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Analysis of NMR Adsorption Isotherms of Zeolite ZSM-5: Adsorption Profiles Derived from the Pressure and Temperature Dependences of ^{129}Xe NMR Chemical Shift and Signal Intensity

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^{129}Xe NMR spectroscopy of nanomaterials, such as zeolites, can provide valuable information on the nanostructure and physicochemical properties of adsorption. In the present study the pressure and temperature dependences of the ^{129}Xe NMR chemical shift and the signal intensity were investigated in detail with a zeolite ZSM-5. The pressure dependence of the signal intensity at constant temperature was analyzed based on the Langmuir and Dubinin-Radushkevich (D-R) models, from which the thermodynamic parameters and energetic profiles of adsorption were obtained together with information concerning the nanospace size. From this isotherm analysis the coverage, θ , was calculated and used for isotherm analysis of the chemical shift. The θ dependence of the chemical shift was successfully fitted by an exponential function, and the results were discussed in relation to the chemical shift at zero coverage, that at full coverage and the curvature of the exponential function. The chemical shift data reported with the zeolites NaA and KA, where separated signals were observed for the different number of encapsulated Xe atoms in the α cage, were analyzed and discussed collectively.

Keywords Nanospace analysis, ZSM-5, ^{129}Xe NMR isotherm, temperature dependence, coverage

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Introduction

Xenon NMR has been used widely as a unique tool in characterizing porous materials, such as zeolites or nanomaterials.¹⁻⁴ It can provide important information regarding the structures of nanospaces as well as the dynamic profiles of Xe atoms distributed in the nanospaces. Recently, the hyperpolarization technique has become more accessible to Xenon NMR.⁵ Hitherto, in ^{129}Xe NMR applications to zeolites or nanomaterials, the temperature dependence has been selected as a first choice of observation for estimating the detailed profiles of adsorption, since the temperature-dependent ^{129}Xe NMR spectra can provide a valuable source data on the presence of multiple sites for Xe adsorption as well as dynamic profiles of Xe distribution and exchange in these sites. Furthermore, from measurements of the temperature dependence in the ^{129}Xe NMR chemical shift it is possible to estimate energetic profiles of adsorption.⁶⁻⁹ By contrast, the pressure dependence of ^{129}Xe NMR parameters has been reported only in rare cases,¹⁰⁻¹³ although the pressure dependence, *i.e.*, the adsorption isotherm,

is an ordinary target of measurement for an adsorption analysis in the fields of physical and analytical chemistry when an adsorption equilibrium is to be studied in a quantitative manner.

The authors have published observations of the pressure dependence in the ^{129}Xe NMR chemical shift and signal intensity for one of the zeolite ZSM-5, and showed a successful determination of the adsorption properties, such as surface area, pore volume, equilibrium constants, and thermodynamic parameters of ΔH , ΔS and the isosteric heat of adsorption, q_{st} .¹² This result encouraged us to pursue the importance of intensity data in the analysis of adsorption profiles of zeolites and nanomaterials, and to show the potential of the ^{129}Xe NMR method for the adsorption isotherm analysis. In the present study, another type of ZSM-5, Zeolyst CBV5524G, was selected, and the pressure dependence of the ^{129}Xe NMR parameter, *i.e.*, the ^{129}Xe NMR adsorption isotherm, is analyzed in detail to discuss the interrelation between the NMR chemical shift and the coverage, θ , which will be useful for developing new analytical tools in the characterization of nanomaterials.

Experimental

Reagents and chemicals

CBV-5524G from Zeolyst International (Zeolite type ZSM-5;

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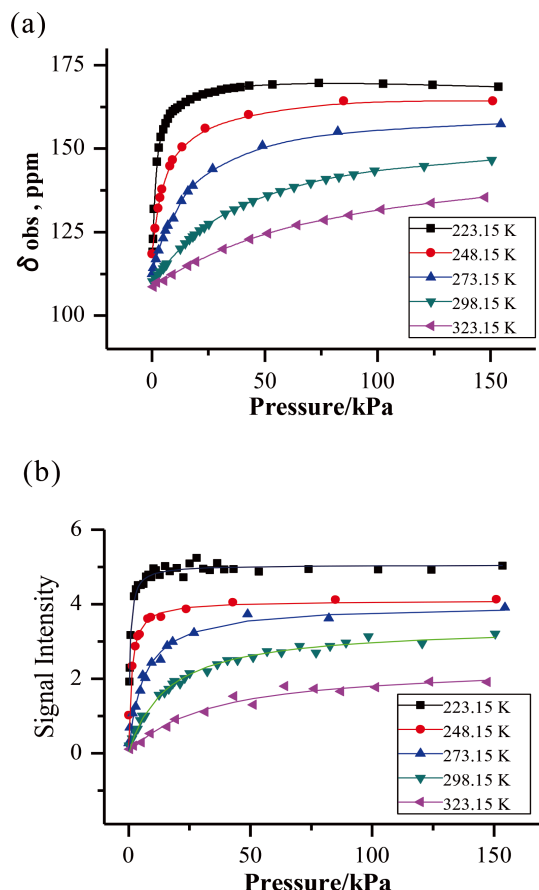


Fig. 1 ^{129}Xe NMR adsorption isotherms of a zeolite ZSM-5 CBV-5524G. (a) Chemical shift δ_{obs} , where experimental data points are connected by a spline function for a guidance of eye; (b) signal intensity (in arbitrary unit), where curves denote calculations based on the Langmuir model.

ammonium form, Si/Al = 25; Surface Area 425 m^2/g) was dried for 8 h at 573 K under a high vacuum of $<10^{-6}$ kPa, and served for the NMR measurement. The Xe standard gas from Japan Air Liquide (purity 99.999 vol% minimum), which contains a natural abundance of 26.24% ^{129}Xe isotope, was purified on the K-Na alloy and directly supplied to the sample in a $\phi 10$ mm glass tube in the NMR magnet. The gas at thermal equilibrium was used throughout the study.

