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Adsorption of Xenon in the Zeolitic Pore in the Henry's Law Region of the Isotherms

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Synopsis. The isotherms and the ^{129}Xe NMR spectra of Xe adsorbed on HY and USY zeolites of faujasite structure were measured. There were two kinds of Xe species, which could be distinguished as one trapped on the internal surface of the supercage and the other freely mobile in the supercage.

Zeolites with their specific and rather well-defined structure show some interesting properties related to the adsorption of gases in the intense potential fields, which exist in cavities of molecular dimensions; this causes an increased intermolecular solid–gas interaction, even in the case of nonpolar gases such as xenon.

In recent years, much effort has been devoted to investigations of adsorption in restricted geometries, such as zeolite structure. It has been proposed that the adsorption of various gasses on activated charcoals and zeolites (5A and 13X) is a superimposed two-site Langmuir adsorption.[1] In the following studies of the adsorption of xenon, the experimental results in zeolitic pore (H-ferrierite) have been fully analyzed by statistical thermodynamics.[2] The ^{129}Xe NMR study of xenon adsorbed on Y zeolites has also revealed characteristic properties of a faujasite structure.[3]

We have now observed the interesting behavior of xenon adsorbed on zeolites (faujasite) in the Henry's law region of the adsorption isotherms. This note is therefore, devoted to the elucidating of the behavior of xenon adsorbed on Y zeolites. The isotherms and the ^{129}Xe NMR spectra of xenon adsorbed on HY and USY zeolites were measured and compared.

Experimental

Commercial synthetic NaY zeolites (Union Showa, Japan) were used. HY zeolite was prepared from NaY type. USY zeolite (Si/Al_2=22.7) was prepared from HY type by dealuminations, steaming and leaching with acid. Before the xenon was adsorbed on the zeolites, these were pretreated for 4 h at 400 °C under vacuum (10^{-5} Torr[4]). The adsorption isotherms of xenon (99.5%) were measured on a volumetric apparatus at −78 °C. NMR absorptions of ^{129}Xe adsorbed on the samples were observed by using FX-90Q (FT-NMR; JEOL, Japan) at a frequency of 24.785 MHz and a magnetic field of 21.1 kG (1G=10^{-4}T) with D lock. The radio frequency field pulse was repeated every second, which was sufficiently long compared to the relaxation time. The reference signal, 24.7850 MHz of ^{129}Xe was taken as that of Xe gas at 5 atm in the presence of about 5% of oxygen as a paramagnetic impurity.[3] All resonance signals of ^{129}Xe adsorbed on zeolites were obtained after 2000 accumulations and shifted to higher frequency relative to the reference.

After the xenon had been adsorbed on each zeolite and the NMR tubes had been sealed at −78 °C, the ^{129}Xe NMR spectra were observed at −78 °C (for HY zeolite, 31.5 Torr of xenon and for USY one, 37.3 Torr of xenon at each adsorption equilibrium) and by cooling to −100 °C (for HY one and for USY one), respectively.

Results and Discussion

The adsorption isotherms of xenon adsorbed on HY (empty circles) and USY (crosses) zeolites at −78 °C are shown in Fig. 1. The amounts of xenon adsorption are proportional to the pressure in the Henry's law region of the isotherms, but these change to a different linear dependence at higher adsorption pressure. These isotherms are at first convex towards the pressure axis at these adsorption equilibria and have an inflection point. The interesting and strange results obtained here are similar to those observed by Aristov, et al.[5] They considered that localized and non-localized xenon adsorptions often co-exist on crystals of zeolites LiX and NaX. These features of the

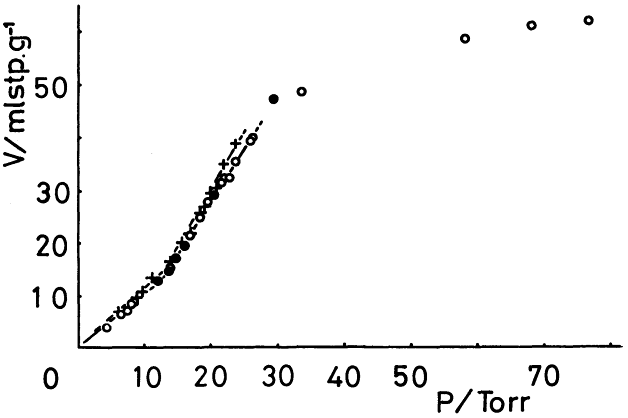

Fig. 1. The amounts for xenon adsorbed vs. pressures of the adsorption equilibrium at −78 °C on HY (circles; ○ for the adsorption, ● for the desorption) and USY zeolites (crosses).

