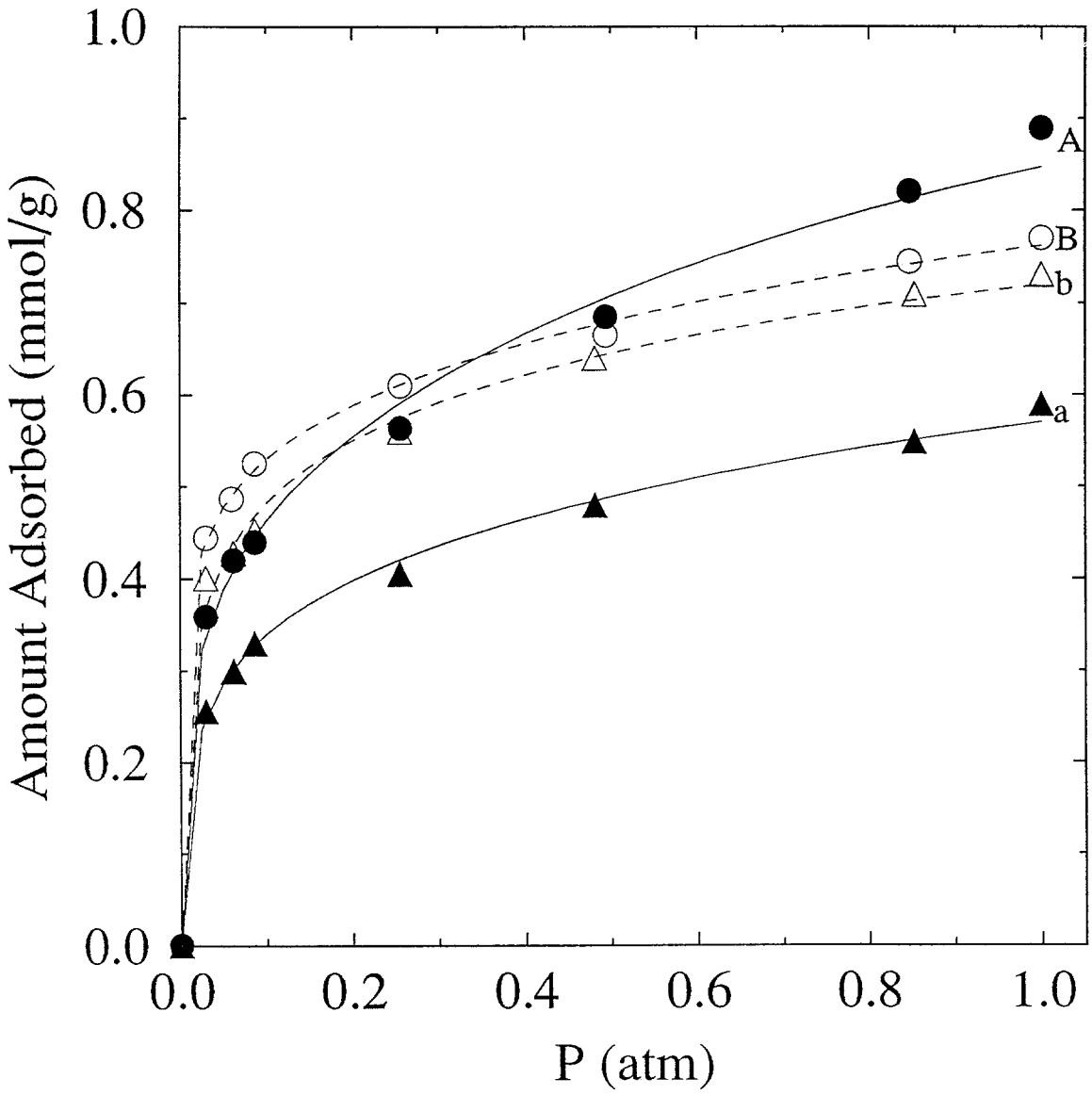

Fig. 9. Comparison of equilibrium isotherms showing differences in the steepness of the portions above the knees. (A) C_3H_6 on $CuCl/TiO_2$-PILC (25°C) (B) C_3H_6 on $CuCl/\gamma$-Al_2O_3 (25°C) (a) C_2H_4 on $CuCl/TiO_2$-PILC (25°C) (b) C_2H_4 on $CuCl/\gamma$-Al_2O_3 (25°C).

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