JOURNAL OF CATALYSIS **88**, 530–534 (1984)

A Frequency Response Technique to Study Zeolitic Diffusion of Gases

In a preceding article (*1*) a frequency response (FR) method has been proposed to determine diffusional time constants of a gas in one- or three-dimensional micropores. The purpose of this note is to present evidence for characteristic functions, δ_{3c} and δ_{3s}, with actual data, which have been derived analytically for the latter case (*1*); systems of Kr (or Xe) over 5A zeolites are investigated and it is shown that the functions are valid to determine not only the diffusional time constant but also a crystal-size distribution.

Commercial synthetic 5A zeolites, Linde 5A (binder free, Union Carbide), and Merck 5A (binder free, Merck), are used. Before the measurements, the powders pelletized (ca. 10 g) were dehydrated at 383 K for 10 h. The temperature was raised to 673 K and evacuated at that level for at least 30 h. Before a subsequent run, the zeolite was degassed at 673 K for at least 20 h.

In the course of the measurements of an equilibrium isotherm, the FR measurements were carried out at an equilibrium pressure. Every isotherm could be regarded as linear (*2*) against the pressure over the range 1 to 10 Torr (1 Torr = 133.3 N m^{-2}) so that Henry constant k could be found directly.

In the FR method, the system is perturbed by changing sinusoidally the volume of a gas space. The change generated could be represented well by

$$V = V_e(1 - ve^{i\omega t}) \qquad (1)$$

where V_e denotes the volume at the equilibrium, v (ca. 5×10^{-2} in standard runs) is the relative amplitude of the volume variation, and ω is the angular velocity of the sinusoidal wave generator. Then, the induced pressure variation could be represented in general by

$$P = P_e\{1 + pe^{i(\omega t+\varphi)}\}. \qquad (2)$$

The relative amplitude p and the phase lag φ depended on ω.

The in-phase and out-of-phase components, $(v/p)\cos \varphi - 1$ and $(v/p)\sin \varphi$, respectively, of the FR of the Kr/Linde 5A system at P_e = 5.8 Torr and T_e = 195 K are plotted together in Fig. 1. The dashed curves (as a first approximation) correspond to two characteristic functions (*1*):

$$\delta_{3c} = (3/\eta)(\sinh \eta - \sin \eta)/(\cosh \eta - \cos \eta) \qquad (3)$$

$$\delta_{3s} = \frac{6}{\eta}\left[\frac{1}{2}\left\{\frac{\sinh \eta + \sin \eta}{\cosh \eta - \cos \eta}\right\} - \frac{1}{\eta}\right] \qquad (4)$$

$$\eta \equiv (2\omega a^2/D)^{1/2} \qquad (5)$$

where a denotes the radius of an isotropic sphere and D is the diffusion coefficient of a gas within it; the value for the parameter D/a^2 of the dashed curves is 2.1 $\min^{-1}$.

Dependence of the FR data obtained from the Xe/Linde 5A systems upon P_e and T_e is exhibited in Fig. 2; the apparent activation energy of D derived from the shift along the abscissa of the solid curves was 5.2 kcal/mol.

In Fig. 3 the FR data of the Kr/Merck 5A system at T_e = 195 K under different equilibrium pressures are plotted together. Evidently, they are independent of the pressures. It should be noted further that they were unaltered even when v was reduced to about one-third.

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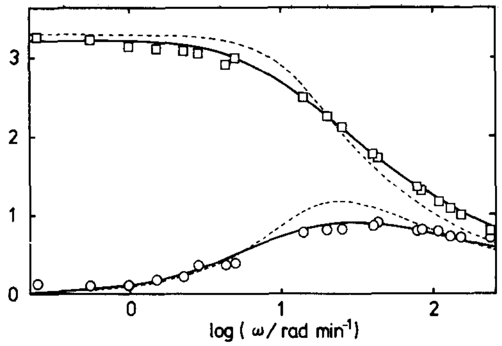

FIG. 1. Frequency response of the Kr/Linde 5A system at $P_e = 5.8$ Torr and $T_e = 195$ K. The in-phase and out-of-phase components, $(v/p)\cos\varphi - 1$ and $(v/p)\sin\varphi$, are shown by the squares and circles, respectively. The solid curves represent the calculated results from Eqs. (6) (upper curve) and (7) (lower curve); the values for the parameters, K, D/a_m^2, and $\bar{\sigma}$, are given in Table 1. The dashed curves correspond to the characteristic functions of Eqs. (3) and (4) applicable to an assembly of *identical* spherical particles.

