Adsorption Uptake Curves Of Ethylene On Cu(I)–NaY Zeolite

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Ethylene is one of the most important petrochemicals. Traditionally ethylene is separated by cryogenic distillation which is high in investment and operation costs. Therefore, efforts to find new processes for ethylene separation continue. Recently, Anderson and Sherman (1984) and Keller (1983) have pointed out the possibility of separating ethylene by new adsorption separation processes. The breakthrough of the technology will depend greatly on the development of new adsorbent with better adsorption selectivity and capability for ethylene.

The synthesis of cuprous exchanged zeolite by Rabo et al. (1977) showed the possibility of ethylene separation by adsorption process. The new adsorbent is capable of reversible complexing reaction between cuprous ion on the surface of the zeolite and ethylene through its π–bond. Due to the limitation of ion exchange equilibrium, Na ions in zeolite can only be partially exchanged with cupric ions. Thus Na and cuprous ions will coexist on the surface of zeolite. Two types of surface act differently for ethylene adsorption: on the surface occupied by Na ions, physical adsorption takes place; on the surface occupied by cuprous ions, complexing reaction takes place. Chai (1988) and Cen (1989) have studied the adsorption isotherms of carbon monoxide on Cu(I)–13X and ehtylene on Cu(I)–NaY zeolite, respectively.

The zeolite pellet consists of small crystals which are pelletized with small amount of binder. Thus, two types of pores exist: micropores in the crystals and macropores in the binder. Because the time constants for diffusion (diffusivity/radius squared) are of the same order of magnitude for both types of pores, both must be considered in the mathematical solution of adsorption kinetics. Ruckenstein et al. (1971) derived a solution for the uptake curves. Haynes (1975) obtained a solution for the chromatographic responses. Time-domain solutions were obtained by Friedrich et al. (1979) for a pulse input and Rasmuson (1982) for a step input. All of the above-mentioned analytical solutions accounted for macropore and micropore diffusion and only for linear isotherms. Those solutions are in the integral form and are very complicated indeed. Cen and Yang (1986) derived a simplified analytic solution for breakthrough curves with bidisperse sorbent under the assumption of parabolic concentration profiles, which is simpler in its form and easier to use.

For nonlinear isotherms, it is generally impossible to obtain an analytic solution for adsorption kinetics. The solution must be done numerically. Experimental studies of diffusion of several hydrocarbons with nonlinear isotherms in 5A zeolite pellets under conditions of macropore diffusion control have been reported by Ruthven and Derrah (1972) and by Youngquist et al. (1971). Yucel and Ruthven (1980) studied the diffusion of CO_2 in 4A and 5A zeolite crystals with virial-type isotherms. Cen and Yang (1988) applied a simplified model to pressure swing adsorption process for multicomponent gas mixture separation with bidisperse sorbent and Langmuir-type isotherms.

Chemical adsorption is studied widely in the area of heterogeneous catalysis. Thomas and Thomas (1977) in their book reviewed the current theories in chemical adsorption including adsorption isotherms and kinetics.

In this work, the uptake curves of ethylene on both NaY and Cu(I)–NaY zeolite were measured. A simultaneous physical and chemical adsorption mechanism was proposed for isotherms of ethylene on Cu(I)–NaY zeolites. A mathematical model for uptake curves was derived, in which both macropore and micropore diffusion and the different rates for physical and chemical adsorption were considered. The parabolic concentration profiles approach was adopted to simplify the numerical solution. The model can simulate the experimental adsorption isotherms and uptake curves well.

Mathematical Model for Adsorption Isotherms and Uptake Curves with Simultaneous Physical and Chemical Adsorption

Adsorption isotherms of C_2H_4 on Cu(I)–NaY zeolite

The adsorption of ethylene on NaY zeolite is of physical adsorption. The adsorption isotherm is Langmuir type:

$$q^p = q^p_m K_p P/(1 + K_p P) \qquad (1)$$

Because of the limitation of ion-exchange equilibrium, only part of the Na ions in NaY zeolite lattice can be exchanged by cupric ions. Both sodium and cuprous ions will remain in the Cu(I)–NaY zeolite after the reduction reaction. Simultaneous physical and chemical adsorption takes place on the heterogeneous surface upon adsorption of ethylene.

