New Sorbents for Olefin/Paraffin Separations by Adsorption via π-Complexation

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New adsorbents for olefin/paraffin separation are synthesized by effective dispersion of Ag(I) and Cu(I) cations on substrates with hydrocarbon-phobic surfaces. These cations bind olefin molecules by a π-complexation bond, a weak chemical bond. Ethane/ethylene and propane/propylene separations are considered. Cation exchange resins and $CuCl/\gamma\text{-}Al_2O_3$ are effective substrates. On the Ag(I) resin at 25°C and 1 atm, the equilibrium adsorption ratio for $C_2H_4/C_2H_6 = 9.2$ and C_2H_4 capacity $= 1.15$ mmol/g; the corresponding values for $C_3H_6/C_3H_8 = 10.4$ and C_3H_6 capacity $= 1.29$ mmol/g. The $CuCl/\gamma\text{-}Al_2O_3$ sorbent shows equally promising results. The sorption rates are pore-diffusion-controlled and rapid. The olefin selectivity, capacity, and rates are much higher than all previous attempts and are suitable for applications in cyclic adsorption processes.

The equilibrium data are correlated with an isotherm equation that accounts for both physical adsorption and π-complexation with energy heterogeneity, using only two true fitting parameters. Molecular orbital calculations using a $C_6H_5SO_3^-$ substrate indicate that the π-complexation bond is contributed mainly by the donation of olefin π-bond electrons to the empty s-orbital of the metal, while the $d\text{-}\pi^*$ back donation contributes only 16%. Moreover, the relative order of the heats of adsorption is correctly predicted.

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. 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 subgroup 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, that is, 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, which 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). Other attempts on solid sorbents for π-complexation will be discussed along with our results. The only apparently successful solid sorbent of this nature is $CuCl/\gamma\text{-}Al_2O_3$ for binding with the π bond of CO (Xie and Tang, 1990; Kumar et al. 1993). 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).

Three basic types of sorbents were selected for study. The first type consisted of ion-exchanged zeolites containing Ag^+ and Cu^+. Even though prior studies (Cen, 1991) indicated that they would not have very high selectivities for olefins, these sorbents provided a baseline against which superior sorbents could be measured. In addition to these zeolites, two new types of ion-carrying substrates were studied: cation-exchanged resins and monolayer salts on alumina. These three sorbent types were studied using two binary hydrocarbon pairs: ethane/ethylene and propane/propylene. To complement the experimental studies and the data interpretation, molecular orbital calculations were also performed in order to gain insight into the π-complexation bonds.

Experimental Studies

Preparation of sorbents

The two basic techniques employed to introduce Ag^+ or Cu^+ on different substrates were ion exchange and spontaneous monolayer dispersion of Ag^+ or Cu^+ containing salts, depending on the type of substrate used. Ion exchange was applied to zeolite (type Y) and polystyrenic resin. The second technique was applied to the substrate of $\gamma\text{-}Al_2O_3$.

Ag^+ Exchanged Y-Zeolites. The Y-zeolite sample was first washed thoroughly with distilled water at 60°C. Then it was added to an aqueous solution of 0.2N $AgNO_3$ at a proportion of 25 mL per 10 g of zeolite. Eight total exchanges were performed at room temperature. The time duration of each exchange increased with the number of exchange and was around 10 min for the first exchange and up to 12 h for the last exchange.

After the exchanges were completed the sample was washed again thoroughly with distilled water at 60°C and was dried *in vacuo* for several hours. The final drying was conducted at 60°C overnight. The dried sample was calcined by heating from 100 to 350°C at a slow heating rate of 0.5°C/min.

Ag^+ Exchanged Resins. A cation-exchange polymeric resin, Amberlyst 15 from Rohm and Haas Company, was used as the substrate for ion exchange. Amberlyst 15 is a functionalized, porous polystyrene cross-linked with 20% divinyl benzene (Albright, 1986). It is available in the form of strong spherical particles in the size range of 16–50 US mesh, with about 50% in the 20–30 mesh range. The BET surface area was 55 m^2/g, and the surface was functionalized by sulfonic acid with a cation (proton) exchange density of 4.7 meq/g. The average pore diameter was 24 nm. Other properties are available from Albright (1986).

The ion exchange procedure involved mainly exchange of H^+ by Ag^+. Prior to ion exchange, the sample was washed successively with distilled/deionized water and methanol, followed by drying in air at 100°C for 2 h. The sample was ready for ion exchange. For each exchange, 5 g of dry resin was added to 250 mL of dilute aqueous solution of $AgNO_3$ (0.014 N). The exchange was allowed for 10 to 14 h at room temperature. After a number of exchanges were made, the resin sample was again subjected to successive washings in water and methanol (twice each) followed by drying at 100°C in air for 2 h. The sample was again weighed. All washings were performed at room temperature with stirring. The use of methanol was to displace the water that remained in the polymer matrix and voids. The extent of ion exchange was determined by the weight gain after ion exchange. The weight gain for complete ion exchange (at 4.7 meq/g exchange capacity of H^+ by Ag^+) was 0.502 g/g dry resin. The accuracy for determining the ion exchange by this procedure was well within 0.1%. After two exchanges, 51.7% H^+ was exchanged by Ag^+, and this was the sample used in this study.

Spontaneous monolayer dispersion of CuCl on $\gamma\text{-}Al_2O_3$. Spontaneous dispersion of monolayer metal oxides and salts on Al_2O_3 and other substrates has been known for nearly 50 years. The procedure for spreading CuCl on $\gamma\text{-}Al_2O_3$ was taken from Xie and Tang (1990). The dispersion being a monolayer of CuCl is due to the matching of crystal lattices and has been supported by a variety of experimental (including spectroscopic) evidence.

The $\gamma\text{-}Al_2O_3$ support was PSD-350 activated alumina kindly supplied by Alcoa Separations Technology, Inc. It had a surface area of 340 m^2/g and a trimodal pore-size distribution with a significant percentage of mesopores (pores larger than 2 nm). The dispersion was achieved by heating a mixture of 0.5 g of CuCl powder with 1 g of $\gamma\text{-}Al_2O_3$ at 350°C for 4 h.

