

One dimensional gas adsorbed in zeolitic pores

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Abstract -- The statistical thermodynamics of one-dimensional fluid was recapitulated and represented in a convenient form for comparison with experiments.

Experimental results of adsorption of Xe and Ar in H-ferrierite were fully analyzed. The one-dimensionality of the adsorbed gas was confirmed. The temperature coefficients of 2nd, 3rd and 4th virial coefficients were determined. The isosteric heat of adsorption was expressed in a form of polynomial function of the adsorbed amount. The coefficients of the polynomials must equal to the the temperature coefficients of the virial coefficients. This was satisfied. The observed virial coefficients were approximately described by an repulsive interaction potential between admolecules.

INTRODUCTION

It was found that some simple molecules adsorbed in mordenite behave as one dimensional (1-D) gas, freely translating along a 1-D channel (ref.1). In the present paper a statistical mechanical theory of 1-D gas in the zeolitic pore is developed and applied to experimental data available to elucidate the interaction between admolecules. In the last section, effects of impurity is discussed which hinder the free translation of admolecule.

THERMODYNAMICS

The equation of state of 1-D gas expressed as

$$\phi = kTc [1 + Bc + Cc^2 + Dc^3 + \dots] \quad (1)$$

with $c = N/L$,

in which N , ϕ and L denote the number of admolecules, 1-D pressure, and total length of pore, respectively. The chemical potential of admolecules, μ_s , is obtained as

$$\begin{aligned} \int dF_s &= -\int \phi dL = -NkT \int \frac{1}{L} [1 + B \left(\frac{N}{L}\right) + C \left(\frac{N}{L}\right)^2 + D \left(\frac{N}{L}\right)^3 + \dots] dL \\ &= -NkT [\ln L - B \left(\frac{N}{L}\right) - \frac{C}{2} \left(\frac{N}{L}\right)^2 - \frac{D}{3} \left(\frac{N}{L}\right)^3 - \dots] \\ \mu_s &= \partial F_s / \partial N = -kT [\ln L + 2B \left(\frac{N}{L}\right) + \frac{3C}{2} \left(\frac{N}{L}\right)^2 + \frac{4D}{3} \left(\frac{N}{L}\right)^3 + \dots] + \text{const.}, \\ &= \mu_s^{\circ} + kT \ln c + kT [2B + (3C/2)c^2 + (4D/3)c^3 + \dots], \end{aligned}$$

where $\mu_s^{\circ} + kT \ln c$ is the chemical potential of the ideal 1-D gas.

The adsorption isotherm is obtained by the aid of a relation,

$$\mu_{\text{gas}} = \mu_g^\circ + kT \ln P = \mu_s,$$

where μ_{gas} and P are the chemical potential and pressure of gas molecule, respectively, which is in equilibrium with the adsorbed phase. Thus we have (ref.2),

$$P = \frac{c}{k_H} \exp \left[2Bc + \frac{3C}{2} c^2 + \frac{4D}{3} c^3 + \dots \right] \quad (2)$$

where k_H denote Henry's constant in adsorption and given by,

$$k_H = \exp \left[(\mu_g^\circ - \mu_s^\circ) / kT \right]. \quad (3)$$

The isosteric heat of adsorption, q_{st} , is given by,

$$\begin{aligned} q_{st} &= -k \left[\frac{\partial \ln P}{\partial (1/T)} \right]_N \\ &= q_{st}^\circ - k \left[2 \frac{dB}{d(1/T)} c + \frac{3}{2} \frac{dC}{d(1/T)} c^2 + \frac{4}{3} \frac{dD}{d(1/T)} c^3 + \dots \right] \end{aligned} \quad (4)$$

where q_{st}° is the initial heat of adsorption and given by

$$q_{st} = -T^2 \frac{d}{dT} \left[(\mu_g^\circ - \mu_s^\circ) / T \right] = h_g^\circ - h_s^\circ$$

It is implicitly assumed in the derivation of Eq.4 that the change of the pore length L is negligibly small. The thermal entropy of the adsorbed 1-D gas molecule s_s° became as,

$$s_s^\circ = s_g^\circ + kT \ln k_H - q_{st}/T,$$

where s_g° is the thermal entropy of gaseous molecule.