Apparatus and procedure

NMR measurements were done on an Agilent Unity INOVA-400WB spectrometer with a 9.4 T superconducting magnet, and the ^{129}Xe resonance frequency was 110.7 MHz. Multiple FID signals, about 4 to 1024 FIDs, were accumulated to obtain a sufficient SN ratio with a pulse angle of 60° (10 μs), spectral width of 25 kHz, acquisition time of 0.4 s, and repetition delay of 5 s. This repetition delay of 5 s was more than ten-times longer than the apparent ^{129}Xe relaxation time, T_1^* , measured for the sample: the T_1^* measured was as short as 0.3 s, probably because of the fast exchange rate between the adsorbed and the gas phase within the sample tube, where the total sample tube length was about 200 mm, whereas the sample was limited within a height of 7 mm, which is comparable to the width of the RF coil. In valuable temperature experiments the NMR measurement was started after holding the sample at a measurement temperature for 10 to 20 min to make sure of the steady state in the temperature distribution.

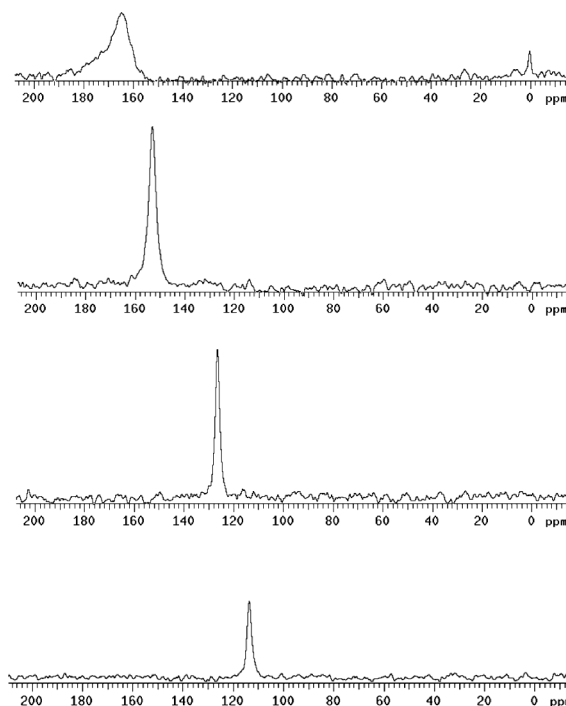


Fig. 2 Pressure dependence of the ^{129}Xe NMR spectrum at 248.15 K. Pressures: 0.5, 3.0, 23.5, and 150.5 kPa from bottom to top.

In preparing the reference sample for the surface area determination, an arbitrary amount of Xe was dissolved in a 0.11 M calixarene solution, 0.283 cm^3 of which was sealed into a small ampoule. After dropping the ampoule into the NMR tube including the zeolite sample, a calibration measurement was done. Here the whole sample volume was minimized so that the reference and zeolite samples were all included within an NMR rf coil. The Xe amount, which induced the signal of the inclusion complex, was calculated from the published NMR data.¹⁴

The gas pressure was measured on a digital Handy Manometer PG-100 from COPAL Electronics within an error of 0.5%. All the sample handling and NMR measurement systems were the same as that in the previous report.¹² The statistical calculations were done on a computer using the software ORIGIN, Lightstone Co., which makes use of the Levenberg-Marquardt algorithm for curve-fitting.

Results

The pressure dependences of the ^{129}Xe NMR chemical shift and the signal intensity, ^{129}Xe NMR isotherm, are shown in Fig. 1. The typical pressure dependence of the spectrum is shown in Fig. 2. The signal intensity reached a plateau at high pressure regions, i.e., above 10 kPa at 223.15 K and above 60 kPa at 323.15 K. This type of isotherm can be successfully reproduced by Langmuir or Dubinin-Radushkevich (D-R) model, according to the conventional way of adsorption analysis. On this contrary, the chemical shift, δ_{obs} , did not show any plateau, and a low-field shift was observed steadily upon increasing the pressure throughout the entire pressure range. The isotherms showed slight upfield shifts at a few measuring points in the high-pressure regions at the lower measuring temperatures of 223.15 and 248.15 K. This would be a spurious result caused by broadening of the peak, probably because of the low exchanging

Table 1 Analysis of the signal intensity isotherms of CBV-5524G based on Langmuir model

Temp./K	223.15	248.15	273.15	298.15	323.15
K/kPa^{-1}	1.893 ± 0.101	0.877 ± 0.048	0.154 ± 0.016	0.065 ± 0.003	0.031 ± 0.005
S_{fc}	5.05 ± 0.03	4.10 ± 0.04	4.08 ± 0.12	3.43 ± 0.05	2.39 ± 0.12
χ^2	0.013	0.004	0.032	0.007	0.010

rate or inhomogeneous distribution of the temperature in the sample. Such a broadening was also responsible for the relatively large errors in the signal intensity: broadening blurred the end points of the peaks in obtaining the signal intensity by integration.