Isotherm and diffusivity measurements

Thermogravimetric analysis (TGA), employing a Cahn system 113 recording microbalance with programmed temperature control, was used to measure uptake rate curves as well as equilibrium isotherms of hydrocarbons. Helium was used as the inert carrier gas and the gas for regeneration. The hydrocarbons used were: ethane (CP grade, Linde, minimum purity 99.0%), ethylene (CP, Matheson, minimum purity 99.5%), propane (CP, Matheson, minimum purity 99.0%), and propylene (CP, Matheson minimum purity 99.0%). The He was of high purity grade from Linde with a minimum purity of 99.995%.

Equilibrium isotherms and diffusion uptake rates were measured in the same manner as described elsewhere (Ackley and Yang, 1991), by which true pore diffusion rates were obtained. At the end of each adsorption experiment a desorption experiment was performed to check the reversibility of the adsorption isotherm. Moreover, measurements were made at two temperatures (25 and 60°C), from which values of heat of adsorption were calculated.

Reproducibility of the data was carefully checked. For all ethylene and propylene isotherms, at least duplicate (in some cases, triplicate) measurements were taken. The paraffin isotherms were very low; however, duplicate measurements were also made for some systems.

Results and Discussion

Isotherm equation and parameters

The adsorption of olefin molecules on the Ag^+ and Cu^+ containing sorbents is the sum of physical adsorption and chemisorption. The physical adsorption can be represented by the Langmuir isotherm. Chemisorption is the result of the following reversible reaction, using C_2H_4 and Ag^+ as an example:

$$C_2H_4(g) + Ag^+(s) \Leftrightarrow C_2H_4Ag^+(s) \tag{1}$$

with equilibrium constant

$$K_P = \frac{a_{C_2H_4Ag^+}}{(a_{Ag^+})(P_{C_2H_4})}. \tag{2}$$

For energetically homogeneous surfaces, the equilibrium also leads to the Langmuir isotherm. This is likely the case for the AgY zeolite, because the Ag^+ sites are well-defined in the crystalline structure. For Ag resin and $CuCl/\gamma Al_2O_3$, however, the surface sites are heterogeneous. The simplest form of energy distribution that also leads to an analytical solution when combined with the Langmuir isotherm is the uniform energy distribution, and the resulting isotherm is (Honig and Reyerson, 1952):

$$q = \frac{q_m}{2s} \ln \frac{1 + \bar{b}Pe^s}{1 + \bar{b}Pe^{-s}} \tag{3}$$

where

$$\bar{b} = b_o \exp \frac{\bar{\epsilon}}{RT} \tag{4}$$

$$s = \frac{\sqrt{3}\,\sigma}{RT} \tag{5}$$

and $\bar{\epsilon}$ and σ are, respectively, the mean and square root of variance of the uniform energy distribution. The parameter, s, is a heterogeneity parameter indicating the spread of the energy distribution. When $s \rightarrow 0$, Eq. 3 is reduced to the Langmuir isotherm.

The total amount adsorbed is

$$q = \frac{q_{mp} b_p P}{1 + b_p P} + \frac{q_{mc}}{2s} \ln \frac{1 + b_c Pe^s}{1 + b_c Pe^{-s}} \tag{6}$$

where subscripts p and c indicate, respectively, physical adsorption and chemisorption.

When a chemical bond is formed (even for a weak bond such as in π-complexation), the electron distribution in the molecular orbitals is altered, resulting in substantial weakening of the van der Waals forces. In this case, the bonding is best described by the molecular orbital theory and the term van der Waals forces is no longer relevant. For this reason, the first term in Eq. 6 represents the adsorption on sites without π-complexation, whereas the second term arises from that with π-complexation.

Equation 6 contains five parameters and their values may be obtained from the experimental isotherm data by nonlinear regression. However, certain constraints must be imposed on some of the parameters in order for them to have physical meaning. For example, empirical values for s are available from the literature (Valenzuela and Myers, 1989; Kapoor and Yang, 1990). The value for s generally falls within the range 0–7, and increases with the carbon number for hydrocarbons as adsorbates. The temperature dependence of s is given by Eq. 5. Constraints may also be placed upon the values for q_m, the monolayer capacity. For example, in the partially Ag^+ exchanged resin, the Ag^+ sites are for π-complexation with olefins, whereas the unexchanged sites are for physical adsorption of olefins. Knowing the extent of Ag^+ exchange, q_{mp} and q_{mc} can be related. For physical adsorption, the values of the Langmuir constant (b_p) are approximately equal between olefin and paraffin with the same carbon number. Consequently, the b value from the paraffin isotherm (which requires only two parameters) is imposed as the upper bound for the corresponding olefin.

The Marquardt nonlinear regression method was used. For each sorbent, the paraffin data were used first to obtain the two parameters in the Langmuir isotherm:

$$q = \frac{q_{mp} b_p P}{1 + b_p P}. \tag{7}$$

Since excellent fit was found, an isotherm with heterogeneity was not needed for the paraffins. Subsequently, Eq. 6 was used to fit the data on π-complexation with imposed values or constraints on q_{mp}, b_p, and s, leaving only two parameters (q_{mc} and b_c) as the true fitting parameters.

Zeolite (Na Y) and Ag^+ exchanged zeolite (AgY)

The equilibrium isotherms for C_2H_6 and C_2H_4 on both NaY and AgY zeolites at 25°C are given in Figure 1. Because of the higher polarizability of C_2H_4, adsorption of C_2H_4 on NaY was stronger than that of C_2H_6. The adsorption of C_2H_4 was enhanced moderately by replacing Na^+ with Ag^+. However, the selectivity ratio of C_2H_4/C_2H_6 on AgY was not strong enough for further consideration. Hence no more isotherms were measured on this sorbent.