STATISTICAL MECHANICS

Now let us derive explicit expressions for the above quantities by using statistical mechanics. If admolecule is monoatomic, translates freely in a 1-D channel, and vibrates against the channel wall as a two-dimensional simple harmonics oscillator with soft frequencies ν' and ν'' , we have,

$$\mu_s^\circ = -\frac{kT}{2} \ln \left(\frac{2\pi mkT}{h^2} \right) - kT \ln \left(\frac{kT}{h\nu'} \frac{kT}{h\nu''} \right) - \chi_0.$$

where χ_0 denotes a work required to bring an admolecule at its lowest state to the lowest state in gas phase. Using the usual formula,

$$\mu_g^\circ = -\frac{3kT}{2} \ln \left(\frac{2\pi mkT}{h^2} \right) - kT \ln(kT)$$

we have

$$\ln k_H = \chi_0/kT - \ln(2\pi m \nu' \nu'') \quad (5)$$

and hence

$$q_{st}^\circ = \chi_0. \quad (6)$$

and

$$s_s^\circ = s_g^\circ - k \ln(2\pi m \nu' \nu'') \quad (7)$$

These equations hold even for diatomic molecules having degrees of freedom of rotation, if the rotation is not hindered in the zeolitic pore. The hindered rotation is not discussed in detail in the present paper.

If admolecules are localized on some sites and oscillate around a potential minimum with soft frequencies ν' , ν'' and ν''' , then μ_s° becomes as

$$\mu_s^\circ(\text{loc}) = -\chi_o - kT \ln \left(\frac{(kT)^3}{h\nu' h\nu'' h\nu'''} \right)$$

and hence

$$\ln k_H(\text{loc}) = \frac{\chi_o}{kT} + \frac{1}{2} \ln(kT) - \ln [(2\pi m)^{3/2} \nu' \nu'' \nu'''] \tag{8}$$

Only very accurate experiments can discriminate the small difference between Eqs.5 and 8.

The virial coefficients are given by

$$B = \frac{1}{2} \int_0^\infty f_{12} dr_{12}, \tag{9}$$

$$C = \frac{1}{3} \int_0^\infty \int_0^\infty f_{12} f_{23} f_{13} dr_{12} dr_{23} \tag{10}$$

$$D = \frac{1}{8} \int_0^\infty \int_0^\infty \int_0^\infty (f_{12} f_{23} f_{34} f_{14} + f_{13} f_{23} f_{24} f_{14} + f_{12} f_{34} f_{13} f_{24} \\ + f_{12} f_{23} f_{34} f_{14} f_{13} + f_{13} f_{23} f_{24} f_{14} f_{12} + f_{12} f_{34} f_{13} f_{24} f_{14} \\ + f_{12} f_{23} f_{34} f_{14} f_{24} + f_{13} f_{23} f_{24} f_{14} f_{34} + f_{12} f_{34} f_{13} f_{24} f_{23} \\ + f_{12} f_{23} f_{34} f_{14} f_{13} f_{24}) dr_{12} dr_{23} dr_{34} \tag{11}$$

and so on,

with $f_{ij} = 1 - e^{-\beta u(r_{ij})}$, and $\beta = 1/kT$ (12)

where r_{ij} and $u(r_{ij})$ designate the distance and the interaction potential between the i -th and j -th admolecules, respectively, and it is assumed that admolecules are aligned in the order of numbering 1,2,3 and 4, and the mutual interchange does not occur in the concerned narrow channel. If the functional form of $u(r_{ij})$ is given, one can calculate values for B, C and D.

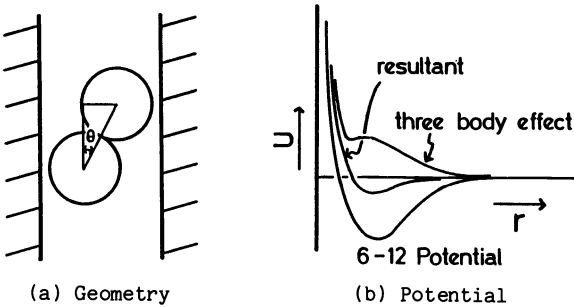


Fig.1. Geometry of a pair of admolecules in the pore and mutual interaction potential