The chemical shift at zero concentration, δ_s , could be obtained by extrapolating the isotherm to zero pressure. Extrapolation could be made by a linear function: the isotherms approached linear relations at low pressures, *i.e.*, below 3 kPa at 223.15 and 248.15 K, below 7 kPa at 273.15 and 298.15 K and below 20 kPa at 323.15 K. A linear extrapolation of these data has given δ_s values of 116.5 ± 2.1 ppm at 223.15 K, 115.6 ± 1.4 ppm at 248.15 K, 113.1 ± 0.3 ppm at 273.15 K, 110.1 ± 0.1 ppm at 298.15 K, and 108.7 ± 0.2 ppm at 323.15 K. The error limit was larger at lower temperatures because of the larger temperature dependence.

The chemical shift at zero concentration, δ_s , showed a linear upfield shift upon elevating the temperature:

$$\delta_s = -0.084(\pm 0.008)T + 135.9(\pm 2.2), \quad R^2 = 0.974, \quad (1)$$

where R means the correlation coefficient.

Discussion

Estimation of the nanospace size from the chemical shift at zero concentration, δ_s

The δ_s value at 298.15 K reflects the size of nanospaces, as exemplified by the equation $\ell = 2.054\{(243 - \delta_s)/\delta_s\}$, where ℓ denotes the mean free path of Xe in the nanospace.² The estimated diameter in this study is 0.69 nm for a cylindrical cavity, which is 20–30% larger than the specific values of the aperture for the cylinder: 0.56×0.54 and 0.55×0.51 nm.¹ In ZSM-5 the nanospace size is known to be wider in the intersection part in the network of cylinders, and the diameter of this part is reported to be 0.8 nm for MFI-type zeolites,¹⁵ to which the zeolite CBV-5524G belongs. Therefore, occupation in this intersection part is strongly suggested as being the reason for a slightly larger channel dimension, estimated from the δ_s value.

Analysis of NMR adsorption isotherms

Adsorption isotherms obtained in NMR measurements can be analyzed by adsorption models, such as Langmuir, D-R or others so long as the measured NMR parameter is dominantly determined by the fractional population of the adsorbed state. In the case of NMR, the signal intensity corresponds to such a parameter when measured under a full avoidance of any NMR saturation effects. As for the model of isotherm analysis, the Langmuir equation is known to be a basic one, but the D-R equation, which is derived under a volume filling model, is also considered to be suitable for Xe adsorption treated in the present case, since the aperture of the cylinder nanospace of ZSM-5 is comparable in size to the diameter of the adsorbate Xe. The isotherms are analyzed based on the Langmuir and D-R models in the following.

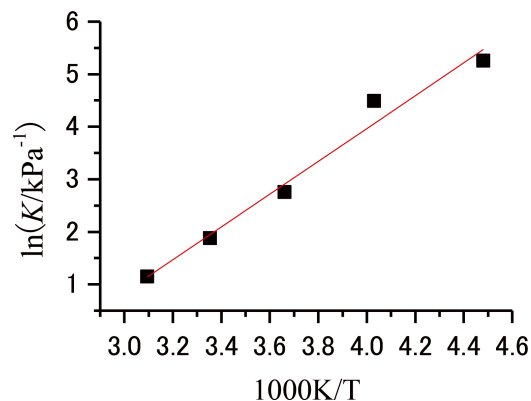


Fig. 3 Van't Hoff plots of the Xe adsorption on CBV-5524G.

Calculations of signal intensity data based on the Langmuir model

The Langmuir model is represented by,

$$\theta = \frac{KP}{1 + KP}, \quad (2)$$

where θ means the coverage, which denotes the fractional surface area covered by the adsorbate; K is the equilibrium constant and P is the pressure. The NMR signal intensity, S_{obs} , observed for the adsorbed Xe is proportional to θ ,

$$S_{\text{obs}} = S_{\text{fc}} \times \theta, \quad (3)$$

where S_{fc} is the limiting intensity at full coverage ($\theta = 1$) when all adsorption sites are occupied.

Here, in the isotherm analysis the independent parameters are S_{fc} and K . The results of calculations are listed in Table 1. χ^2 is the reduced chi square, which is minimized in the fitting and equal to the residual sum of squares divided by the degrees of freedom. The thermodynamic parameters of adsorption are derived from the temperature dependence of the equilibrium constants (Eq. (4)): $\Delta H = -25.9 \pm 2.2$ kJ/mol and $\Delta S = -109.3 \pm 8.3$ J/K/mol (Fig. 3). The ΔS value is dependent on the unit of pressure; when changed to atm unit, $\Delta S = -70.9 \pm 8.3$ J/K/mol is obtained by an addition of $R \ln(1 \text{ atm}/1 \text{ kPa}) = R \ln(101.33) = 38.4$ J/K/mol, which allows for the difference in the standard states of 1 atm and 1 kPa.

$$\ln K = -\frac{\Delta H}{R} \frac{1}{T} + \frac{\Delta S}{R}. \quad (4)$$

Calculations of the chemical shift: dependence on the coverage θ in Langmuir analysis