The equilibrium data were fitted by the Langmuir isotherm (Eq. 7) for C_2H_6/NaY, C_2H_4/NaY, and C_2H_6/AgY, and by Eq. 6 for C_2H_4/AgY, as shown in Figure 1 and Table 1. The π-complexation of C_2H_4 on Ag^+ takes place on well-defined sites in the Ag Y zeolite (Yates, 1966). Therefore, s was assumed to be zero in the regression. Moreover, the physically adsorbed C_2H_4 on the non-Ag^+ sites in AgY should not exceed the total adsorption of C_2H_6 in AgY. It was then reasonable to impose an upper bound for q_{mp} and b_p by using the corresponding values for C_2H_6/AgY, leaving only q_{mc} and b_c as the two fitting parameters. The resulting values, given in Table 1, showed that q_{mp} was actually lower than the upper bound (2.62 vs. 3.26 mmol/g), with a q_{mc} value of 1.303 mmol/g for π-complexation. The regression value for b_c (which indicated the bond strength) was 165 atm^{-1}, as compared to 1.13 atm^{-1} for physical adsorption. All of the regression results were reasonable and meaningful.

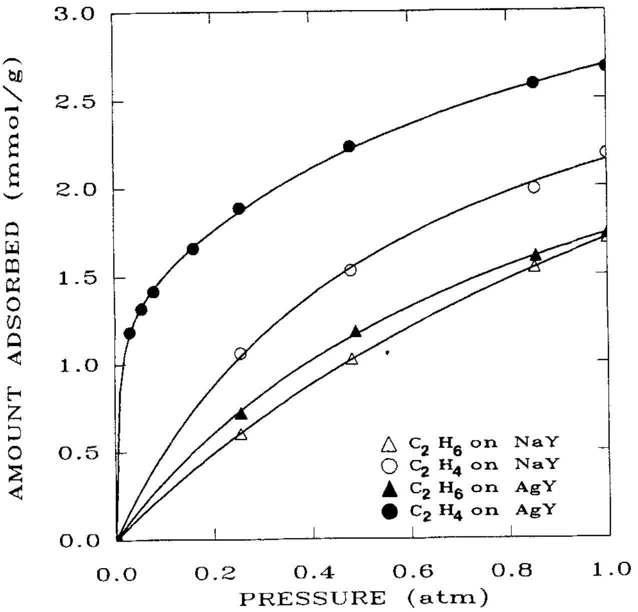

Figure 1. Equilibrium isotherms of C_2H_6 and C_2H_4 on NaY and AgY zeolites at 25°C.

Solid lines are fitted by Eqs. 6 and 7.

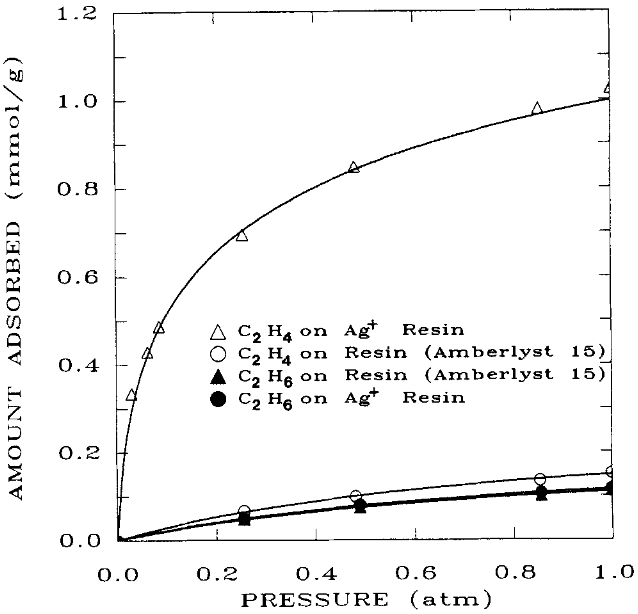

Figure 2. Equilibrium isotherms of C_2H_6 and C_2H_4 on Amberlyst 15 cation (H^+ form) exchanged resin and Ag^+ exchanged resin at 25°C.

Solid lines are fitted by Eqs. 6 and 7.

Ag^+-exchanged cation-exchange resin

A series of macroreticular cation-exchange polystyrenic resins are available commercially (Albright, 1986). The functional group for cation exchange is $C_6H_5SO_3^- H^+$ where H^+ can be replaced by the cation subjected for exchange, and the benzene group is polymerized through a vinyl group that is polymerized with other vinyl groups. The resins are known to be both hydrophobic as well as lyophobic, that is, with a low affinity for hydrocarbons as well. Although hydrocarbons have high polarizabilities, the lyophobicity results from the weakness of the electric field on the surfaces of the resins. This property makes the resin an ideal candidate for cation exchange of π-complexation, so high olefin/paraffin selectivities can be achieved. The most commonly used cation-exchange resin is Amberlyst 15; its properties are described earlier and elsewhere (Albright, 1986).

Figure 2 shows the equilibrium adsorption data for C_2H_6 and C_2H_4 on the H^+ form resin and the Ag^+ exchanged resin, both at 25°C. On the H^+ form resin (that is, unexchanged), the amounts adsorbed were low for both C_2H_6 and C_2H_4, and there was a small selectivity (about 25% higher) for C_2H_4. Both hydrocarbons adsorbed by van der Waals forces. The preference toward C_2H_4 was due to its higher polarizability. However, the selectivity was not high enough to be of practical value. After Ag^+ exchange, the adsorption of C_2H_6 remained essentially the same, while the amounts of adsorbed C_2H_4 exhibited a dramatic sevenfold increase.