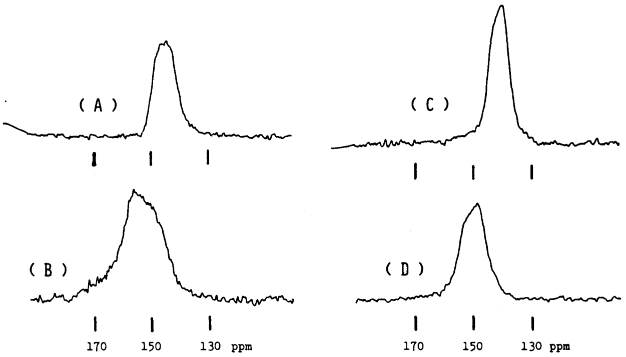

Fig. 2. ^{129}Xe NMR spectra of xenon adsorbed, on HY zeolite at −78 °C under 31.5 Torr of xenon at the adsorption equilibrium (A) and then cooled to −100 °C (B), and on USY zeolite at −78 °C under 37.3 Torr of xenon (C) and also cooled to −100 °C (D), respectively.

isotherms can also be interpreted by a superimposed two-site Langmuir model.1) The data obtained were highly reproducible. No hystereses of these isotherms were observed, that is, the amount adsorbed for xenon in the adsorptive process equals strictly that in the desorptive one at the same equilibrium pressure, shown by full circles in Fig. 1. From this, it follows that the xenon adsorption occurs in intense potential fields, not by pore filling.6) The isosteric differential heat of adsorption, q_{iso} of xenon was 16—18 kJ mol^{-1} in the Henry's law region of the isotherms on HY and USY zeolites, different from the heat of vaporization of xenon 12.6 kJ mol^{-1}.7)

Figure 2 shows the ^{129}Xe NMR spectra of xenon adsorbed at −78 °C and −100 °C, on HY and USY zeolites. Each ^{129}Xe line shape is characteristic in width and suggests it consists of two signals. The NMR signal of ^{129}Xe adsorbed on zeolite shifts increasingly with increasing the xenon pressure at the adsorption equilibrium. When the ^{129}Xe NMR spectra were observed by cooling the NMR tubes to −100 °C, the two NMR signals in Fig. 2 (B) or (D) could be clearly separated into one peak, 146 or 148 ppm and another, 152 or 158 ppm shifted to the reference, respectively.

The distinguishable differences between the two NMR signals and between two heats of xenon adsorption corresponded to each NMR signals are extremely small. The relaxation time for the higher field signal and for the other were approximately 10 and 70 ms, respectively. Comparatively speaking, the xenon species adsorbed and corresponding to the higher field signal is considered to be strongly trapped on the internal surface of the supercage and the other to be freely mobile in the supercage of the faujasite structure. We deduce therefore, that the higher field signal for our NMR spectra appeared at lower xenon densities (within 7—9 xenon atoms/unit cell) must be due to the interactions between a xenon atom and the internal surface of the supercage. Another lower field signal appeared at higher xenon densities is also deduced to be caused by mutual interactions between xenon atoms in the supercage.3) This conclusion agrees perfectly with that of the superimposed two-site Langmuir model.1)

The superimposed two-site Langmuir model was not based on spectroscopical evidence. Here we propose this supporting evidence based on the NMR signals of ^{129}Xe adsorbed on zeolites. We infer the adsorption states of Xe adsorbed on HY zeolite are comparatively similar to those on USY one.

References

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