The ^{129}Xe NMR signal of Xe atoms encapsulated in the α cage of zeolite NaA is reported to be separated depending on the number of Xe atoms included in the cage, n , the chemical shift being gradually increased with the number n .⁹ Here, the exchange rate of Xe is slow enough to separate the signal from

the cages different in the number n . In the present study, however, the exchange rate is fast, and only a single peak appears as a statistical average of the distribution in multiple adsorption sites. To discuss the pressure dependence of the ^{129}Xe chemical shift, in the present study, the coverage, θ , is selected as an independent parameter instead of the number of Xe atoms in the cage. The θ value can be calculated according to Eq. (2) under the given values of K and P . Plots of the chemical shift observed, δ_{obs} , against θ are shown in Fig. 4. The value of δ_{obs} increases with the increase of θ , and the amount of increase becomes larger as θ increases. A similar trend has been observed in the case of the n dependence in the chemical shift of Xe atoms encapsulated in the α cage of zeolite NaA.¹⁶

In the present study an exponential function is assumed to reproduce such a dependence on θ :

$$\delta_{\text{obs}} = A + B \exp(C\theta). \quad (5)$$

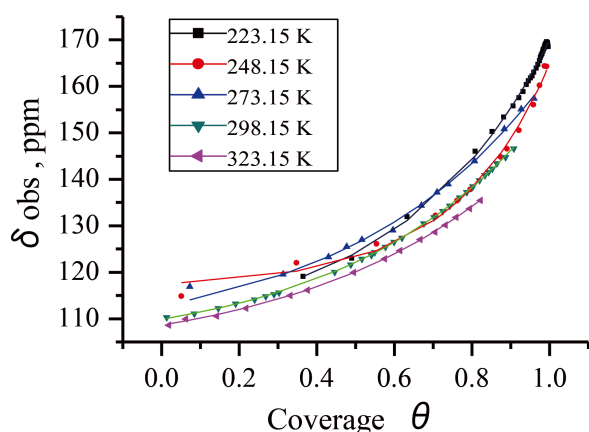


Fig. 4 Plots of the ^{129}Xe chemical shift, δ_{obs} , against the value of coverage θ .

The results of this fitting are listed in Table 2. The independent parameters used in the least-square data fitting, which was conducted using the ORIGIN software, were A, B and C. Furthermore, an estimation of the chemical shift at zero coverage or zero pressure, δ_0 , was done by adopting δ_0 , B and C as independent parameters in the fitting, while considering the relation $\delta_0 = A + B$. Similarly, the chemical shift at full coverage ($\theta = 1$), which is expressed as $\delta_1 = A + B \exp(C)$, was determined by a fitting that adopted δ_1 , B and C as independent parameters. It may be noteworthy that δ_0 or δ_1 can be calculated from the relation $\delta_0 = A + B$ or $\delta_1 = A + B \exp(C)$ by using the values of A, B and C obtained in a fitting using A, B and C as independent parameters, but that error estimation of these parameters fails since the errors in δ_0 and δ_1 are not simply the sum of those in A, B and C. In practice, the basic equations used were Eq. (5a), where the independent parameters are δ_0 , B and C, and Eq. (5b), where the independent parameters are δ_1 , B and C, for the case of error estimations in δ_0 and δ_1 , respectively:

$$\delta_{\text{obs}} = (\delta_0 - B) + B \exp(C\theta), \quad (5a)$$

$$\delta_{\text{obs}} = \delta_1 + B \{ \exp(C\theta) - \exp(C) \}. \quad (5b)$$

The chemical shift at zero coverage or zero pressure, δ_0 , listed in Table 2 corresponds well with δ_s , which was determined by extrapolating the pressure dependence at a lower-pressure region to zero pressure, as described in the Results section. This means that the isotherm is well reproduced by the model of Langmuir for a whole range of coverage. However, at the lowest temperatures of 223.15 K the values of δ_0 show a slight deviation from δ_s . This is probably because the chemical shift shows major changes at low pressures, especially at low temperatures (Fig. 1), and hence deviations in between the fittings in the whole pressure regions and those in the very low-pressure regions have become conspicuous at the lowest temperature. When δ_0 is fixed at the value of δ_s , the results of the fitting showed discernible changes in B and C from those listed in Table 2. When δ_0 is fixed at 116.5, $B = 2.22 \pm 0.20$,

Table 2 Analysis of δ_{obs} as a function of coverage θ : $\delta_{\text{obs}} = A + B \exp(C\theta)$ where θ is calculated based on the Langmuir model

Temp./K	223.15	248.15	273.15	298.15	323.15
A	107.5 ± 1.5	119.0 ± 0.9	105.3 ± 1.0	102.8 ± 0.2	100.8 ± 0.5
B	4.41 ± 0.64	0.529 ± 0.132	7.55 ± 0.70	7.04 ± 0.16	7.79 ± 0.45
C	2.64 ± 0.12	4.47 ± 0.24	2.03 ± 0.08	2.02 ± 0.02	1.82 ± 0.05
χ^2	0.378	1.04	0.291	0.017	0.032
δ_0^a	111.9 ± 0.9	117.6 ± 0.9	112.8 ± 0.3	109.9 ± 0.1	108.6 ± 0.1
δ_1^b	169.9 ± 0.2	164.9 ± 0.9	162.5 ± 0.5	156.0 ± 0.1	148.8 ± 0.4

a. The chemical shift at zero coverage: $\delta_0 = A + B$. Errors are estimated in the fitting where δ_0 , B and C are used as independent parameters.

b. The chemical shift at full coverage, $\theta = 1$: $\delta_1 = A + B \exp(C)$. Errors are estimated in the fitting where δ_1 , B and C are used as independent parameters.