Electron micrographs of the two kinds of 5A are compared in Fig. 4. The crystal-size distribution of Linde 5A has been determined empirically by a photomicrographic technique to be approximately normal on a weight or volume fraction basis, of which (relative) standard deviation was 0.3–0.4 depending on the samples from different batches (*3*). It is assumed therefore that the size distribution of both zeolites is also normal.

The solid curves in Fig. 1 represent the theoretical ones calculated from

$$(v/p)\cos\varphi - 1 = K\bar{\delta}_{3c} \qquad (6)$$

$$(v/p)\sin\varphi = K\bar{\delta}_{3s} \qquad (7)$$

where the characteristic functions modified by the distribution are given explicitly as

$$\bar{\delta}_{3j} = \frac{1}{\sqrt{2\pi}\sigma}\int_0^\infty \delta_{3j}\left(\frac{D}{a_x^2}\right) \exp\left\{-\frac{(a_x - a_m)^2}{2\sigma^2}\right\} da_x \qquad (8)$$

$$(j = \text{c or s})$$

which contain two parameters, D/a_m^2 and $\sigma/a_m(\equiv \bar{\sigma}$; named relative standard deviation).

The values for the three parameters characteristic of the *two* solid curves were determined by a computer as follows. The value of D/a_m^2 was expected to be about 2.1 min^{-1} as noted above; that of $\bar{\sigma}$ was estimated to be around 0.4 as discussed above; that of K, on the other hand, can be derived

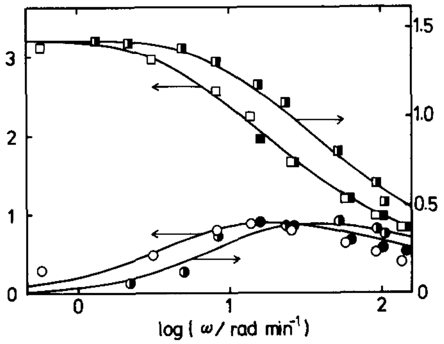

FIG. 2. Temperature and pressure dependence of the FR data on the Xe/Linde 5A system. ◨ and ◑; the in-phase and out-of-phase components of the data, respectively, obtained at $T_e = 273$ K (at $P_e = 7.4$ Torr). The other symbols correspond to the data at $T_e = 253$ K (□ and ○, at $P_e = 1.9$ Torr; ■ and ●, at $P_e = 5.0$ Torr). The solid curves are similar in shape with the ones in Fig. 1; the values for the parameters characteristic of the curves are given in Table 1.

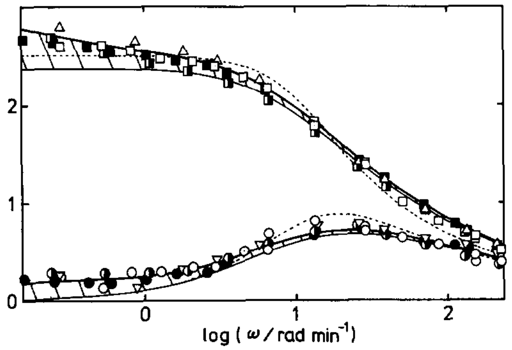

FIG. 3. Frequency response of the Kr/Merck 5A system at $T_e = 195$ K. □ and ○ indicate the in-phase and out-of-phase components at $P_e = 0.9$ Torr, respectively; ◨ and ◑, at $P_e = 5.6$ Torr; ■ and ●, at $P_e = 5.4$ Torr; △ and ▽, at $P_e = 4.2$ Torr, which were obtained under a reduced amplitude of the volume change, $v = 1.84 \times 10^{-2}$.

