Surface Diffusion on Energetically Heterogeneous Surfaces

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Surface diffusion of the adsorbed species is of considerable importance and can be dominating in intraparticle mass transfer. Several models have been suggested in the literature to describe surface diffusion on a homogeneous surface. These models have recently been reviewed by Kapoor et al. (1989).

It has been shown that surface diffusivity is a strong function of the adsorbed phase concentration and temperature (Sladek et al., 1974; Okazaki et al., 1981; Ross and Good, 1956; Tamon et al., 1981); surface diffusivity increases with increase in adsorbed phase concentration and temperature. The Arrhenius-type temperature dependence suggests that surface diffusion is an activated process. It has also been suggested (Gilliland et al., 1974; Sladek et al., 1974) that the activation energy for surface diffusion can be related to the energy of adsorption, i.e., the bond energy between the adsorbate and the surface.

Recently, Seidel and Carl (1989) studied surface diffusion on an energetically heterogeneous surface. They assumed that surface diffusivity is related to the adsorption isotherm through adsorption energy distribution. By fitting the equilibrium adsorption data to different isotherms (e.g., the Freundlich isotherm, Dubinin-Radushkevich isotherm, and Toth isotherm) different adsorption energy distributions were calculated. These energy distributions were then used to describe the concentration dependence of surface diffusivity. However, their basic premise was that surface diffusivity was independent of adsorbate concentration on a homogeneous surface, and that the concentration dependence arose due to the surface heterogeneity. The resulting functional forms of surface diffusivity dependence on adsorbate concentration showed incorrect behaviors. In the limit of zero adsorbate concentration, surface diffusivity becomes zero. The results of Seidel and Carl (1989) are in contrast to results obtained earlier, experimentally (Ross and Good, 1956; Carman and Raal, 1951; Gilliland et al., 1974) and theoretically (Higashi et al., 1963; Yang et al., 1973; Tamon et al., 1981), i.e., surface diffusivity is finite at zero adsorbate concentration. However, Seidel and Carl showed qualitatively that surface diffusivity increases with an increase in adsorbate concentration, a finding consistent with results reported in the literature.

Simple expressions have been derived, which describe the effects of adsorbate concentration, temperature and heterogeneity on surface diffusivity. The heterogeneity parameter is obtained directly from the equilibrium adsorption data. Comparisons are given between the theoretical predictions and experimental data taken from literature.

Theory

Adsorption on an energetically heterogeneous surface can be described by the following equation (Ross and Olivier, 1964):

$$n(T,P) = \int_{\epsilon_{\min}}^{\epsilon_{\max}} n(T,P,\epsilon) f(\epsilon)\, d\epsilon \tag{1}$$

where $n(T, P, \epsilon)$ is the local adsorption isotherm on a homogeneous patch with adsorption energy ϵ, $f(\epsilon)$ is the energy distribution function, and $n(T, P)$ is the overall isotherm on the heterogeneous surface. A similar expression can be written for surface diffusivity on an energetically heterogeneous surface by assuming that the surface consists of a series of parallel paths such that each path has uniform but different energy, and the surface flow is in the direction of these parallel paths.

$$D_s^{\mathrm{Het}} = \int_{\epsilon_{\min}}^{\epsilon_{\max}} D_s^{\mathrm{Hom}}(T,P,\epsilon) f(\epsilon)\, d\epsilon \tag{2}$$

where D_s^{Hom} is the surface diffusivity on a homogeneous patch with energy ϵ, and D_s^{Het} is the overall surface diffusivity on a heterogeneous surface. The parallel-path assumption is the same as that in the parallel-pore models for pore diffusion in random porous materials.