Table 1. Equilibrium Isotherm (Eq. 6) Parameters for Zeolite and Ag^+-Exchanged Zeolite at 25°C

	q_{mp} (mmol/g)	b_p (1/atm)	q_{mc} (mmol/g)	b_c (1/atm)	s
C_2H_6 on NaY	4.52	0.605	—	—	—
C_2H_4 on NaY	3.39	1.73	—	—	—
C_2H_6 on AgY	3.26	1.13	—	—	—
C_2H_4 on AgY	2.62	1.13	1.303	165	0

From Figure 2, the amount adsorbed for C_2H_4 on Ag^+ resin at 1 atm and 25°C was 1.15 mmol/g, compared to 0.125 mmol/g for C_2H_6. The selectivity ratio was 9.2. The selectivity from binary mixture would be much higher than 9.2 since the stronger component dominates in mixture adsorption (Yang, 1987). Moreover, the low-pressure region of the isotherm (for C_2H_4 on Ag^+ resin) was not a steep one, because the π-complexation bond was not strong as compared with that on AgY zeolite. These features, combined with the fast rates to be discussed later, make the Ag^+ resin an excellent sorbent for C_2H_6/C_2H_4 separation by cyclic adsorption processes such as pressure swing adsorption (Yang, 1987). Since 51.7% H^+ was exchanged by Ag^+, the ratio of C_2H_4/Ag^+ at 1 atm and 25°C was approximately 1/3.

The temperature dependence for C_2H_4/Ag^+ resin is shown in Figure 3, from which a heat of adsorption of 10.0 kcal/mol was obtained. The equilibrium adsorption data for C_3H_8 and C_3H_6 on the Ag^+ exchanged resin are shown in Figure 4. A dramatic increase in the C_3H_6 adsorption upon Ag^+ exchange was again caused by π-complexation. The ratio for the amounts adsorbed of C_3H_6/C_3H_8 at 1 atm and 25°C was 10.4, and the ratio was nearly 20 at 60°C. Similar to that for C_2H_4, the low pressure region of the C_3H_6 isotherm was not steep. Although the rates of adsorption and desorption were lower than that for C_2H_4, which will be discussed shortly, they should be suitable for cyclic adsorption processes (Yang, 1987). The features just described also make Ag^+ resin an excellent sorbent for C_3H_8/C_3H_6 separation.

The equilibrium data for C_2H_6 and C_3H_8 were correlated well with the Langmuir isotherm (Eq. 7). Equation 6 was used

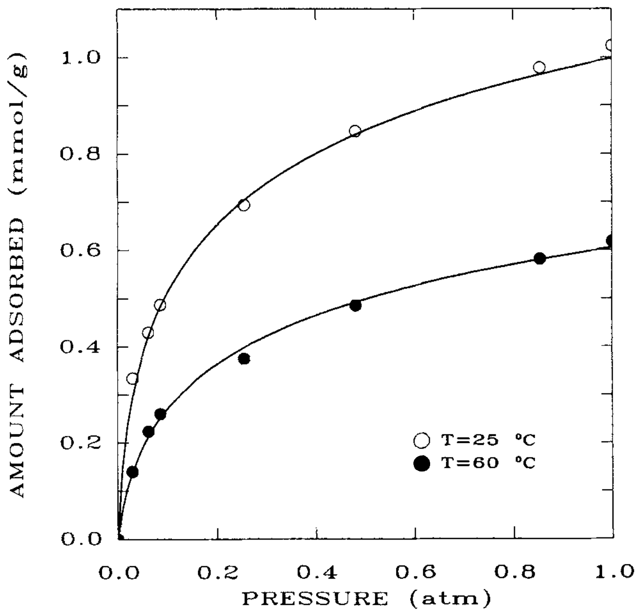

Figure 3. Temperature dependence of C_2H_4 π-complexation on Ag^+ exchanged resin.

Solid lines are fitted by Eq. 6.

for correlating the equilibrium data for C_2H_4 and C_3H_6 on Ag^+ resin where π-complexation was involved. The portion contributed by π-complexation to the isotherm could be estimated by subtracting the C_2H_6 isotherm from that of C_2H_4 (and C_3H_8 from C_3H_6). The π-complexation portion of the isotherm for C_2H_4 on AgY (see from Figure 1) was essentially a stepped isotherm, or "irreversible isotherm." Here the Ag^+ sites in AgY zeolite were well defined and were energetically homogeneous. The Ag^+ resin sorbent, however, exhibited a rather different behavior. The portions contributed by π-complexation for both C_2H_4 and C_3H_6 increased continually with pressure (Figures 2 and 4), although both had a high "knee" due to π-complexation. This behavior was typical of adsorption on heterogeneous surfaces. For meaningful correlation using Eq. 6, physically reasonable constraints on the parameters were imposed. Values for the heterogeneity parameter, s, could be obtained empirically. For C_2 hydrocarbons (such as C_2H_4) on various carbon surfaces at 25°C, an empirical value of $s = 3.5$ appeared to be reasonable (Valenzuela and Myers, 1989; Kapoor and Yang, 1990). Similarly, $s = 5$ was a reasonable empirical value for C_3H_6 at 25°C. The temperature dependence for s is given by Eq. 5. Thus, the following s values were assigned for Ag^+ resin: $C_2H_4 =$ 3.5 (25°C) and 3.13 (60°C); $C_3H_6 = 5.0$ (25°C) and 4.5 (60°C). Constraints could also be placed upon the two Langmuir parameters for the physical adsorption contribution (q_{mp} and b_p). Physical adsorption of C_2H_4 took place on the sites not exchanged by Ag^+; 48.3% of the H^+ sites were unexchanged. Consequently, 48.3% of the q_m values (that is, "monolayer" values) of C_2H_4/H^+-resin were used for C_2H_4 on the partially Ag^+ exchanged resin. In addition, the b constants from the unexchanged resin were used as the upper bounds for b_p in C_2H_4/Ag^+-resin. All fitting parameters for both unexchanged and exchanged resins are given in Table 2. The actual number of fitting parameters for C_2H_4 on Ag^+-resin was only two: q_{mc} and b_c. The fitted curves are shown in Figures 2–4. The fitted values for q_{mc} and b_c (Table 2) were both higher than their corresponding values from physical adsorption; this was a reasonable result. The b_c value is an indication for the bonding strength. If no preassigned values were used, that is, all five parameters in Eq. 6 were fitting parameters, the regression results for C_2H_4/Ag^+-resin (25°C) showed meaningless values for s (over 10) and $b_c \sim 10^{-3}$ atm^{-1}. The same procedure was used for correlating the equilibrium data of C_3H_8 and C_3H_6. Again, both meaningful parameters (Table 2) and reasonable fitting (Figure 4) were obtained.