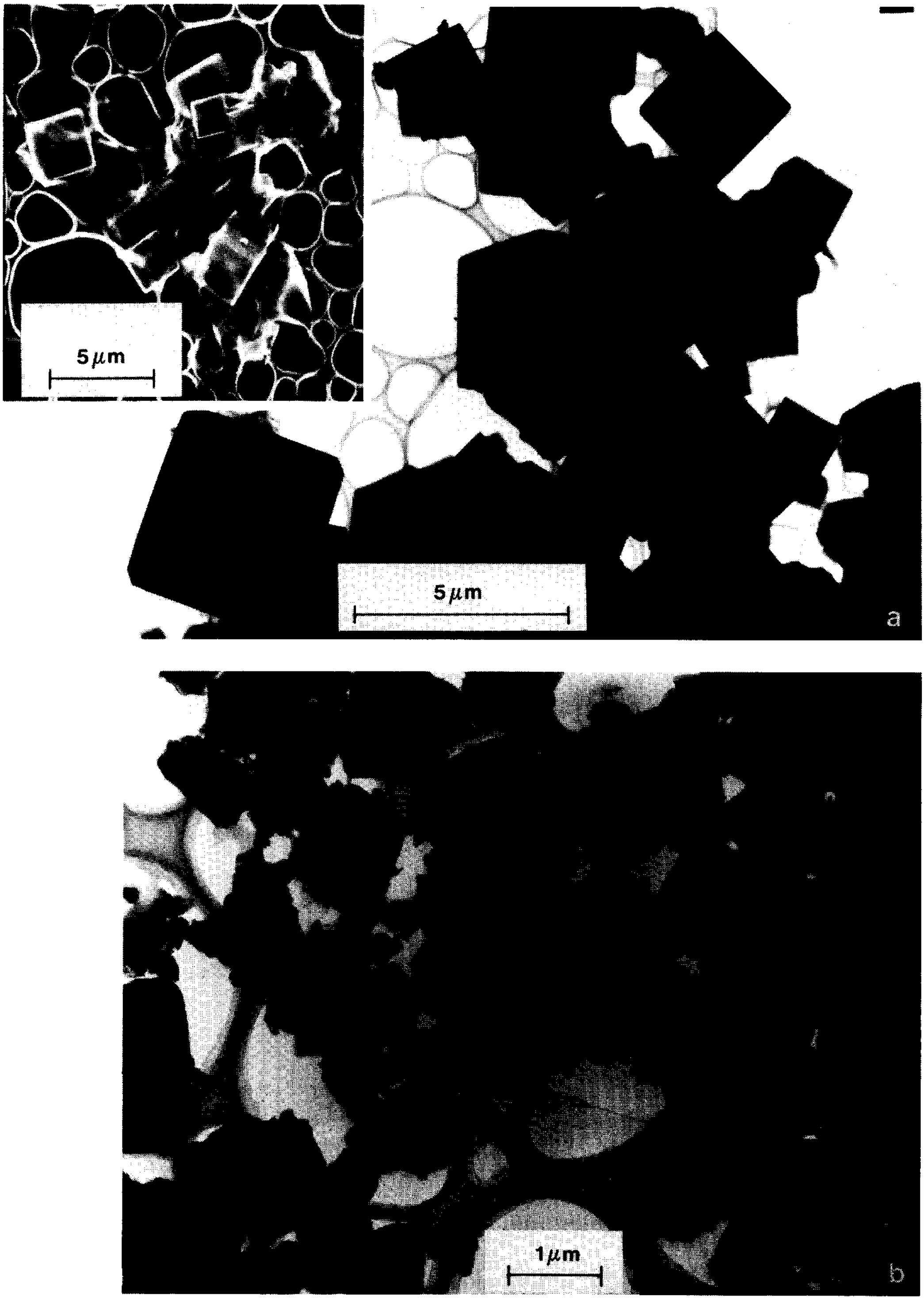

FIG. 4. Electron micrographs: (a) SEM and TEM of Linde 5A and (b) TEM of Merck 5A samples.

TABLE 1

Results Obtained by Data Analysis

System	T_e (K)	K_H	K	(D/a_m^2) (min^{-1})	$\bar{\sigma}$	K/K_H
Kr/Linde 5A	195	3.43	3.30 (±0.05)	2.20 (±0.05)	0.50 (±0.05)	0.96
Xe/Linde 5A	253	3.53	3.3	1.3	0.5[a]	0.9_3
	273	1.50	1.5	2.8	0.5[a]	1.0
Kr/Merck 5A	195	3.01	$(K_1 =)$2.40 (±0.05) $(K_2 =)$0.60 (∓0.05)	$(D_1/a_1^2=)$1.75 (±0.05) $(D_2/a_2^2 =)1.6 \times 10^{-2}$ $(\pm 0.3 \times 10^{-2})$	$(\bar{\sigma}_1 =)$0.45 (±0.05) 0.45[a]	1.00

[a] Each value was presumed to be 0.50 or 0.45.

from the gradient of the isotherm provided only one kind of admolecules exist (*1*). Most probable values of them given in Table 1 were obtained after the repeated calculation for various choices of the parameters around the initial values. The value of K calculated from the gradient of the isotherm or the Henry constant k, K_H, according to the equation of $K_H = (RT_0/V_e)k$ (*1*) (V_e was 1.2 dm^3 in the present work), is compared with K in Table 1.