The functional form of $D_s^{\mathrm{Hom}}(\theta)$ was derived by Higashi et al. (1963), based on a random walk of molecules from adsorption site to adsorption site on the solid surface. Assuming that the

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transit time between sites is negligible compared to the residence time on each site, and the molecule immediately bounces off if it encounters a site already occupied by another molecule, they derived the following expression (HIO Model: Higashi, Ito, and Oishi):

$$\frac{D^{\mathrm{Hom}}_{s,\theta}}{D^{\mathrm{Hom}}_{s,\theta=0}} = \frac{1}{1-\theta} \tag{3}$$

where θ is the fractional surface coverage. The temperature dependence of surface diffusivity is given by

$$D^{\mathrm{Hom}}_{s,\theta} = \frac{D_{so}}{1-\theta} \exp\left(-E/RT\right) \tag{4}$$

where D_{so} is the frequency factor and E is the activation energy, for surface diffusion. Parameter D_{so} is independent of temperature, E and θ. The activation energy for surface diffusion can be assumed to vary linearly with adsorption energy (Gilliland et al., 1974):

$$E = a\epsilon \tag{5}$$

where a is a constant less than unity. For diffusion of physically adsorbed species, the value of a is either 1 or ½ (Sladek et al., 1974). Since the introduction of the HIO model in 1963, several modifications have been suggested in the literature (Yang et al., 1973; Tamon et al., 1981; Suzuki and Fujii, 1982). In the present work, however, we use the HIO model as a first approximation.

Assuming that adsorption on a homogeneous surface can be described by the Langmuir isotherm, Eq. 1 gives

$$n(T, P) = \int_{\epsilon_{\min}}^{\epsilon_{\max}} \frac{q_m bP}{1 + bP} f(\epsilon)\, d\epsilon \tag{6}$$

Combining Eqs. 4 and 5, and substituting in Eq. 2 yields

$$D^{\mathrm{Het}}_{s} = \int_{\epsilon_{\min}}^{\epsilon_{\max}} \frac{D_{so} \exp\left(-a\epsilon/RT\right)}{1 - \dfrac{bP}{1 + bP}} f(\epsilon)\, d\epsilon \tag{7}$$

where

$$b = b_o \exp\left(\epsilon/RT\right) \tag{8}$$

Equations 6 and 7 can be solved by substituting an energy distribution function. In principle, any suitable distribution function can be used. However, for mathematical simplicity, a uniform distribution function is used here. The uniform distribution is given as

$$f(\epsilon) = \frac{1}{\epsilon_{\max} - \epsilon_{\min}} \quad \text{for } \epsilon_{\min} \le \epsilon \le \epsilon_{\max}$$

and

$$f(\epsilon) = 0 \quad \text{for } \epsilon < \epsilon_{\min}; \quad \epsilon > \epsilon_{\max} \tag{9}$$

The mean ($\bar{\epsilon}$) and square root of variance (σ) of the uniform distribution are given as

$$\bar{\epsilon} = (\epsilon_{\max} + \epsilon_{\min})/2 \tag{10a}$$

and

$$\sigma = (\epsilon_{\max} - \epsilon_{\min})/(2\sqrt{3}) \tag{10b}$$

Substituting Eq. 9 into Eq. 6, an overall isotherm, Langmuir with uniform distribution (LUD), has been derived (Myers, 1984).

$$n(T, P) = \frac{q_m}{2s} \ln \frac{1 + \bar{b}Pe^{s}}{1 + \bar{b}Pe^{-s}} \tag{11}$$

where

$$\bar{b} = b_o \exp\left(\bar{\epsilon}/RT\right) \tag{11a}$$

$$s = \sqrt{3}\sigma/RT \tag{11b}$$

and s is a heterogeneity parameter, the value of which indicates the extent of surface heterogeneity.

For $a = 1$, substituting Eq. 9 into Eq. 7 gives

$$\frac{D^{\mathrm{Het}}_{s,\theta}}{D^{\mathrm{Het}}_{s,\theta=0}} = 1 + \frac{2s}{(e^{s} - e^{-s})} \left\{ \frac{e^{2s\theta} - 1}{e^{s} - e^{s(2\theta-1)}} \right\} \tag{12}$$

Similarly for $a = ½$, the surface diffusivity on a heterogeneous surface can be calculated by substituting Eq. 9 into Eq. 7 to give:

$$\frac{D^{\mathrm{Het}}_{s,\theta}}{D^{\mathrm{Het}}_{s,\theta=0}} = 1 + \frac{e^{2s\theta} - 1}{e^{s} - e^{s}(2\theta - 1)} \tag{13}$$

Equations 12 and 13 describe the surface diffusion on an energetically heterogeneous surface as a function of adsorbate concentration (θ) and heterogeneity parameter (s). Parameter s is obtained by fitting the equilibrium adsorption data to Eq. 11.