The Lennard-Jones 6-12 potential is most frequently used as an interaction potential. The interaction potential between admolecules is considerably deformed from the 6-12 one by the following two causes. First, the pore diameter is usually larger than that of molecules, and a situation shown in Fig.1(a) occurs in collisions of admolecules. In other words, the strict one-dimensionality cannot be realized, but the phenomena are treated as pseudo 1-D problems. Second, the three-body effect strongly operates between two admolecules and adsorbate solid, and the attractive force between admolecules is seriously reduced (ref.3). A plausible potential profile in this system is depicted in Fig.1(b). This potential form may be approximated by a function,

$$u(r) = U_o \left[\left(\frac{r_o}{r_{12}} \right)^{12} - \eta \left(\frac{r_o}{r_{12}} \right)^6 \right] \quad \text{with} \quad \eta < 2 \tag{13}$$

in which values for r_o and U_o might differ from corresponding ones in 3-D gas, owing to the above reason, depending upon the geometry.

By substitutions,

$$r_0 = \sigma |\eta|^{1/6}, \text{ and } \beta U_0 \eta^2 = 1/t, \tag{14}$$

Eq.9 is reduced as

$$B = \frac{\sigma}{2} t^{-1/12} [1.056 \mp 0.177t^{-1/2} - 0.0440t^{-1} \mp 0.00336t^{-3/2} \dots] \tag{15}$$

in which \mp correspond to $\eta > 0$ and $\eta < 0$ cases, respectively. In the derivation of Eq.15, the use is made of the usual method, developed by Lennard-Jones (ref.4).

Analytical-expressions for C and D are difficult to obtain and numerically calculated.

ANALYSIS OF EXPERIMENTAL DATA

Only limited experimental data are available which are so accurate to be compared with the above theory in detail. One of such is adsorption of rare gases (Xe, and Ar) with ferrierite having a composition of $H_{3.7}(Al_{3.7}Si_{32.3}O_{72})$ (ref.5). Observed values for $\ln k_H$, B, C and D are plotted against $1/T$, and q_{st} against c in Figs 2-6. The straight line in the plots of $\ln k_H$ vs $1/T$ has a correlation coefficient of 0.99997, and it is concluded with confidence that Eq.5 holds, and that the adsorbed molecule freely translates in the 1-D channel and vibrates against the channel wall with soft frequencies.

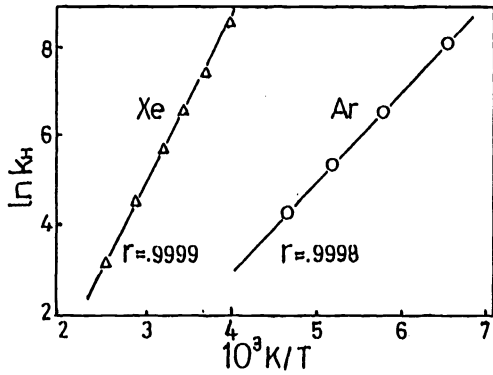


Fig.2. Temperature dependence of Henry's constant. Xe and Ar adsorbed in H-ferrierite; q_{st} : 31.5 kJ mol⁻¹ for Xe; 17.07 kJ mol⁻¹ for Ar.

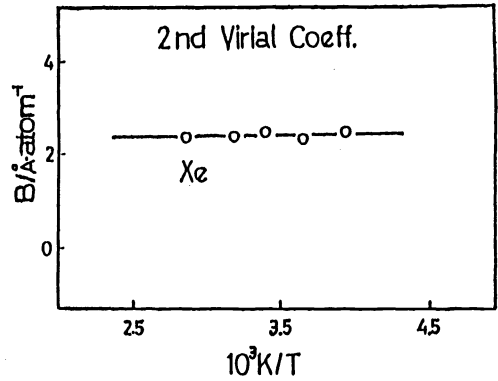


Fig.3. Temperature dependence of second virial coefficient. Xe adsorbed in H-ferrierite.

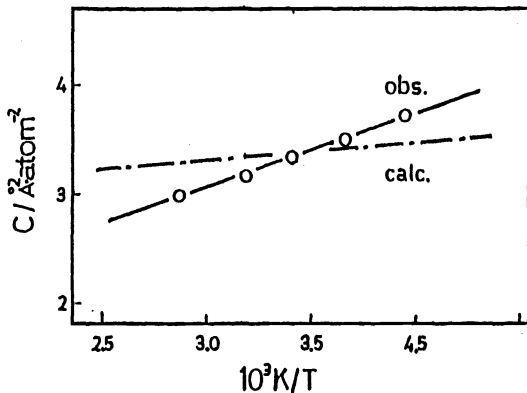


Fig.4. Temperature dependence of 3rd virial coefficient. Xe adsorbed in H-ferrierite.