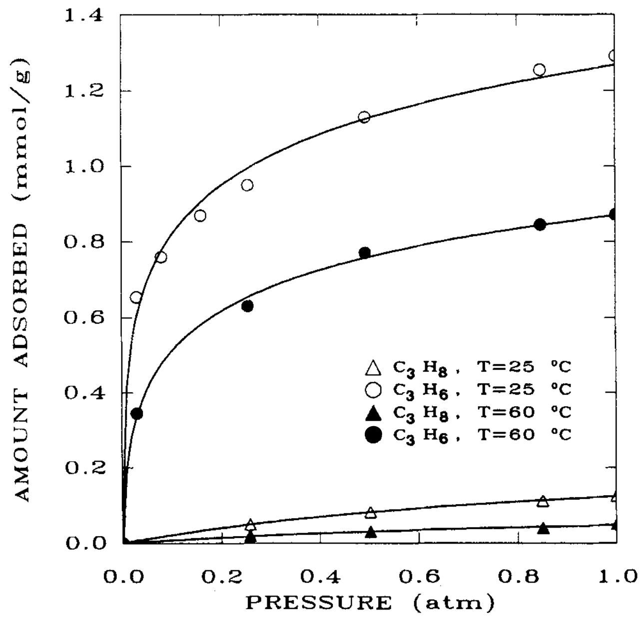

Figure 4. Equilibrium isotherms of C_3H_8 and C_3H_6 on Ag^+ exchanged resin at two temperatures.

Solid lines are fitted by Eqs. 6 and 7.

A comparison of our results with previous attempts is in order. In the review by Quinn (1971), a number of early attempts for C_2H_6/C_2H_4 and C_3H_8/C_3H_6 separations by ion-exchange resins treated with silver salts were discussed. Apparently due to low Ag^+ dispersion, low capacities (less than 3% C_2H_4/Ag^+ ratio for the best samples) made these sorbents only useful in gas chromatography. The more recent work by Hirai et al. (1985a, b) appeared to be more successful than the earlier attempts. In their work, however, *anion* (not cation) exchange resins were used—only as a support, not to effectively disperse the Ag^+ ions. The result was low C_2H_4/C_2H_6 selectivities, low C_2H_4 capacities, as well as low diffusion rates. The low diffusion rates (such as $D/R^2 = 9 \times 10^{-5}$ s^{-1} for C_2H_4 at 20°C., Hirai et al., 1985b) were apparently caused by blockage of the pores by the doped salts. The lyophobility of the resin was, however, utilized in their work, that is, resin would be a better support than activated carbon since the latter would adsorb paraffins strongly. Nevertheless, using cation exchange resins can effectively disperse the Ag^+ ions and at the same time avoid blockage of the pores. The Ag^+-resin yielded superior C_2H_4/C_2H_6 selectivities, C_2H_4 capacities (per Ag^+ ion), and diffusion rates as compared to all previous attempts.

Table 2. Equilibrium Isotherm Parameters (Eq. 6) for Amberlyst 15 Resin and Ag $^{+1}$-Exchanged Resin at Two Temperatures

	q_{mp} (mmol/g)	b_p (atm^{-1})	q_{mc} (mmol/g)	b_c (1/atm)	s
C_2H_6/Resin (25°C)	0.208	1.12	—	—	—
C_2H_4/Resin (25°C)	0.267	1.22	—	—	—
C_2H_6/Ag Resin (25°C)	0.212	1.18	—	—	—
C_2H_6/Ag Resin (60°C)	0.212	0.610	—	—	—
C_2H_4/Ag Resin (25°C)	0.102	0.911	1.46	3.07	3.50
C_2H_4/Ag Resin (60°C)	0.102	0.610	0.920	2.22	3.13
C_3H_8/Ag Resin (25°C)	0.258	0.921	—	—	—
C_3H_8/Ag Resin (60°C)	0.106	0.809	—	—	—
C_3H_6/Ag Resin (25°C)	0.125	0.921	1.77	6.35	5.00
C_3H_6/Ag Resin (60°C)	0.051	0.809	1.37	2.00	2.40

CuCl/γ-Al$_2$O$_3$

CuCl can be spread into a nearly monolayer distribution on the surface of γ-Al_2O_3 upon heating (Xie and Tang, 1990). Adsorption of C_2H_4 on CuCl/γ-Al_2O_3 has been reported (Gui et al., 1984; Xie and Tang, 1990).

Figure 5 shows the equilibrium data for C_2H_6 and C_2H_4 on CuCl/γ-Al_2O_3 at two temperatures. Both C_2H_4/C_2H_6 adsorption ratios and C_2H_4 capacities were high, although they were not as high as those on Ag^+ resin. Equilibrium data for C_3H_8 and C_3H_6 on the same sorbent at two temperatures are given in Figure 6. High C_3H_6/C_3H_8 selectivities and C_3H_6 capacities were also obtained. At 1 atm pressure and 25°C, the molar ratio $C_2H_4/Cu^+ = 0.22$ and that for $C_3H_6/Cu^+ = 0.24$, assuming monolayer coverage of CuCl on the surface of Al_2O_3. These low ratios were expected for steric reasons: the Cu^+-to-Cu^+ distance was approximately 3.6 Å, as well as energetic factors discussed below.