Results and Discussion

Effect of heterogeneity on surface diffusion was studied in terms of relative surface diffusivity as a function of θ, at various values of s. The results for $a = 1$ (Eq. 12) and $a = ½$ (Eq. 13) are shown in Figure 1. The curve for $s = 0$ corresponds to the HIO model which shows the behavior on a homogeneous surface. It is seen from Figure 1 that the effect of heterogeneity on surface diffusion is very different, depending on the value of a, i.e., the relationship between E and ϵ dictates the effect of heterogeneity on surface diffusion. For $a = 1$, the case when the activation energy of surface diffusion is equal to the energy of adsorption, the relative surface diffusivities on all heterogeneous surfaces are lower than that on the homogeneous surface with the same average ϵ. The higher the extent of heterogeneity (greater values of s), the lower is the relative surface diffusivity for a given surface coverage. However, the case when the activation energy of surface diffusion is one half of the energy of adsorption ($a = ½$), the relative surface diffusivities on heterogeneous surfaces are lower than that on the homogeneous surface (with the same $\bar{\epsilon}$) for low-surface coverages, and higher at higher-surface coverages, i.e., as the value of s increases, the relative surface diffusiv-

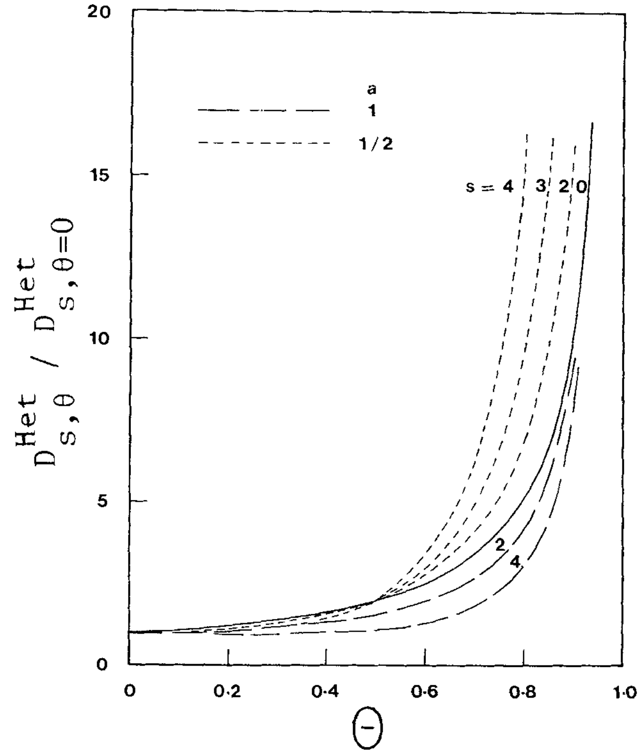

Figure 1. Effect of heterogeneity on surface diffusion.
All surfaces have the same average adsorption energy, $\bar{\epsilon}$.

ity vs. θ curve sharpens. These curves for different values of s intersect with each other at $\theta = 0.5$. These observations can be explained qualitatively as follows. At low values of θ, adsorption occurs mostly on high-energy patches and the adsorbate molecules are held strongly on the surface. This results in a lower overall surface diffusivity at low values of θ. At high surface coverages (high values of θ), however, significant adsorption occurs at low-energy patches, which also contribute to the overall relative surface diffusivity. For $a = 1/2$, this contribution from molecules on low-energy patches compensates, more than enough, for the low-surface diffusivity on high-energy patches, to give an overall increase in surface diffusivity compared to that on a homogeneous surface. It is different, however, for the case of $a = 1$. For $a = 1$, even on the low-energy patches, significantly more energies are required for surface diffusion, which makes the contribution from molecules on low-energy patches not enough to compensate for the low local surface diffusivities on the high-energy patches. Thus, the overall surface diffusivities on heterogeneous surfaces for $a = 1$ are lower than that for the homogeneous surface.