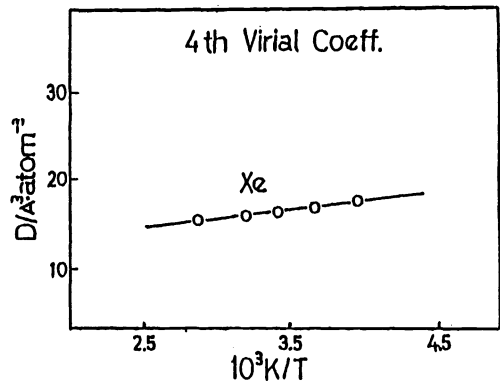


Fig.5. Temperature dependence of 4th virial coefficient. Xe adsorbed in H-ferrierite.

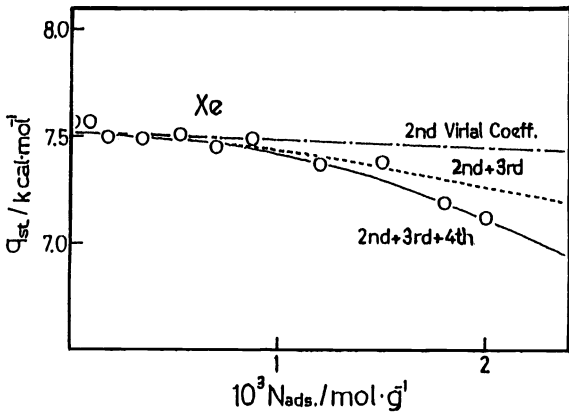


Fig.6. Isosteric heat of adsorption vs. adsorbed amount.

Xe in H-ferrierite at $-40 \sim 120^\circ\text{C}$.

Circle, observed values ;

Curves, calculated values:

- · — · — , only 2nd virial coeff. included ;
- · · · · , 2nd and 3rd virial coeff. included ;
- , 2nd, 3rd and 4th virial coeff. included.

The curve of q_{st} vs. c can be calculated by using Eq.4. If the terms referred to $dB/d(1/T)$, $dC/d(1/T)$, and $dD/d(1/T)$ are successively taken into account in Eq.4, calculated curves gradually approach to and coincide with the observed one, as can be seen in Fig.6. This is the first experimental verification of the thermodynamic relation Eq.4. As the correctness of the present data is ensured, we can proceed further in detailed analysis.

The curve of B vs. $1/T$ is described by a equation

$$B = 2.17 + 60.3/T \quad (\text{in } \text{Å} \text{ unit}) \quad (16)$$

The positive gradient means that the repulsive force predominantly operates in the observed temperature region. Let us use provisionally an approximation, $\eta = 0$, in the analysis of Xe adsorption data. Then, Eq.15 is reduced to

$$B = 0.526 r_0 (U_0/kT)^{1/12}, \quad (17)$$

and

$$\frac{dB}{d(1/T)} = \frac{BT}{12} \quad (18)$$

Introducing the observed values for B at $T = 300 \text{ K}$ ($B = 2.4 \text{ Å}$) into Eq.18 and 17, we have

$$\frac{dB}{d(1/T)} = 60 \quad \text{and} \quad r_0 (U_0/300k)^{1/12} = 4.56$$

the former of which is in good agreement with Eq.16.

Introducing $U_0/k = 225 \text{ K}$, which is a value for 3-D gas, we have

$$r = 4.67 \text{ Å}$$

which is almost same to the value for 3-D gas of Xe, 4.6 Å . Thus it is concluded that θ in Fig.1(a) is almost zero.

Values for C and D are calculated by using the above values for the parameters, but results are not completely satisfactory as shown in Fig.4, as $\eta = 0$ is a tentative approximation to have a semi-quantitative conclusion on the form $u(r)$. However, it is concluded that the three body effect strongly operates to reduce drastically the attractive force between admolecules.

THREE-BODY EFFECT

The interaction potential between a pair of admolecules differs considerably from that between an isolated pair in vacuum, as before mentioned. The difference stems from the three-body effect, i.e., a third-order perturbation energy in a system of three bodies. In 3-D gas, the effect is small, while fairly large in the adsorption phenomena (ref.3,6). As for 1-D gas adsorbed in a zeolitic pore, a theory was developed by the present author (ref.7), and its essential part is reviewed and criticized in the following.