The reaction between ethylene and the cuprous ions is reversible complexing. The stoichiometric relation of the reaction is:

$$\mathrm{Cu}(I) + \mathrm{C_2H_4} \underset{k_{-I}}{\overset{k_I}{\rightleftharpoons}} \mathrm{Cu}(I)\cdot \mathrm{C_2H_4} \tag{2}$$

The chemical adsorption is monolayer. And if all Na ions are exchanged by cuprous ions, the Langmuir equation can also apply:

$$q^c = q^c_m K_c P/(1 + K_c P) \tag{3}$$

Assuming fraction of Na ions exchanged by cuprous ions is f, and ethylene adsorption on either Na or cuprous is independent, the total adsorbed amount of ethylene on Cu(I)–NaY zeolite can be calculated by:

$$q = f \cdot q^c + (1 - f) \cdot q^p \tag{4}$$

Uptake curves of C_2H_4 on Cu(I)-NaY zeolite

The simplifying assumptions in the model are: isothermality, spherical in shape for both pellets and crystals, and adsorbate adsorbed and diffused independently in the heterogeneous surface of adsorbent.

The mass balance equations of adsorbate in crystal for both chemical and physical adsorption on heterogeneous surface are:

$$\frac{\partial q^c}{\partial t} = \frac{D^c_c}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial q^c}{\partial r}\right) \tag{5}$$

$$\frac{\partial q^p}{\partial t} = \frac{D^p_c}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial q^p}{\partial r}\right) \tag{6}$$

The initial and boundary conditions are as follows:

$$q^c|_{t=0} = q^{co}, \left.\frac{\partial q^c}{\partial r}\right|_{r=0} = \left.\frac{\partial q^p}{\partial r}\right|_{r=0} = 0,$$

$$q^c|_{r=r_0} = q^{c*}\,(C_p|_{r=r_0}),\ q^p|_{r=r_0} = q^{p*}(C_p|_{r=r_0}) \tag{7}$$

If the surface fraction for chemical adsorption is f, the total adsorbed amount of adsorbate on the surface can be calculated from Eq. 4

$$\frac{\partial q}{\partial t} = f\frac{\partial q^c}{\partial t} + (1 - f)\frac{\partial q^p}{\partial t} \tag{8}$$

The mass balance equation for the pellets is

$$\frac{\partial C_p}{\partial t} + \frac{1-\epsilon}{\epsilon}\rho\frac{\partial \bar{q}}{\partial t} = \frac{D_p}{R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial C_p}{\partial R}\right) \tag{9}$$

where

$$\bar{q} = \frac{3}{R_0^3}\int_0^{R_0} R^2 q\, dR$$

The initial and boundary conditions are:

$$C_p|_{t=0} = C^p_0,\ q|_{t=0} = q^0,$$

$$\left.\frac{\partial C_p}{\partial R}\right|_{r=0} = 0,\ C_p|_{R=R_0} = C_f \tag{10}$$

If the ideal gas law is applicable, then

$$C_f = \frac{P}{RT} \tag{11}$$

Equations 5 to 11 can be solved numerically, but the process is tedious. Liaw et al. (1979) suggested a parabolic concentration profile in the pellet. Cen and Yang (1986) extended the assumption into bidisperse sorbent. The simplified solutions are in good agreement with Rosen's numerical solution (1952, 1954). In this work, the assumption is adopted again, so that:

$$q = a_0 + a_2 r^2 \tag{12}$$

$$C_p = b_0 + b_2 R^2 \tag{13}$$

Substituting Eqs. 12 and 13 into Eqs. 5, 6 and 9, we obtain:

$$\frac{\partial \bar{\bar{q}}^c}{\partial t} = \frac{15 D^c_c}{r_0^2}\,[\bar{q}^{c*}(C_p) - \bar{\bar{q}}^c] \tag{14}$$

$$\frac{\partial \bar{\bar{q}}^p}{\partial t} = \frac{15 D^p_c}{r_0^2}\,[\bar{q}^{p*}\,(C_p) - \bar{\bar{q}}^p] \tag{15}$$

$$\frac{\partial \overline{C_p}}{\partial t} + \frac{1-\epsilon}{\epsilon}\rho\frac{\partial[f\bar{\bar{q}}^c + (1-f)\bar{\bar{q}}|]^p]}{\partial t} = \frac{15 D_p}{R_0^2}(C_f - \overline{C_p}) \tag{16}$$

with the following initial conditions:

$$\bar{\bar{q}}^c|_{t=0} = \bar{\bar{q}}^{co}, \bar{\bar{q}}^p|_{t=0} = \bar{\bar{q}}^{po},\ \overline{C_p}|_{t=0} = \overline{C}^0_p \tag{17}$$

Equations 14 to 17 can be solved numerically. A two-point implicit method is used to guarantee convergence. If f equals to zero, i.e., homogeneous surface without chemical adsorption, Eqs. 14 to 17 are used to describe the uptake curves with physical adsorption alone.

