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IR Spectra of CH_4 Adsorbed on an NaZSM-5 Zeolite under Pressures up to 1 MPa

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A special cell for measuring IR spectra of adsorbed species under pressures up to 1.5 MPa has been made. With this cell, the IR ν_1 absorption of methane adsorbed on an NaZSM-5 zeolite is obtained even at room temperature and at a moderately high pressure. The ν_1 absorption intensity increases linearly with the amount of methane adsorption. The electric field strength in the zeolite pore has been evaluated to be 3.6×10^9 $V \cdot m^{-1}$.

Although the ν_1-vibration of methane is IR inactive under ordinary conditions, the absorption for this vibrational mode becomes observable when methane is adsorbed by an adsorbent containing cationic adsorption sites. Thus the IR spectroscopy coupled with an adsorption measurement provides us with important information about the adsorption force of cations in the adsorbent pore as revealed by the work of Cohen de Lara et al.[1-6] in an NaA-CH_4 system. In their reports[1,4] Cohen de Lara et al. have stressed that IR measurements at low temperatures are necessary in order to have reliable information about methane molecules entrapped in the zeolite cavity. The purpose of the present work is to show that the low temperature is not always indispensable in obtaining the IR ν_1-absorption of methane. The IR spectra of adsorbed methane are obtainable even at room temperature under pressures below 1 MPa.

The IR absorption cell unit used in the present work is illustrated in Fig. 1. This unit is made of stainless steel and consists of a cell body with a side arm. The cell body is equipped with two NaCl windows of 8 mm thickness and 25 mm diameter. Preliminary experiments ensured that the window withstood repeated pressurizings up to 1.5 MPa. The optical path length between the windows was 12 mm. In addition, the cell body is equipped with a strain pressure gauge (2 MPa;MINEBEA CO., LTD. PRB-20K). The side arm facilitated an in situ out-gassing of the sample without exposing the windows at high temperatures. A sample holder (aluminum)-guide block assembly inserted in the side arm served for a smooth and exact setting of the sample at the out-gassing position or at the IR irradiating position. The displacement of the sample holder was carried out by handling an outer magnet.

An NaZSM-5 zeolite (SiO_2/Al_2O_3=23.3 mole ratio) was adopted as an adsorbent and methane (99.95%) was used as an adsorbate gas. Zeolite was pressed into a disk with ≈100 μm thickness and 13 mm diameter. After an in situ out-gassing at ≈573 K for 8 h under a vacuum of 10^{-3} Pa, methane was introduced into the cell. The IR spectra were recorded (100 or 200 scans) at 8 cm^{-1} resolution on a JEOL JIR-100 FT-IR spectrometer with TGS detector. The data processings including subtraction of the IR absorption of methane in the gaseous phase were carried out using a computer of the spectrometer. The temperature of the sample disk under an IR irradiation was measured separately. Adsorption isotherms necessary for analyzing the IR data were measured by means of a constant volume high pressure adsorption technique reported in earlier papers.[7-10)]