Table 3 Analysis of the signal intensity isotherms of CBV-5524G based on the D-R model

Temp./K	223.15	248.15	273.15	298.15	323.15
S_{fc}	5.02 ± 0.04	4.15 ± 0.14	4.08 ± 0.16	3.21 ± 0.09	2.07 ± 0.23
$P_{\text{eq}}/\text{kPa}^{-1}$	20.8 ± 2.1	109.4 ± 51.7	213.8 ± 78.0	247.2 ± 45.6	310.1 ± 178.3
$RT/\beta E_0$	0.224 ± 0.009	0.160 ± 0.010	0.238 ± 0.019	0.289 ± 0.013	0.335 ± 0.049
χ^2	0.023	0.012	0.020	0.006	0.010
$q_{\text{st}}/\text{kJ mol}^{-1}$	20.9 ± 0.3	25.5 ± 0.8	22.1 ± 0.7	21.2 ± 0.3	20.6 ± 1.0

$C = 3.23 \pm 0.09$ and $\chi^2 = 0.729$ were obtained at 223.15 K, which do not affect the discussion in the following.

The chemical shift at full coverage ($\theta = 1$), δ_1 , increases with decreasing the temperature. This is also the case for δ_0 , except for the lowest temperature.

Calculations of the signal intensity data based on the D-R model

In the case of the D-R model, the basic equation is,

$$\left[\left(\ln \frac{S_{fc}}{S_{obs}} \right) \right]^{1/2} = \left(\frac{RT}{\beta E_0} \right) (\ln P_{eq} - \ln P) \quad (6)$$

where βE_0 is the effective potential energy of a micro-pore to adsorb Xe, and P_{eq} is the quasi-saturated vapor pressure when the pore volume is completely filled. In this equation the intensity ratio, S_{obs}/S_{fc} , corresponds to the weight ratio, w_a/w_a^0 , given in the original equation,¹⁷ where w_a and w_a^0 are the amounts of Xe adsorbed at P and P_{eq} , respectively. Here, in the isotherm analysis, the independent parameters are S_{fc} , P_{eq} and $RT/\beta E_0$. The results of calculations are listed in Table 3 and shown in Fig. 5. The estimated values of S_{fc} are consistent with those determined in the Langmuir model (Table 1). The quasi-saturated vapor pressure, P_{eq} , increases with the increase of the temperature in Table 3, indicating that higher pressure is needed to completely fill the pore volume. The estimated errors in P_{eq} are large in Table 3, except for the one at 223.15 K. The error in P_{eq} is large when the error in S_{fc} is large, which suggests an interference of the two parameters in the fitting calculation: P_{eq} and S_{fc} contribute compensatively to the isotherm of S_{obs} vs. P .

In D-R analysis, the isosteric heat of adsorption, q_{st} , can be calculated from βE_0 according to Eq. (7),¹⁸ where ΔH_v is the enthalpy of vaporization at the boiling point, and equals to 12.6 kJ/mol:

$$q_{st} = \Delta H_v + \beta E_0. \quad (7)$$

The isosteric heat of adsorption, q_{st} , thus determined from the ^{129}Xe signal intensity data, amounts to 21.2 ± 0.3 kJ/mol at 298.15 K (Table 3).

This value is comparable to the previously reported data of 22.0 ± 0.2 kJ/mol for ZSM-5 JRC-Z5-70Na,¹² and to the available data: 22.1 – 22.9 kJ/mol for the activated carbon fibers (P5, P10 and P20) measured by a gravimetric method below 3 MPa,¹⁹ but smaller than 30.6 ± 1.0 kJ/mol for ZSM-5 from Tosoh corp. as well as 26.6 ± 1.0 kJ/mol for molecular sieves 5A measured below 10 MPa,¹¹ and 26.0 ± 1.0 kJ/mol for the activated carbon fiber 10A measured below 5 MPa.¹⁰ The value of $P_{eq} = 247 \pm 46$ kPa at 298.15 K, is larger than the previously reported value of 91 ± 6 kPa obtained for JRC-Z5-70Na⁷ and smaller than the available data: 717 – 2980 kPa,¹⁹ 5 ± 1 MPa for ZSM-5 as well as 6 ± 1 MPa for molecular sieves 5A¹¹ and 9.3 ± 1.0 MPa.¹⁰ It may be said that the parameters determined in the present study are small compared to the reported data because the maximum measuring pressure of 150 kPa is much lower than those adopted in the reported case of 3 – 10 MPa. Probably, a tight structure of Xe filling at the entrance of nanospace is responsible for this tendency, as suggested¹⁹ to be due to ink bottle-type micropores.