Experimental Study

Original NaY zeolite pellet (1 mm in diameter, from Wenzhou Zeolite Works) was pretreated in 1 N $NaNO_3$ solution and then treated with 0.1 N Cu $(NO_3)_2$ solution for ion exchange at the room temperature.

The resulting Cu(II)–NaY zeolite is light blue in color and is washed with distilled water and then dried at 110°C. The Cu(II)–NaY zeolite was analyzed with atomic absorption spectrometry (AAS). The result indicated that the cupric content was 5.037% by weight.

In a reducing atmosphere, Cu(II)–NaY zeolite can be easily

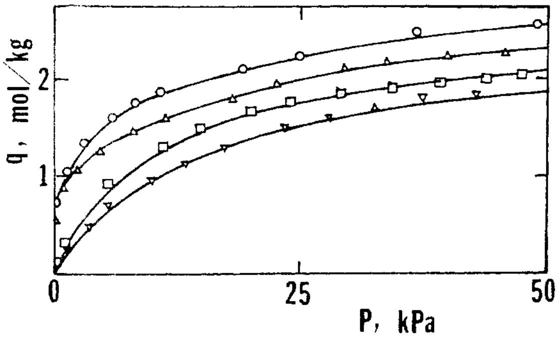


Figure 1. Adsorption isotherms of ethylene on NaY and Cu(I)–NaY zeolite.

□, *ethylene/NaY*, 30°C; ▽, *ethylene/NaY*, 50°C; ○, *ethylene/Cu(I)–NaY*, 30°C; △, *ethylene/Cu(I)–NaY*, 50°C; Solid lines: calculated by Eq. 4.

reduced to Cu(I)–NaY zeolite, such as by hydrogen or carbon monoxide. In this work, ethylene itself was used as reduction agent. The reduction was completed in a CAHN–2000 electronic balance. The Cu(II)–NaY zeolite was first dehydrated at 150°C and 10^{-6} mm Hg (1.3 mPa), then ethylene was introduced into the balance to reduce the Cu(II) to Cu(I) at 250°C for 4 hours. The final Cu(I)–NaY zeolite was grey white in color. From the comparison of the adsorbed amount of ethylene in the untreated NaY zeolite and Cu(I) exchanged NaY zeolite, the reduction was complete.

Adsorption uptake curves of ethylene on both untreated and cuprous exchanged NaY zeolites were also measured in the CAHN–2000 electronic balance at 30 to 50°C, respectively.

Results and Discussion

Adsorption isotherms of ethylene on NaY and Cu(I)–NaY zeolites

Adsorption isotherms of ethylene on NaY zeolite obtained from uptake curve measurement are shown in Figure 1. The isotherms are of Langmuir type and are physical adsorption in nature. The parameters q_m^p and K_p in Eq. 1 are correlated from the experimental data and listed in Table 1. Adsorption isotherms of ethylene on Cu(I)–NaY zeolite are also shown in Figure 1. The differences between two sets of the isotherms are:

- The adsorption capability of ethylene on the Cu(I)–NaY zeolite is much higher than that on NaY zeolite.
- At very low adsorption pressure, isotherms of ethylene on the Cu(I)–NaY zeolite are very steep and then become parallel to those of ethylene on NaY zeolite.

There are five parameters in Eq. 5, where q_m^p and P_p have already been obtained from ethylene-NaY isotherms; and the combined parameter $f \cdot q_m^c$, which represents the maximum adsorbed amount by chemical adsorption, can be calculated according to the stoichiometric reaction (Eq. 2) and Cu–ion exchanged amount:

$$f \cdot q_m^c = (1{,}000) \times (5.037\%)/(63.54)$$
$$= 0.7929 \text{ mol/kg Cu(I)} - \text{NaY} \quad (18)$$