Let E_{ij} be the dispersion energy between a pair of particles specified by i and j , then the total dispersion energy of a system composed of particles 1,2, and i , E_{tot} , is given by

$$E_{tot} = E_{12} + E_{1i} + E_{2i} + E_{12i},$$

that is, it contains a non-additive term E_{12i} . E_{12i} is small in a system of three particles in gas phase. In the adsorption phenomena, we must consider quantities such as $\sum E_{1i}$, $\sum E_{2i}$ and $\sum E_{12i}$ ($= E_{12s}$), where the summation is carried out over an adsorbent solid, and these terms becomes fairly large. The first and second term contribute to the adsorption energy, and $E_{12} + E_{12s}$ is observed as an interaction potential between a pair of admolecules.

For a model shown in Fig.7, E_{12s} was numerically calculated and approximated, in a limit of accuracy of 15%, as

$$E_{12s} = \frac{\pi}{4} n_s \alpha_s \frac{\Delta_s (2\Delta_1 + \Delta_s)}{(\Delta_1 + \Delta_s)^2} \left[1.5 - \frac{1.72 R}{r_{12}} \right] E_{12} \quad (19)$$

where n_s and α_s are the number of atoms constituting solid in a unit volume, and their mean polarizability, respectively, Δ_1 and Δ_s the mean excitation energy of the admolecule and solid, respectively, and R the radius of the zeolitic pore. Eq.19 contains two unknown parameters Δ_s/Δ_1 and α_s , the former of which may not much differ from unity. The value of α_s for zeolites was not known previously, but now can be determined by measuring the Auger parameter in Si-KLL line with XPS techniques (ref.8). Only values for zeolite A and mordenite were obtained as to be 2.5 and 2.2 Å³, respectively (ref.9).

As for ferrierite, let us provisionally chose the following values:

$$\Delta_s/\Delta_1 = 1, \quad \alpha_s = 2.2 \text{ \AA}^3, \quad \text{and} \quad R = 2.5 \text{ \AA},$$

then Eq.19 becomes as $E_{12s} = \left[1.1 - \frac{3.16}{r_{12}} \right] E_{12}$

and hence we have $u_{12} = U_0 \left[\left(\frac{r_0}{r_{12}} \right)^{12} - 0.9 \left(\frac{r_0}{r_{12}} \right)^6 - \frac{3.16}{r_{12}} \left(\frac{r_0}{r_{12}} \right)^6 \right]$

in which r_{12} is given in unit of Å and the 6-12 potential is used for an isolated pair potential.

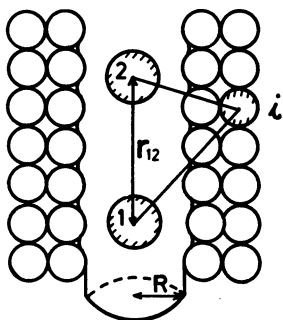


Fig.7. Admolecules and atoms constituting adsorbent.

The above potential contains non-negligible attractive terms and does not fit quantitatively to the experimental result. E_{12s} in Eq.19 was derived by using a jelly model for the solid, and a lattice model may give a larger value for E_{12s} . More accurate quantum mechanical and numerical calculations are required to obtain a best-fit potential which self-consistently describes B, C, and D.

ON THE EFFECTIVE PORE LENGTH

Zeolite crystal, usually used in adsorption experiments, is larger than $0.5 \mu\text{m}$ but smaller than $5 \mu\text{m}$ in its edge. Colloidal impurities or larger ions are frequently located on the wall of the channel, and partially hinder the free translation of admolecules. Admolecule must overcome these barrier to diffuse into the pore with some activation energy (See Fig.8). Thus the effective length of the pore, in which admolecule freely translates, is seriously reduced as well as the rate of diffusion of admolecule. The thermodynamic functions of admolecules, however, are not influenced by such a reduction of the pore length, as the usual approximation,

$$Q_{\text{trans}} = \sum_n \exp[-n^2 h^2 / (8mkTL^2)] = \int_0^\infty \exp[-n^2 h^2 / (8mkTL^2)] dn = L \sqrt{2\pi mkT} / h ,$$

valids even for $L = 10 \text{ nm}$ for Ar.