Calculations of the chemical shift: dependence on the coverage, θ , in D-R analysis

In D-R analysis the coverage, θ , can be calculated as:

$$\theta = \exp[-\{(RT/\beta E_0)\ln(P_{eq}/P)\}^2]. \quad (8)$$

Therefore, the coverage dependence of the chemical shift can be investigated by plotting the observed chemical shift, δ_{obs} , against θ calculated from Eq. (8). This plot showed a similar trend with Fig. 4, and a fitting by Eq. (5) gave the results listed in Table 4. A comparison of the results of D-R analysis (Table 4) with those of Langmuir analysis (Table 2) shows that the estimated errors in A, B and C are about an order larger (Table 4). This is probably because in the D-R analysis the number of adjustable parameters is 3 in Eq. (6), i.e., $RT/\beta E_0$, P_{eq} and S_{fc} , and estimated errors are large in P_{eq} (Table 3), while in the case of Langmuir analysis it is 2, K and S_{fc} , where the errors are reasonably small (Table 1). Therefore, the θ values calculated from Eq. (8) include certain levels of errors, which are considered to be a reason for increased errors in A, B and C in the D-R analysis. When the number of adjustable parameters is reduced to 2 by introducing the chemical shift at zero coverage or zero pressure, δ_0 , as a fixed parameter in the fitting of δ_{obs} vs. θ plots, the results turn out as listed in Table 5. In practice, the basic equation in this case is,

$$\delta_{obs} = \delta_1 + (\delta_0 - A)\{\exp(C\theta) - \exp(C)\}. \quad (5c)$$

By fixing the value of δ_0 in the fitting of δ_{obs} vs. θ plots, the estimated errors in A and B are greatly reduced. That is, the

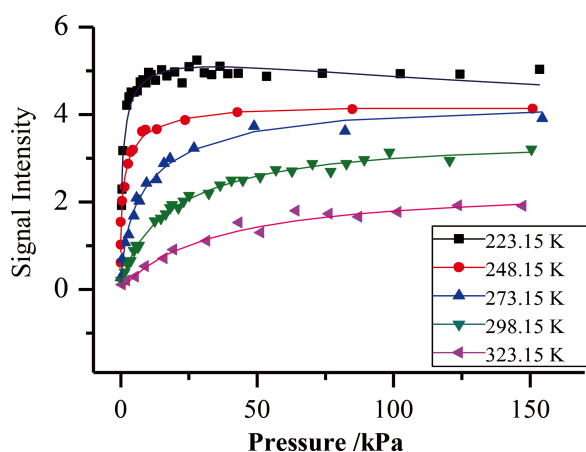


Fig. 5 Signal intensity data fitted by the D-R model. The curves denote calculations based on the D-R model.

Table 4 Analysis of δ_{obs} as a function of the coverage θ , $\delta_{obs} = A + B \exp(C\theta)$, where θ is calculated based on the D-R model

Temp./K	223.15	248.15	273.15	298.15	323.15
A	87.0 ± 20.5	109.0 ± 3.3	89.9 ± 9.8	94.5 ± 3.9	95.8 ± 10.8
B	17.6 ± 14.4	2.90 ± 1.36	20.0 ± 8.4	13.7 ± 3.3	12.3 ± 9.7
C	1.521 ± 0.56	2.98 ± 0.43	1.24 ± 0.29	1.35 ± 0.17	1.21 ± 0.56
χ^2	10.0	6.60	4.30	1.55	3.64

Table 5 Analysis of δ_{obs} as a function of the coverage θ , $\delta_{\text{obs}} = A + B \exp(C\theta)$, where θ is calculated based on the D-R model and δ_0 is fixed at the value of δ_s

Temp./K	223.15	248.15	273.15	298.15	323.15
A	112.1 ± 1.1	113.9 ± 0.2	103.3 ± 1.5	102.4 ± 0.4	100.4 ± 0.4
B	4.41 ± 1.12	1.70 ± 0.23	9.8 ± 1.5	7.7 ± 0.4	8.4 ± 0.4
C	2.50 ± 0.24	3.41 ± 0.14	1.76 ± 0.14	1.80 ± 0.05	1.80 ± 0.05
χ^2	5.32	1.71	2.27	0.303	0.040
δ_0^a	116.5	115.6	113.1	110.1	108.7
δ_1^b	164.4 ± 0.3	164.6 ± 0.6	159.6 ± 0.8	148.5 ± 0.2	138.7 ± 0.2
S_{fc}	5.02 ± 0.04	4.15 ± 0.14	4.08 ± 0.16	3.21 ± 0.09	2.07 ± 0.21

a. δ_0 is fixed at the chemical shift at zero concentration, δ_s , derived in the Results section. b. Errors are estimated in the fitting adopting δ_1 , A and C as independent parameters.

Table 6 The chemical shift data of ^{129}Xe encapsulated in the α cages of zeolite NaA and KA, and the results of fitting by Eq. (5)

Sample		$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$	$n = 6$	$n = 7$	$n = 8$
NaA	$\delta(\text{Xe}_n)^a$	74.8	92.3	111.7	133.1	158.4	183.5	228.3	272.3
	θ	0.125	0.25	0.375	0.5	0.625	0.75	0.875	1.0
	Fitting by Eq. (5): $A = 3.1 \pm 14.0$, $B = 61.2 \pm 11.2$, $C = 1.48 \pm 0.14$, $\chi^2 = 8.66$								
Sample		$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$	$n = 6$		
KA	$\delta(\text{Xe}_n)^a$	79.5	98.4	119.7	145.4	180.5	—		
	θ	0.167	0.333	0.5	0.667	0.833	—		
	Fitting by Eq. (5): $A = -57.3 \pm 12.4$, $B = 117.0 \pm 11.8$, $C = 0.98 \pm 0.07$, $\chi^2 = 0.118$								

a. The ^{129}Xe chemical shift of Xe_n cluster in the α cage.^{15,16}

Table 7 The results of the coverage θ dependence of $\delta(^{129}\text{Xe})$ for some zeolites^a