where 63.54 is atomic weight of copper. Therefore, only two parameters, f and k_c, are remained to be determined from the experimental adsorption data. The correlated f and K_c values are also listed in Table 1. The comparisons between the experimental data and model calculation are shown in Figure 1. The good agreement indicates that the assumed mechanism is correct, i.e., simultaneous physical and chemical adsorption take place when ethylene is adsorbed on Cu(I)–NaY zeolite. Furthermore, from Table 1, we see that the correlated f values at 30°C and 50°C equal to 0.1834 which is almost the same as the cupric ion exchanged fraction (0.1805) calculated from the formula of NaY zeolite, $Na_{56}(AlO_2)_{56}(SiO_2)_{136}$, and 5.037% cupric content, if small amount of binding material is neglected. It also explains the correctness of assumed adsorption mechanism and stoichiometric reaction (Eq. 2) and the completeness of reduction of Cu(II) into Cu(I). Also, from Table 1, the correlated chemical adsorption equilibrium constant, K_c, which is four orders of magnitude larger than physical adsorption equilibrium constant, k_p, explains that chemical adsorption of ethylene on Cu(I) occupied surface is much more irreversible than the physical adsorption of ethylene on the Na occupied surface. The irreversibility is a general characteristics of chemical adsorption.

Uptake curves on ethylene on NaY zeolite

The typical uptake curves of ethylene on NaY zeolite are shown in Figure 2. It is obvious from Figure 2 that with the increase of adsorption pressure the uptake curves become sharper. The results of model simulation are also shown in Figure 2 and are in good agreement with experimental data.

The diffusion constant in macropore, $15D_p/r_0^2$, is considered a constant at certain temperature as listed in Table 1, whereas the diffusion constant in micropores, $15D_c^p/r_0^2$, changes with the adsorption pressure according to Darken's equation:

$$D_c = D_c^* \frac{d \ln P}{d \ln q} \quad (19)$$

where D_c^* is the self-diffusivity which should be independent of P. The micropore diffusion constants, which are obtained from the uptake curves, are shown in Figure 2. Although the variation in micropore diffusion constants does not closely follow the Darkin's equation strictly, its tendency to increase with the increase of adsorption pressure is obvious. Also, from Figure 3, micropore diffusion constant increases when increasing temperature.

Table 1. Parameters Used in the Mathematical Models

T °C	q_m^p mol/kg	K_P kPa^{-1}	K_C kPa^{-1}	$f \cdot q_m^c$ mol/kg	f	$15D_P/r_0^2$ s^{-1}	$15D_C/r_0^2$ s^{-1}	ϵ	ρ kg/m^3
30	2.573	0.09716	149.3	0.7929	0.1834	0.0841	0.0087	0.497	998
50	2.415	0.07263	95.7	0.7929	0.1834	0.0859	0.0115	0.497	998

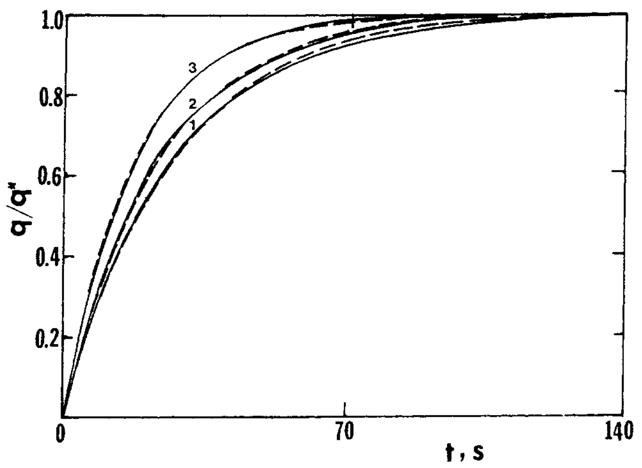


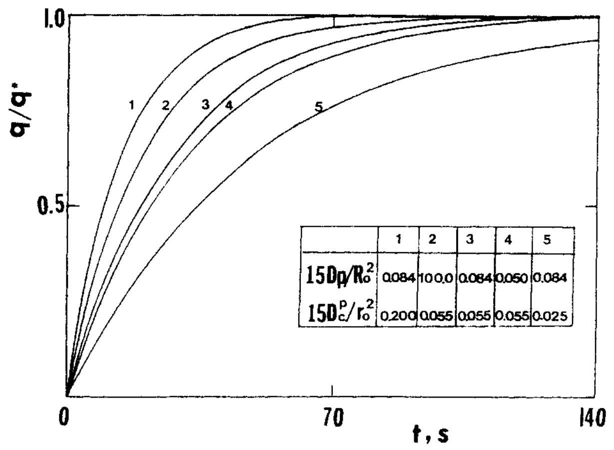
Figure 2. Uptake curves of ethylene on NaY zeolite at 30°C.