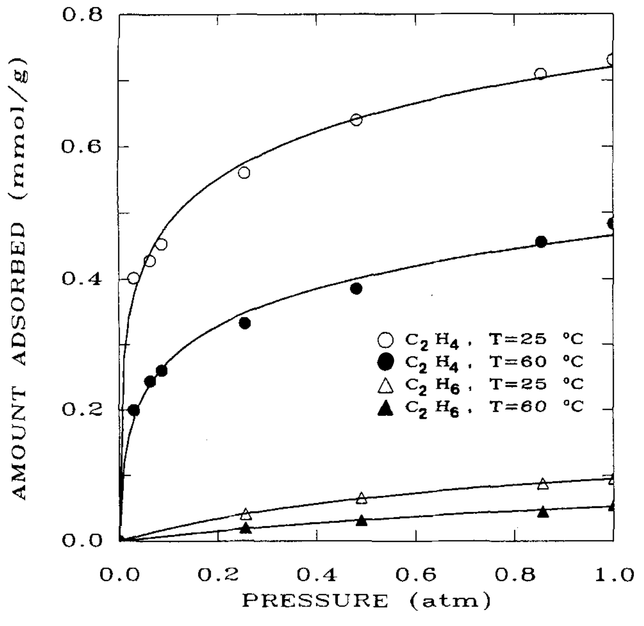

Figure 5. Equilibrium isotherms of C_2H_6 and C_2H_4 on near monolayer CuCl/γ-Al_2O_3.

Solid lines are fitted by Eqs. 6 and 7.

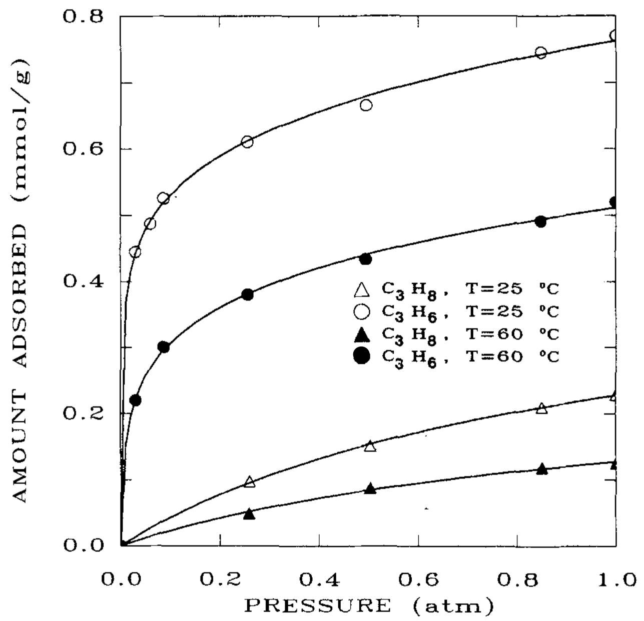

Figure 6. Equilibrium isotherms of C_3H_8 and C_3H_6 on near monolayer CuCl/γ-Al_2O_3.

Solid curves are fitted by Eqs. 6 and 7.

The surface of the γ-Al_2O_3 support was energetically heterogeneous. Upon spreading of CuCl on its surface, Cu^+ filled the vacancies on the surface and could be 4, 5, or 6 coordinated with O^{-2} ions. The olefin molecules could only form π-complexation with the 4-coordinated Cu^+, and the 4-coordinated Cu^+ only occupied a small fraction of the surface (Gui et al., 1984). Our results indicated that less than approximately 30 percent of the Cu^+ ions were 4-coordinated.

The equilibrium adsorption of C_2H_4 on CuCl/γ-Al_2O_3 at 1 atm pressure and 14−18°C was reported by Xie and Tang (1990) and Gui et al. (1984). Their best result was 0.29 mmol/g for an Al_2O_3 support with a surface area of 340 m^2/g (which was the surface area for both their sample and our sample). Our result of 0.73 mmol/g at 25°C and 1 atm was more than double their value. The difference was likely caused by the difference in the γ-Al_2O_3 supports. The source and pore structure of their γ-Al_2O_3 were not given. The equilibrium amount adsorbed C_2H_4 at 25°C and 1 atm on their γ −Al_2O_3 was 0.038 mmol/g. The corresponding value for our γ-Al_2O_3 was 0.50 mmol/g. Therefore, the supports were different, and the difference in the resulting CuCl/γ-Al_2O_3 was not unexpected.

The equilibrium data were correlated by Eq. 6. The results are listed in Table 3. The paraffin data could be well fitted by the two-parameter Langmuir isotherm. Due to the highly heterogeneous nature of the Cu^+ sites, as well as a small fraction of uncovered Al_2O_3 surface, the values for the heterogeneity parameter (s) were greater than those for Ag^+ resin. Consequently, $s = 5$ was used for C_2H_4 at 25°C and $s = 6$ for C_3H_6 at 25°C. For the reason discussed in the foregoing, it was estimated that 2/3 of the surface sites were available for physical adsorption (of olefin), whereas the other 1/3 was the Cu^+ sites capable of π-complexation. Consequently the q_{mp} value for the olefin was assumed to be two-thirds of that of the corresponding paraffin. For example,

Table 3. Equilibrium Isotherm (Eq. 6) Parameters for $CuCl/\gamma\text{-}Al_2O_3$

	q_{mp} (mmol/g)	b_p (atm^{-1})	q_{mc} (mmol/g)	b_c (1/atm)	s
C_2H_6 (25°C)	0.168	1.28	—	—	—
C_2H_6 (60°C)	0.138	0.615	—	—	—
C_2H_4 (25°C)	0.112	1.14	0.858	16.4	5.0
C_2H_4 (60°C)	0.092	0.615	0.647	4.60	4.5
C_3H_8 (25°C)	0.443	1.05	—	—	—
C_3H_8 (60°C)	0.260	0.951	—	—	—
C_3H_6 (25°C)	0.296	0.562	0.783	66.7	6.0
C_3H_6 (60°C)	0.174	0.547	0.721	3.84	5.4

Table 4. Heats of Adsorption (ΔH)

Sorbent	Sorbate	$-\Delta H$, kcal/mol
Ag^+ Resin	Ethane	4.8
	Ethylene	10.0
	Propane	5.1
	Propylene	10.3
$CuCl/\gamma\text{-}Al_2O_3$	Ethane	5.3
	Ethylene	11.7
	Propane	5.6
	Propylene	14.2

$q_{mp} = 0.168$ mmol/g for C_2H_6 at 25°C, hence the corresponding value for C_2H_4 was taken as 0.112 mmol/g. It was also reasonable to impose the b_p value from the paraffin as the upper bound for the olefin. In this manner, only two parameters in Eq. 6 remained as fitting parameters. The results, as shown in Table 3, were reasonable. The fitted curves are also shown in Figures 5 and 6.