	Si/Al	δ_0^b	δ_1^b	$A (= \delta_0 - B)$	B	C	χ^2
Zeolite A, NaA	1	64.3 ± 3.1	271.9 ± 2.6	3.1 ± 14.0	61.2 ± 11.2	1.48 ± 0.14	8.66
Zeolite A, KA	1	59.7 ± 0.6	253.7 ± 1.1	-57.3 ± 12.4	117.0 ± 11.8	0.98 ± 0.07	0.118
CBV-5524G	25	109.9 ± 0.4	156.0 ± 0.1	102.8 ± 0.2	7.04 ± 0.16	2.02 ± 0.02	0.017
ZSM-5-70Na	92.5	127.0 ± 1.1	177.3 ± 0.9	126.9 ± 1.1	0.11 ± 0.04	6.12 ± 0.38	0.803

a. Calculated based on the Langmuir model for CBV-5524G. For ZSM-5-70Na the raw data of isotherm are cited from Ref. 12. b. The error is estimated by the fitting using δ_0 or δ_1 as one of the independent parameters instead of A.

errors are greatly reduced by fixing the total value of $A + B$ at δ_0 instead of varying the two parameters, A and B, independently. In contrast, the errors in C are not changed very much by fixing the δ_0 value. This is reasonable since C denotes the curvature of the δ_{obs} vs. θ plots and is related to the rate of the exponential increase in these plots.

The value of C exhibits a tendency of a decrease on temperature increase (Tables 2, 4 and 5). This reflects that the curvature of the δ_{obs} vs. θ plots is decreased with increasing temperature, or that the δ_{obs} vs. θ plots is likely to be close to a line on increasing the temperature, although the tendency is not so specific because of an interruption from the experimental errors. Similarly, the value of A is seen to be decreased upon increasing the temperature (Tables 2, 4 and 5). This is in consistent with the results of a decrease (upfield shift) in the δ_0 value upon increasing the temperature. Here, $\delta_0 = A + B$ holds and since A is about an order larger than B in numerical values, this tendency is considered to be a result of the dominant role of A in the value of δ_0 . In contrast, the temperature dependence of B is not so clear as that of A (Tables 2, 4 and 5), which may be interpreted in a way that a more precise observation of δ_0 is necessary for determining the temperature dependence of B more clearly.

The chemical shift dependence on the coverage θ : comparison with the reported case

The chemical shift dependence on the coverage, θ , can also be discussed while incorporating a few reported data of zeolites NaA. The α cage in NaA is known to encapsulate Xe atoms as clusters and the windows interconnecting the cages are comparable in size with the diameter of the Xe atom. This has made the exchange rate of Xe atoms in between the cages slow enough to separate the signals from α cages with different numbers of encapsulated Xe atoms. The largest number of Xe atoms encapsulated is 8 for NaA.¹⁶ Therefore, the coverage θ is estimated to be $n/8$ for the α cage when the number of encapsulated Xe atoms is n . This is also the case with KA, for which the largest number of Xe atoms encapsulated in the α cage is 6.²⁰ From the data listed in Table 6 the dependence of the ^{129}Xe chemical shift on θ can be analyzed by Eq. (5). The results are included in Table 6.

The results of fitting by Eq. (5) are summarized in Table 7 for different zeolites. The chemical shift ^{129}Xe in zeolite nanospace is reported to be dependent on several factors [1]:

$$\delta_{\text{obs}} = \delta_0 + \delta_s + \delta_E + \delta_M + \delta_{\text{Xe}}, \quad (9)$$

where δ_o , δ_s , δ_E and δ_M are the reference, contributions due to collisions between Xe and cage or channel walls, electric field created by the cations, and magnetic properties of the solids, respectively; the last term expresses the contributions from intermolecular interactions of Xe atoms,

$$\delta_{Xe} = \delta_{Xe-Xe} \cdot \rho_{Xe} \quad (10)$$

where δ_{Xe-Xe} is associated with Xe-Xe collisions and ρ_{Xe} is the local density of Xe adsorbed in the cavities and/or channels. According to Eq. (10), the chemical shift dependence on the local density of Xe is proportional to the Xe density. In the present study, however, Xe-Xe interactions are regarded as being increased exponentially, and not linearly, with the Xe density, as depicted in Eq. (10). This may be interpreted as being due to the high density of Xe atoms entrapped in the small nanospace of zeolites, which makes the density dependence not simple, as described in a linear relation, making the dependence increasingly larger with increasing the density. The exponential function can be extended to polynomials as follows:

$$\delta_{obs} = A + B \exp(C\theta) = A + B \{1 + (C\theta/1!) + (C\theta)^2/2! + (C\theta)^3/3! + (C\theta)^4/4! + \dots\}, \quad (11)$$

and hence the treatment with exponential functions is considered to reflect the inclusion of Xe-Xe interactions higher than the two-body collisions. Alternatively, it may be pointed out that the coefficient in Eq. (10), δ_{Xe-Xe} , is not a constant throughout the whole range of the coverage, and becomes large on increasing the number of Xe atoms in the nanospace.