Solid lines, experimental data; dashed lines, calculated by the model 1, 0.16 kPa; 2, 5.25 kPa; 3, 28.9 kPa)

Both macropore and micropore diffusion constants correlated from the uptake curves are of the same order of magnitude; therefore, neither of them can be neglected. The relative importance of macropore and micropore diffusion constants to the uptake curves can be seen from the sensitivity analysis as shown in Figure 4. It indicates that the uptake curves are more sensitive to change in the micropore diffusion constant.

Uptake curves of ethylene on Cu(I)–NaY zeolite

Typical uptake curves of ethylene on Cu(I)–NaY zeolite are shown in Figure 5. At low pressure, the adsorption uptake curves are very smooth and take very long time to reach equilibrium. It is completely different from those in ethylene/NaY system. The low uptake rate can be explained by a slow chemical reaction rate. For the ethylene/Cu(I)–NaY system, the adsorbed amount of ethylene is contributed by both chemical and physical adsorption. Comparing adsorption isotherms of ethylene on the Cu(I)–NaY zeolite (as shown in Figure 1), the isotherms of ethylene on the NaY zeolite are smooth and are of the Langmuir type, but isotherms of ethylene on Cu(I)–NaY zeolite is very steep at low adsorption pressure and then becomes smooth and almost parallel to the isotherms of ethylene on NaY zeolite. These facts indicate that vacant sites occupied by Cu(I) are almost saturated by ethylene molecules even at very low adsorption pressure. Therefore, at low adsorption pressure ethylene uptake by Cu(I)–NaY zeolite is caused mainly by chemical adsorption. Despite the reversibility of complexing reaction between ethylene and Cu(I), the interaction is much stronger than that on the Na surface, resulting in slow uptake rate.



	1	2	3	4	5
$15D_p/R_o^2$	0.084	100.0	0.084	0.050	0.084
$15D_c^p/r_o^2$	0.200	0.055	0.055	0.055	0.025

Figure 4. Relative sensitivity of calculated uptake curves to macro- and micropore diffusion constant 30°C and 0.156 kPa.

With an increase in adsorption pressure, Cu(I) ions are almost saturated with ethylene, the further increase of adsorbed amount is caused mainly by physical adsorption on Na ions surface. Thus, the uptake curves become similar to those for physical adsorption. For example, when P = 3.08 kPa, the

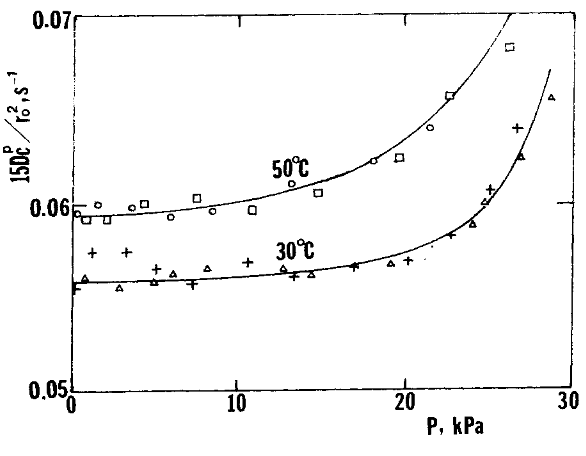


Figure 3. Micropore diffusion constants of physical adsorption, D_c^p/r_0^2, vs. adsorption pressure for both C_2H_4/NaY and C_2H_4/Cu(I)– NaY systems.

+, *C_2H_4/NaY*, 30°C; ○, *C_2H_4 Cu(I)–NaY*, 50°C; △, *C_2H_4/Cu(I)–NaY*, 30°C; □, *C_2H_4/NaY*, 50°C

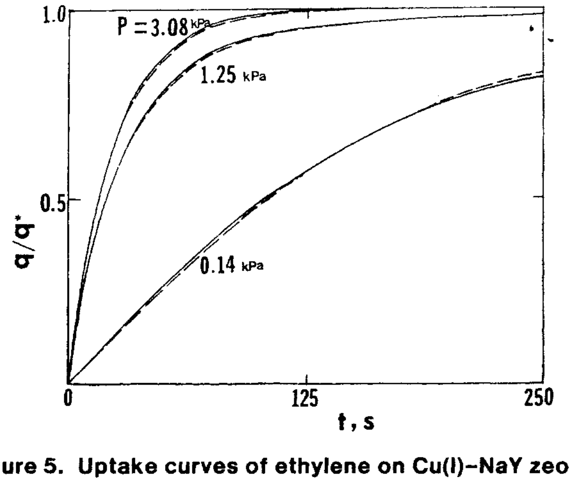


Figure 5. Uptake curves of ethylene on Cu(I)–NaY zeolite at 30°C.