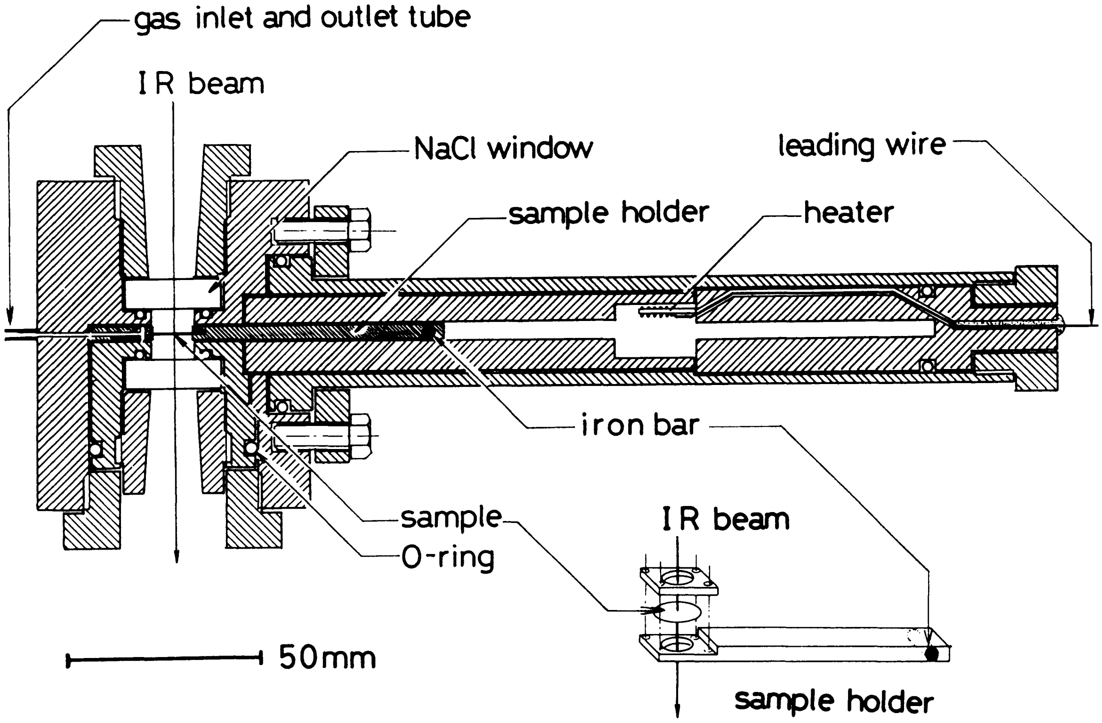

Fig.1. A schematic diagram of the high pressure IR absorption cell.

Illustrated in Fig. 2 is an example of IR spectrum of methane adsorbed on the NaZSM-5 zeolite. A broad and strong band around 3000 cm^{-1} is assigned to the ν_3-vibration of methane. The absorption peak at 2890 cm^{-1} is assigned to the ν_1-vibration (the Raman ν_1-peak of gaseous methane appears at 2914 cm^{-1}). Although the intensity of the ν_1-peak varied on changing the pressure, the peak position (2888-2890 cm^{-1}) as well as the peak width (18-20 cm^{-1}) did not show significant change.

The pressure dependence of the intensity (area intensity) of the ν_1-band is shown in Fig. 3, where S is the area intensity in cm^{-1} and W is the sample weight per cross sectional area in $g \cdot cm^{-2}$. It is clear that the ν_1-absorption can be

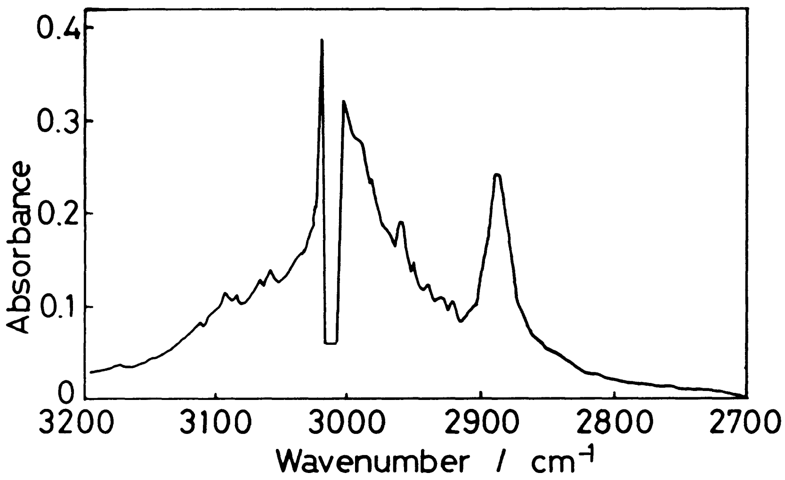

Fig. 2. An example of IR spectrum of methane adsorbed on the NaZSM-5 zeolite; temperature = 300 K, pressure = 0.57 MPa.

measured at room temperature in particular under moderately high pressures up to 0.8 MPa. It is seen in the figure that the intensity-pressure curve representing the high pressure IR data can also represent the low pressure IR data obtained another IR cell.[11)]

Another aspect of the IR ν_1-absorption is revealed by the data shown in Fig. 4, where the absorption intensity (S/W) is plotted as a function of the amount of methane adsorption (N). A linear relation between S/W and N is evident. The IR absorption intensity vs. the amount of methane adsorption relation enables us to evaluate an average electric field strength (E) of the