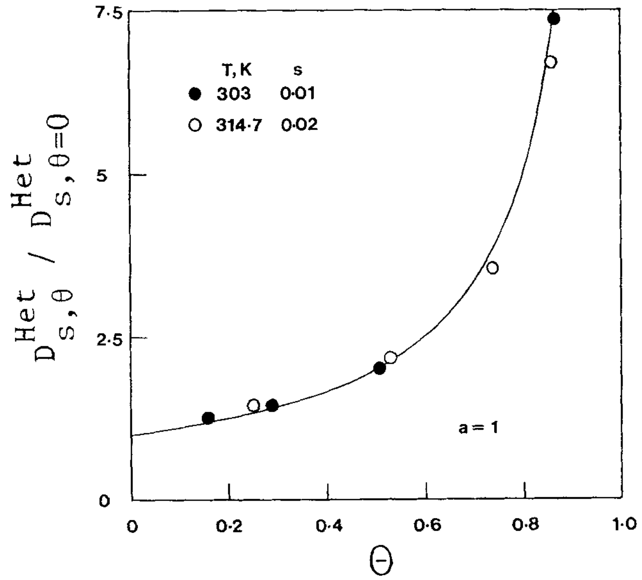

Figure 2. Surface diffusion of *n*-butane on Spheron 6 carbon black at 303 and 314.7 K.
Data points from Ross and Good (1956)

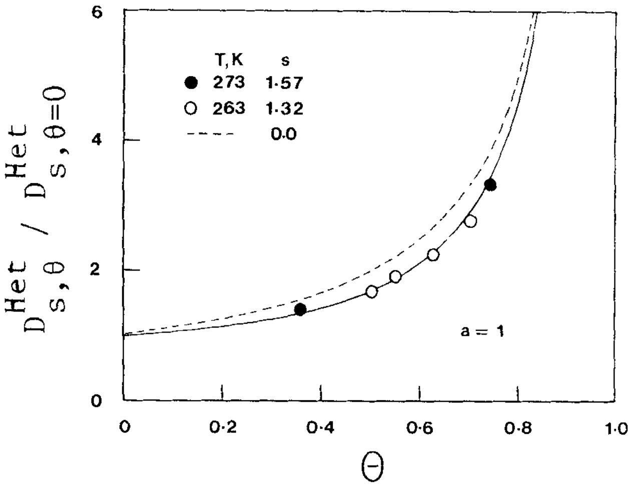

Figure 3. Surface diffusion of SO_2 on Linde silica at 263 and 273 K.
Data points from Carman and Raal (1951)

Comparison with Experimental Data

Experimental data on equilibrium adsorption and surface diffusivity for the case, $a = 1$, given in the literature (Ross and Good, 1956; Carman and Raal, 1951) were correlated by Eqs. 11 and 12. The comparisons between the experimental and predicted surface diffusivities are shown in Figures 2 and 3.

Ross and Good (1956) measured the adsorption isotherms and surface diffusivities of *n*-butane on Spheron 6 (2,700°) carbon black at two temperatures (303 and 314.7 K). The adsorption data were obtained for pressures up to 60 cm Hg (80 kPa). The adsorption data were correlated by Eq. 11, and the parame-

Table 1. Heterogeneous Isotherm Parameters

System	T, K	q_m(mol/kg)	$\bar{b}$(l/atm)	s
n-Butane*	303	0.419	21.21	0.010
	314.7	0.431	11.83	0.023
SO_2**	263	3.273	6.81	1.322
	273	4.046	2.43	1.570
SO_2†	252.3	7.395	8.29	1.952
	239.4	12.52	3.61	3.953

*Spheron 6 carbon black (Ross and Good, 1956)
**Linde silica (Carman and Raal, 1951)
†Carbolac I carbon (Ash et al., 1963)