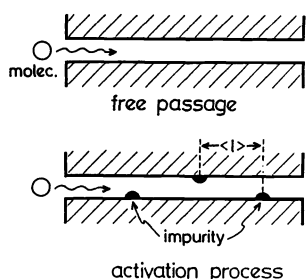


Fig.8. 1-D channel and impurities on the wall, blocking translation of admolecules.

To investigate the presence or non-presence of such a reduction, we must measure dynamic properties of admolecules, e.g., the relaxation time of electron spin or nuclear spin. Molecular oxygen has unpaired electrons and is similar to Ar as adsorbate, having similar molecular diameter and adsorption heat. Let us use molecular oxygen as a probe molecule to investigate the presence of impurities on the wall of the pore channel.

Oxygen molecule in the pore of mordenite freely translates and rotates, and its ESR spectrum is just same to that of 3-D gas (ref.10). The shape of each ESR line is expressed by a Lorentzian function,

$$S(\Delta B) = \frac{1}{\pi} \frac{(\Delta B_{\text{half}}/2)}{(\Delta B)^2 + (\Delta B_{\text{half}}/2)^2} , \quad \text{with } \Delta B = B - B_0$$

where B_0 is the magnetic flux density at the peak, and ΔB_{half} denotes the half-breadth of the observed absorption curve. The magnitude of ΔB_{half} is determined by the life time of a concerned quantum state, τ . There is a relation, in the present experimental condition,

$$1/\tau = 1.59 \times 10^6 \pi \Delta B_{\text{half}} = 8.63 \times 10^6 \Delta B_{\text{p-p}} \quad (\text{in } \text{s}^{-1}), \quad \text{with } \sqrt{3} \Delta B_{\text{p-p}} = \Delta B_{\text{half}},$$

where $\Delta B_{\text{p-p}}$ denotes the peak-to-peak width in the derivative curve of ESR usually recorded, and is given in unit of gauss.

This life time is decomposed into two terms as,

$$1/\tau = 1/\tau_{\text{coll}} + 1/\tau_s,$$

in which the first term is referred to the mutual collision of admolecules (pressure

broading), and the second stems from perturbations due to the adsorbent solid. We have

$$\tau_{\text{coll}} = (L/N_m)/\langle v \rangle, \quad \text{and} \quad \tau_s = \langle l \rangle / \langle v \rangle$$

where L/N_m is the concentration of adsorbed O_2 , $\langle v \rangle$ the mean velocity of O_2 , and $\langle l \rangle$ the mean length of a part of pore in which O_2 can freely translates as shown in Fig.8.

Thus $1/\tau_{\text{coll}}$ linearly increases with N_m at a rate $\langle v \rangle / L$. At a temperature of -57°C , we have

$$\langle v \rangle = 188 \text{ m s}^{-1}, \quad \text{and} \quad L = 1.29 \times 10^{11} \text{ m/g for mordenite,}$$

and hence $\langle v \rangle / L = 1.45 \times 10^{-9}$

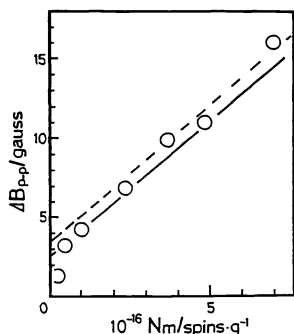


Fig.9. Line breadth of ESR of O_2 , adsorbed in 1-D channel of mordenite against spin concentration.

Temperature, -57°C ;
lines, calculated as 1-D gas.

Fig.9 shows observed results of ΔB_{p-p} vs. N_m , in which two linear lines have the calculated tangential 1.68×10^{-16} ($= 1.45 \times 10^{-9} / 8.63 \times 10^6$) (ref.11). The intersect of the ordinate of the broken line may give an upper limit of $1/\tau_s$, and we have

$$1/\tau_s = \langle v \rangle / \langle l \rangle < 3.5 \times 8.63 \times 10^6, \quad \text{or} \quad \langle l \rangle > 6.2 \mu\text{m}$$

This means that there is no obstacle which hinders the free translation of adsorbed O_2 in the pore channel, as the edge length of mordenite used is shorter than $6 \mu\text{m}$.

The measurement of the line breadth may be an effective means to check the non-presence of blocking impurity on the wall of the channel.

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