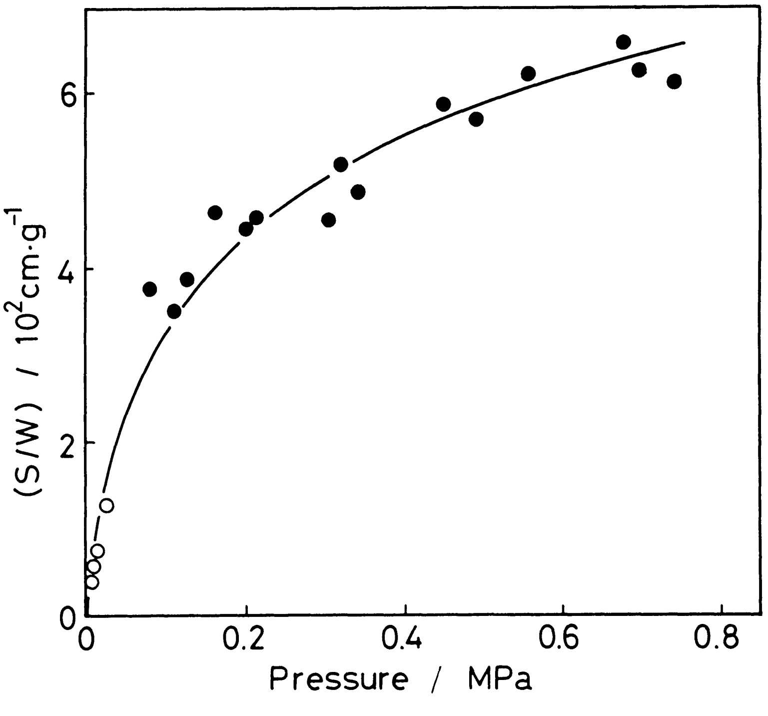

Fig. 3. Pressure dependence of the intensity of the ν_1-adsorption of methane adsorbed on NaZSM-5 at 300 K. (●) data obtained by the high pressure IR cell shown in Fig. 1. (○) data obtained with another cell.[11)]

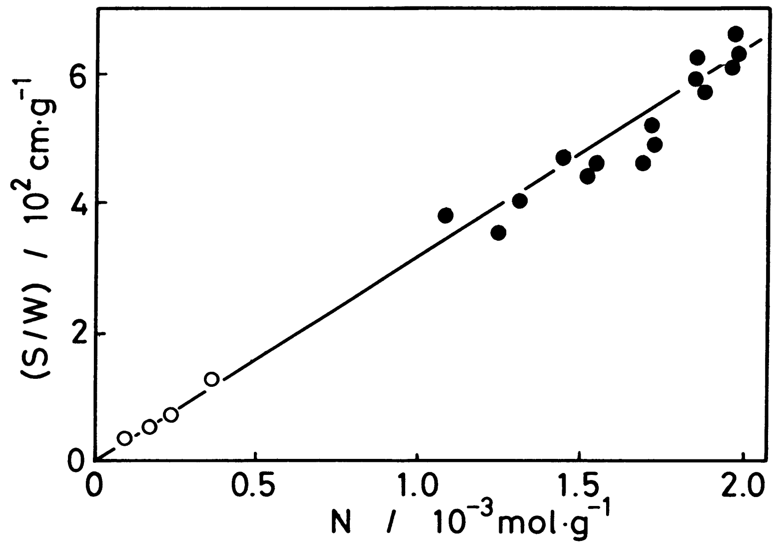

Fig. 4.
A linear relationship between the IR ν_1-intensity and the amount of methane adsorption.

cationic adsorption site in the pore of the NaZSM-5 zeolite. For this purpose the following relation[4)] is available:

$$(1/C_m \cdot l) \int_{\text{band}} \log(I_0/I)\, d\nu = (\pi/3c)(\partial\alpha/\partial Q)^2 E^2 \qquad (1)$$

where C_m is the molecular density of adsorbed methane, l is the thickness of the sample disk, $\log(I_0/I)$ is the absorbance, ν is the frequency in Hz, c is the velocity of light, and $\partial\alpha/\partial Q$ is the average of the first derivatives of the polarizability (α) with respect to normal coordinates (Q).

Putting the IR data and the reported value[12)] of $\partial\alpha/\partial Q$ $=2.27\times10^{-16} \cdot N^{1/2}\,cm^2 \cdot g^{-1/2}$ into Eq.1, we obtained $E = 3.6 \times 10^9\ V \cdot m^{-1}$ (1.2×10^5 esu). This value is comparable with the field strength $4.8\text{-}7.8 \times 10^9\ V \cdot m^{-1}$ ($1.6\text{-}2.6 \times 10^5$ esu) reported for the NaA zeolite.[4)]

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