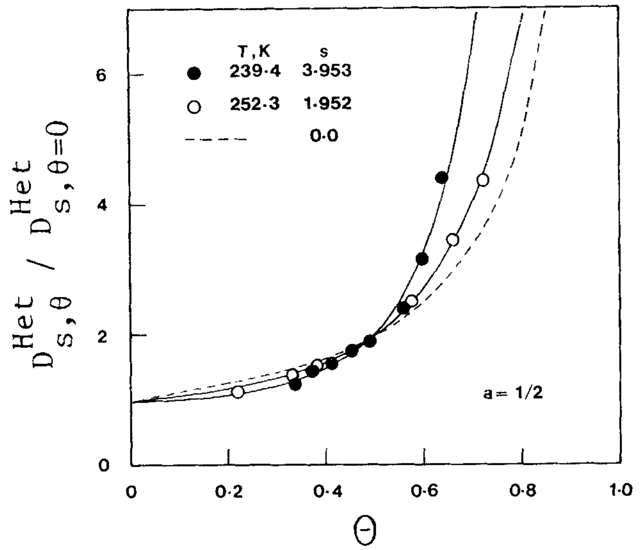

Figure 4. Surface diffusion of SO_2 on Carbolac I carbon at 239.4 and 252.3 K.
Data points from Ash et al. (1963)

ters, q_m, $\bar{b}$ and s are listed in Table 1. The small values of s showed that carbon black is fairly homogeneous. The average relative error between the experimental adsorption amount and the amount calculated from Eq. 11 was less than 3%. A comparison between experiment and model predictions for surface diffusivity is shown in Figure 2. The two curves obtained by Eq. 12 for $s = 0.01$ and 0.023 were very close to the one predicted by the HIO model.

Carman and Raal (1951) studied diffusion of gases on Linde silica at 263 and 273 K. The adsorption data of SO_2 on Linde silica were correlated by Eq. 11. The average relative error of fit was 3.0% at 263 and 1.7% at 273. The adsorption isotherm parameters are also listed in Table 1. The values of s (1.322 and 1.57) show the extent of heterogeneity of Linde silica. The experimental and predicted results for surface diffusivity are compared in Figure 3. The diffusivity curve for $s = 1.322$ is slightly higher than that for $s = 1.57$. Also shown is the curve for the homogeneous surface ($s = 0$), i.e., predictions by the HIO model. It is seen that the inclusion of the effect of heterogeneity gives a better fit of the experimental data.

All the experimental data discussed above belonged to the case of $a = 1$. Ash et al. (1963) measured the adsorption isotherm and surface diffusion of SO_2 on carbon. For the SO_2/carbon system, Sladek et al. (1974) found that $a = 1/2$. The adsorption data of SO_2/carbon at 239.4 and 252.3 K were correlated by Eq. 11. The average relative error was less than 4%. The isotherm parameters, q_m, $\bar{b}$ and s are listed in Table 1. Reasonably large values of s (1.952 and 3.953) show that these systems are heterogeneous in nature. The experimental surface diffusivity data were correlated by Eq. 13, which is derived for $a = 1/2$. A comparison between experimental and theoretical values is shown in Figure 4. Also shown are the predictions by the HIO model for a homogeneous surface. The effects of heterogeneity on surface diffusivity are clearly shown in Figure 4.

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Notation

b = constant in the Langmuir isotherm, 1/kPa or 1/atm
$\bar{b}$ = defined by Eq. 11a
D = diffusivity, m^2/s
E = activation energy for surface diffusion, kJ/mol
f = energy distribution function
nq = amount adsorbed, mol/kg
P = pressure, kPa or atm
R = gas constant
s = heterogeneity parameter, defined by Eq. 11b, dimensionless
T = temperature, K

Greek letters

ϵ = energy or heat of adsorption, kJ/mol
$\bar{\epsilon}$ = average value of ϵ, kJ/mol
θ = fractional surface coverage
σ = square root of variance for energy distribution, kJ/mol

Subscripts

m = monolayer
min = minimum value
max = maximum value
o = constant
s = surface

Superscripts

Het = on heterogeneous surface
Hom = on homogeneous surface

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