Validity of isotherm equation

The reason for invoking energy heterogeneity in deriving the isotherm equation (Eq. 6) was a practical one. For complexation of C_2H_4 on AgY zeolite, the value for s was zero: two Langmuir equations could fit the data (Figure 1). This was a direct consequence of the homogeneous crystalline structure that existed in the zeolite. For Ag^+ resin and $CuCl/\gamma\text{-}Al_2O_3$, however, the experimental data could not be fitted by two Langmuir equations. In these cases, large values for the heterogeneity parameter (s) were needed. This was particularly true for $CuCl/\gamma\text{-}Al_2O_3$. As discussed earlier, Cu^+ filled the vacancies on the Al_2O_3 surface with various coordination numbers, hence the Cu^+ sites were heterogeneous for π-complexation. The chemical/structural reason for heterogeneity supports the choice of a heterogeneous isotherm equation.

Heats of adsorption

The heats of adsorption (ΔH) were calculated from the temperature dependence of equilibrium adsorption, and are given in Table 4. The adsorption of ethane and propane was dominated by van der Waals forces. Consequently, the heats of adsorption for propane were higher than ethane due to a higher polarizability. Also, the heats of adsorption for both paraffins were higher on $CuCl/\gamma\text{-}Al_2O_3$ than on Ag^+ resin because the electric field on the resin surface was weaker.

The heats of adsorption for the olefins on Ag^+ and Cu^+ were in the range 10–14.2 kcal/mol. It is significant that the heat of adsorption of C_3H_6 was substantially higher than that of C_2H_4 on Cu^+ (14.2 vs. 11.7 kcal/mol), whereas they were approximately equal on Ag^+ (10.3 vs. 10.0 kcal/mol). This contrast was predicted by the molecular orbital theory results, to be discussed shortly.

An interesting comparison can be made with the heats of adsorption in other π-complexation systems. For the π-complexation of C_2H_4 in aqueous solutions of Ag NO_3, Keller et al. (1992) reported heats of complexation of 4.8–6 kcal/mol (for concentrations 3–6 M). This low value was apparently caused by the interactions of Ag^+ with the surrounding hydrates, which weakened its π-complexation bond with C_2H_4. For the π-complexation of C_2H_4 with zeolites, Huang (1980) reported heats of adsorption of 18.1 kcal/mol for C_2H_4 on AgY zeolite and 15.9 kcal/mol on Cu(I)Y zeolite. These high values were apparently contributed partly by the interactions of C_2H_4 with the framework structure of zeolite and the unexchanged cations (Na^+). From this comparison, it is evident that the chemical environment (including anions) has a strong influence on the strength of π-complexation.

It should be noted that the values of heats of adsorption were calculated at high loading values, above 50% saturation at 60°C. Due to the heterogeneous nature of the cation sites, the heats of adsorption at very low loadings were expected to be higher than the values given here. However, since only two temperatures were used, values at low loadings would not be accurate so they are not given.

Diffusion rates and adsorption reversibility

Uptake rates for all sorbate/sorbent pairs discussed earlier were measured at 25°C and 60°C. The fact that the uptake rates were controlled by diffusion, rather than π-complexation, was established from the results that the uptake rates depended upon only the sorbate molecular size and were not influenced by olefin vs. paraffin: the π-complexation with olefin did not influence the rates.

The diffusion in $CuCl/\gamma\text{-}Al_2O_3$ was rapid, and was dominated by Knudsen diffusion. For all uptake curves, the diffusion was nearly completed (that is, well over 90 percent completion) within one minute. For example, at 25°C and at $t = 1$ min, the fractional completions were approximately: 96 percent for C_2H_4 and 92–95 percent for C_2H_6, C_3H_6, and C_3H_8.

A number of studies on diffusion in cation exchange resins have been published, and reviewed by Quinta Ferreira and Rodrigues (1993). Each particle of the resin is an ensemble of numerous microspheres, thus it has a bidisperse pore structure. Diffusion in the Ag^+ exchanged resin was slower than that in $CuCl/\gamma\text{-}Al_2O_3$. However, for C_2H_6 and C_2H_4, well over 70 percent completion was achieved within one minute, as shown in Figure 7; these were high rates for practical applications. The diffusion of C_3H_8 and C_3H_6 was considerably slower, as also shown in Figure 7. The overall diffusion time constants, D/R^2, are given in Table 5.

The desorption rates were, for several cases, slightly lower than the adsorption rates. Also, small residual amounts remained in the sorbents from π-complexation on strong sites. Since desorption rates and residual amounts are of impor-

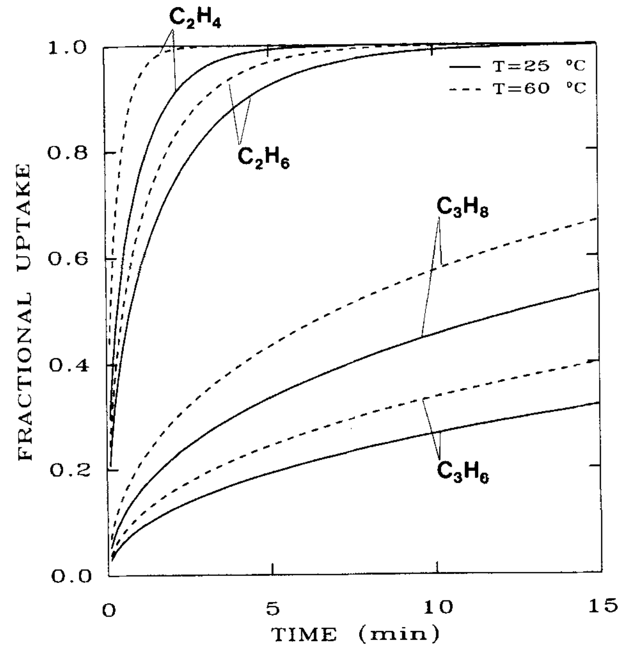

Figure 7. Uptake rates (at $P = 0.26$ atm) on Ag(I) exchanged Amberlyst 15 resin at two temperatures: 25°C (——) and 60°C(---).