The coefficient C , which expresses the rate of exponential increase in the chemical shift, as denoted by Eq. (5), is large when Si/Al ratio is large (Table 7). This is also the case with δ_o . When Si/Al ratio is large, the number of counter ions of Na or K is increased to neutralize the total charge. This increase is considered to deshield the Xe nucleus in the cavity to move the chemical shift of isolated Xe, δ_o , toward the low field side, *i.e.*, toward higher values. This will also apply to the Xe-Xe collision coefficients, δ_{Xe-Xe} , which is possible to be increased in a more enhanced way with the increase of the Xe concentration in nanospace when the Xe concentration becomes higher.

Calculation of the surface area from ^{129}Xe NMR data

The surface area of nanomaterials can be calculated from the above ^{129}Xe NMR data with the aid of the NMR data for a reference sample. In the present study, the calixarene inclusion complex of Xe dissolved in water¹⁴ was used as a reference, and the signal intensity ratio was determined after a calibration measurement with the sample including both of the zeolite and the reference. In Fig. 6, the ^{129}Xe NMR spectrum was measured for a sample containing 0.012 g CBV-5524G under the Xe gas at 62.8 kPa after the addition of a 0.283 cm³ reference solution enclosed in an ampoule. In the reference ampoule, a 0.11 M calixarene aqueous solution was enclosed, to which Xe gas was bubbled preliminarily. The Xe concentration in the ampoule was determined from the ^{129}Xe chemical shift data with the aid of the inclusion complex formation profile published in a reference.¹⁴

The surface area A is expressed as

$$A = \left(\frac{S_{fc}}{S_{obs,P}} \right)_{\text{isotherm}} \left(\frac{S_{obs,P}}{S_{ref}} \right)_{\text{calib}} \left(\frac{C_{ref} V_{ref} S_{Xe} N_A}{W_{\text{sample}}} \right), \quad (12)$$

where the meaning of the symbol is as follows: $S_{obs,P}$ in the isotherm blanket is the signal intensity measured at P kPa in the isotherm; $S_{obs,P}$ and S_{ref} in the calib blanket are the signal intensity

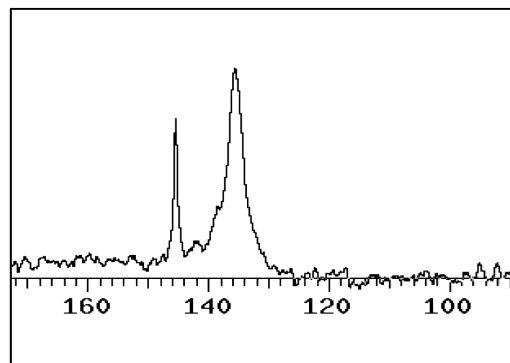


Fig. 6 ^{129}Xe NMR spectrum of the sample containing 0.012 g CBV-5524G under the Xe gas at 62.8 kPa with a 0.283 cm³ reference ampoule. The ^{129}Xe signal entrapped in the calixarene and adsorbed on CBV-5524G appear at 145.26 and 135.37 ppm, respectively.

at the same P kPa and the signal intensity from the reference sample, respectively; C_{ref} is the concentration of Xe in mol/dm³; V_{ref} is the sample volume in the reference sample; S_{Xe} is the surface area occupied by a single Xe atom, 0.232 m² and N_A is the Avogadro number; and W_{sample} is the weight of zeolite used for calibrating the peak area. Then, the saturated amount of Xe adsorption w_a^0 (g/g, sample) is obtained by converting the surface area A to w_a^0 through the relationship $w_a^0 = A/(S_{Xe} N_A / MW_{Xe})$, where MW_{Xe} is the atomic weight of Xe, 131.29.

The calculation gives $A = 320$ m²/g, which corresponds to $w_a^0 = 0.300$ g/g. This surface area is a little smaller than the specific value, 425 m²/g, listed as a nominal value, and a reported value of BET surface area 409.0 m²/g for the calcinized zeolite,²¹ but close to a value of the micro porous surface area of 354.0 m²/g.²¹ This trend is similar to the previously reported case of ZSM-5 JRC-Z5-70Na,¹² and may be due to the ink-bottle¹⁹ or inlet effect.¹²

Conclusions

^{129}Xe NMR adsorption isotherms were measured with a zeolite ZSM-5 CBV5024G below 150 kPa at 223.15, 248.15, 273.15, 298.15 and 323.15 K using natural abundance Xe gas at thermal equilibrium. The isotherms for the chemical shift were extrapolated to zero pressure in the low-pressure region to obtain the chemical shift at zero concentration, δ_s , which gave a the reasonable cavity size for the cylindrical nanospace. The isotherms for the signal intensity were analyzed based on the Langmuir and D-R models, and the applicability of the two models was confirmed. The main difference in the application of the two models is that for deriving the energetic profiles of the adsorption, the Langmuir model needs observation of the temperature dependence of the isotherm, while the D-R model does not. In this contrast, in the D-R model, 3 independent parameters are involved in the isotherm analysis and a more precise measurement is needed for successfully determining the parameters compared to the Langmuir model in which the number of independent parameters are 2, equilibrium constant and signal intensity at full coverage.

The isotherms for the chemical shift did not show a similar trend to the intensity data, and was investigated on the dependence on coverage θ derived from the intensity data. This dependence showed a steady increase with θ , and especially a

higher increase in the higher θ region, which was able to be fitted by an exponential function. The fitting, which was done by including other available data of zeolites, showed that the curvature of the exponential function tends to increase with increasing the Si/Al ratio in zeolites.

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