Solid lines, experimental data; dashed lines, calculated by the model.

At P = 3.08 kPa, the calculated uptake curves for $15D_c^p/r_0^2$ = 0.0087 s^{-1} and 1,000 s^{-1} are identical.

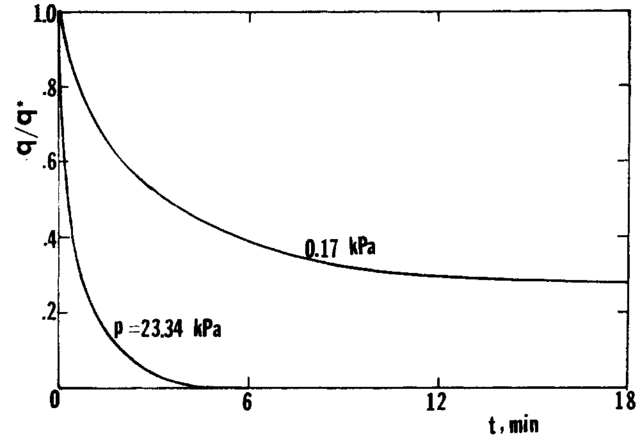


Figure 6. Experimental desorption curves of ethylene on the Cu(I)–NaY zeolite at 30°C.

uptake curves calculated with $15D_c^c/r_0^2 = 0.0087\ s_1^{-1}$ and 1,000 s^{-1}, respectively, are almost the same as shown in Figure 5, which shows that the uptake rate by chemical adsorption can be neglected.

The model simulation for the uptake curves of ethylene on Cu(I)–NaY zeolite is satisfactory as shown in Figure 5. The correlated micropore diffusion constant of physical adsorption changes with adsorption pressure in a similar manner as shown in Figure 2. The model simulation indicates that the micropore diffusion constant of chemical adsorption is much smaller than that of physical adsorption, and it increases from 0.0087 s^{-1} to 0.015 s^{-1} when temperature is increased from 30 to 50°C.

Desorption curves of ethylene on Cu(I)-NaY zeolite

The experimental desorption curves of ethylene on Cu(I)–NaY zeolite are shown in Figure 6. The desorption curves behave differently when adsorption pressure changes. When adsorption pressure is decreased from 0.17 kPa to 0.10 kPa, the desorbed rate is very slow and the desorbed amount is smaller than the adsorbed amount. According to the isotherm equation, at low pressure chemical adsorption dominates. When the adsorption pressure is decreased from 23.34 to 18.05 kPa, the desorption rate is fast and the amount desorbed is almost equal to the amount adsorbed. In this pressure range, the physical adsorption dominates and the chemical adsorption can be neglected based on the adsorption isotherm study. The desorption curve also shows the feature of physical adsorption.

Acknowledgment

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Notation

C_f = concentration in gas phase, kmol/m^3
C_p = concentration in macropore, kmol/m^3
$\overline{C}_p$ = average value of C_p averaged over the pellet, kmol/m^3
D_c = diffusivity in crystal, m^2/s
D_p = diffusivity in pellet, m^2/s
f = surface fraction occupied by Cu(I)
K_c = parameter in Langmuir equation for chemical adsorption, kPa^{-1}
K_p = parameter in Langmuir equation for physical adsorption, kPa^{-1}
q = adsorbed amount, kmol/m^3
$\overline{q}$ = average value of q averaged over the crystal, kmol/m^3
$\overline{\overline{q}}$ = average value of $\overline{q}$ averaged over the pellet, kmol/m^3
q_m = parameter in Langmuir equation, kmol/m^3
r = radial distance in crystal, m
r_0 = radius of crystal, m
R = radial distance in pellet, m
t = time, s

Greek letters

ϵ = intrapellet void fraction
ρ = density of adsorbent, kg/m^3

Superscripts

c = chemical adsorption
p = physical adsorption
o = initial conditions
$*$ = equilibrium

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