The two couples of the solid curves in Fig. 2 are similar in shape with the ones in Fig. 1; the values for the parameters except $\bar{\sigma}$ were determined by curve fitting, because $\bar{\sigma}$ of the Xe/Linde 5A system is expected to be identical with that of the Kr/Linde 5A system. The results are summarized in Table 1.

In the data analysis of the Merck 5A system, however, it is found that

$$(v/p)\cos\varphi - 1 = K_1\bar{\delta}_{3c}^{(1)} + K_2\bar{\delta}_{3c}^{(2)} \quad (9)$$

$$(v/p)\sin\varphi = K_1\bar{\delta}_{3s}^{(1)} + K_2\bar{\delta}_{3s}^{(2)} \quad (10)$$

are preferable to Eqs. (6) and (7). The heavy solid curves in Fig. 3 represent the calculated results; the components of the first terms are represented by the light solid curves and those of the second terms are indicated by the shaded areas. The values for the six parameters determined by the computation are summarized in Table 1.

Additional FR measurements of Kr/Linde 5A were performed with a reduced amount of the sorbent (ca. 5 g). Both in-phase and out-of-phase components were proportional within experimental errors to the amount of the sorbent. The fact would support the assumption in Eqs. (6) and (7) and Eq. (8) that contributions of various particles may be given by their linear combinations.

Mean cube side of Linde 5A is reported to be 3.05–3.91 μm depending on batches (*3*). Therefore, the mean radius of the Linde 5A, a_m, is assumed to be 1.8 μm. Considering the diffusional time constant in Table 1, one finds $D = 1.2 \times 10^{-9}\ \text{cm}^2/\text{s}$; the concentration of Kr was 0.23 molecules/cavity at that equilibrium pressure. The value of D seems one order of magnitude larger than that obtained by a microbalance (*4*).

Most remarkable discrepancy is in the dependence of D upon P_e or the amount of molecules absorbed. In contrast to inverse concentration dependence reported (*4*), the results in Figs. 2 or 3 lead evidently to a constant diffusion coefficient. It has been reported that in small crystals such as Linde 5A, sorption rates of CF_4 and n-C_4H_{10} are controlled by combined effects of external heat transfer and intracrystalline diffusion (*5*). It should be emphasized, however, that the intrusion of heat transfer resistance can be neglected in the present work, because these FR data were independent of the amplitude of the volume change, v (see Fig. 3).

The micrographs in Fig. 4 show striking contrast; there are many amorphous fragments in Merck 5A, while only cubic crystals in Linde 5A. The second terms of Eqs. (9) and (10) added may be attributed to the fragments as follows. Additional experiments were performed with Merck 4A (prepared from the Merck 5A by exchanging Ca^{2+} for Na^+). The FR data on the Kr/Merck 4A system at $T_e = 195$ K revealed that the diffusion corresponding to the first terms vanished by the cation exchange, whereas that of the second terms was not affected.

Every value of K/K_H and $(K_1 + K_2)/K_H$ in Table 1 may be regarded as unity within experimental errors. Therefore, additional terms would not be required in Eqs. (6) and (7) and also in Eqs. (9) and (10).

Since the FR technique may be applied to *every* gas system at various equilibrium temperatures and pressures, it would be a viable way for determination of not only intracrystalline diffusion coefficients but also to characterize zeolites. It should be emphasized further that the range of diffusivities accessible to reliable measurement by the FR technique could be extended to both ranges (being far apart) by the sorption-rate and NMR techniques so that large discrepancy between diffusion coefficients observed by both techniques (*6, 7*) might be resolved in a case by the present technique.

ACKNOWLEDGMENTS

The authors are grateful to Mr. Nobuaki Sato and to Mr. Kinya Mori for help in the measurements of the Merck 5A systems. The authors are also grateful to Professor Ikuya Matsuura for fruitful discussions and to Professor Tatsuaki Yashima of Tokyo Institute of Technology for advice about zeolites.

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Received September 27, 1983

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