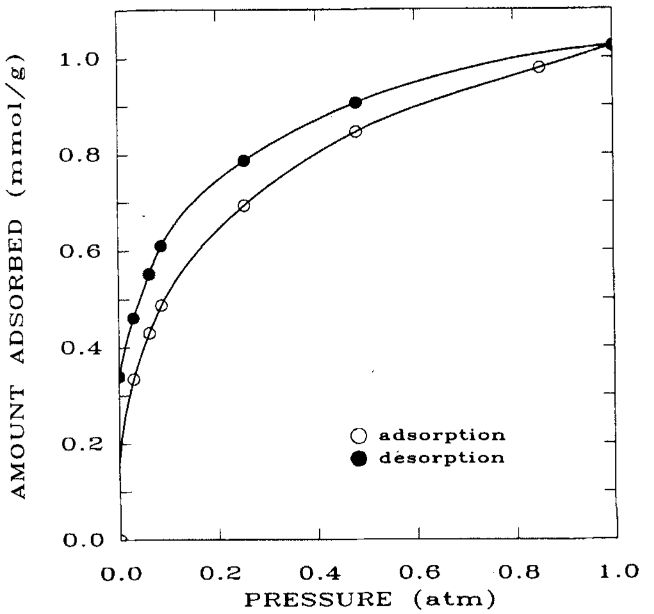

Figure 8. Equilibrium adsorption and desorption isotherms of C_2H_4 on Ag^+ exchanged resin at 25°C.

tance in practical applications, they are subjects for further investigation. These subjects are, however, clearly related to the strengths of π-complexation. In the case of AgY and Cu(I)Y zeolites, severe problems arose in desorption of C_2H_4 due to the strong π-complexation bonds (Huang, 1980). For π-complexation of C_2H_4 in aqueous solution of Ag^+, complete reversibility was achieved without difficulty (Keller et al., 1992); this was due to a weak π-complexation bond. The bond strengths in our case, as given by the heats of adsorption, were between these two cases. The residual amounts of adsorption in our cases (for Ag resin and CuCl/γ-Al_2O_3) were also between these two cases. Among the least reversible adsorption was C_2H_4 on Ag^+ resin at 25°C. The adsorption/desorption isotherms are shown in Figure 8. The residual amounts, however, were desorbed completely and rapidly at 100°C, and the adsorption capacities were completely restored. Cyclic adsorption/desorption is also under further investigation.

Molecular orbital calculations

The basic concept for π-complexation was described in a qualitative theory by Dewar (1951). The outer shell orbitals for Cu(I) and Ag(I) consist 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 (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 (that is, back donation of electrons to the empty olefin antibonding orbital). An extended Hückel molecular orbital (EHMO) study was undertaken to gain an understanding of the bonding of C_2H_4 with $Ag^+SO_3C_6H_5^-$, $Cu^+SO_3C_6H_5^-$, and Ag^+ and Cu^+ on other anions. The EHMO computation program and other details were the same as those described earlier (Yang and Chen, 1989; Chen and Yang, 1989). The detailed results are beyond the scope of this study, so only the relevant result will be discussed here.

Table 5. Overall Diffusion Time Constant (D/R^2) for Diffusion in Ag^+ Exchanged Resin

	D/R^2, 1/s	
	25°C	60°C
Ethane	7×10^{-4}	1×10^{-3}
Ethylene	1.0×10^{-3}	3.7×10^{-3}
Propane	4×10^{-5}	7.2×10^{-5}
Propylene	1.2×10^{-5}	2.0×10^{-5}

The π-σ donation was the major contribution to the π-complexation, whereas the back donation of the d-orbital electrons from the metal made only a minor contribution. For the example of C_2H_4 on $AgSO_3C_6H_5$, the σ donation accounted for 84% of the bond, whereas the d-π^* back donation accounted for only 16%. More important, however, is the relative heats of adsorption calculated from the EHMO theory. The relative heats of adsorption were: -29.6 kcal/mol for C_2H_4/Ag^+, -24.6 kcal/mol for C_3H_6/Ag^+, -27.6 kcal/mol for C_2H_4/Cu^+, and -48.8 kcal/mol for C_3H_6/Cu^+. It is known that the energy scale in the EHMO theory is dependent upon one's choice of Coulomb integrals and formula for the resonance integral used in the calculation and is therefore arbitrary. However, the relative values from the same calculations are meaningful (Turner, 1974). The EHMO results showed a clearly higher heat of adsorption for C_3H_6 on Cu^+, while the heats of adsorption for the other three pairs were lower and were close to each other. The experimental results given in Table 4 yielded -14.2 kcal/mol for

C_3H_6 on Cu^+ with weaker values for the other three pairs falling in the range -10 to -11.7 kcal/mol. The experimental results were in agreement with the EHMO predictions.

Acknowledgments

The research was supported by the National Science Foundation under grant CTS-9212279 and a Praxair Endowed Chair. We would like to thank J. P. Chen for performing the molecular orbital calculations (the results of which will be published elsewhere) and J. A. Miers of Rohm and Haas Company for discussions and donation of the resins.

Notation

a = activity
b = Langmuir constant
D = diffusivity
P = pressure
q = equilibrium amount adsorbed
q_m = monolayer or saturated amount adsorbed
R = gas constant or particle radius in D/R^2
s = heterogeneity parameter
T = absolute temperature

Greek letters

ϵ = bond energy for adsorption
σ = square root of variance of uniform energy distribution

Subscripts

c = chemisorption or π-complexation
p = physical adsorption

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Manuscript received Dec. 28, 1993, and revision received Apr. 21, 1994.