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著者名、タイトル、雑誌名、発行年月、巻号、ページ、URL等を自動で作成する機能
Motion of methanol adsorbed in porous coordination polymer with paramagnetic metal ions†

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Abstract

In recent years, porous coordination polymers containing transition metal ions and organic ligands, whose properties are promising for chemistry and application in storage, separation, and catalysis as well as zeolites, have been extensively studied.§ This feature is associated with their complete regularity, high porosity, and highly desirable and dynamic frameworks, which, in certain cases, are beyond the scope of the zeolites and activated carbons. Generally, the discussion of the behaviour of guest molecules in porous coordination polymers has been based on X-ray diffraction and thermodynamic data such as adsorption isotherms. Therefore, little in-depth information on the dynamic behaviour of guest molecules in micropores, which is essential for evaluation and understanding of micropore filling and design of new functions, has been obtained. To date solid state NMR techniques have been demonstrated to be a powerful tool for monitoring the dynamic behaviour of guest molecules confined in microporous materials like zeolites.§

Herein, we have succeeded in observing solid state 1H NMR spectra for a guest adsorbed in a porous coordination polymer with paramagnetic metals. In this report, we have employed a pillared-layer type coordination polymer, [Cu(pzdc),py] (CPL-1; pzdc = pyrazine; pzdc = pyrazine-2,3-dicarboxylate), whose structure was determined previously by single crystal X-ray crystallography and elemental analysis, and the channel dimension was estimated to be about 4 × 6 Å² along the a axis.§ We have chosen the CH₃OH molecule (3.8 × 4.0 Å²) as a guest, which is interesting as a probe because it not only has a size comparable with that of the channel of CPL-1, but also a structure having hydrophilic (OH) and hydrophobic (CH₃) groups. CPL-1 shows a high adsorption affinity for CH₃OH even at 298 K with type 1 isotherms.

To investigate the structural change of the framework before and after adsorption of CH₃OH, we performed in-situ high resolution synchrotron X-ray diffraction measurements at SPring-8, BL02B2 and Rietveld analysis.§ The crystal structure of CPL-1 at 298 K determined by refinement of the powder data reveals that the porous structure is identical to that of as-synthesized compound CPL-1·MCH₃OH with only a slight structure distortion (Fig. 1(a)).§ The refinement also shows that the space group of CPL-1·CH₃OH (P2c/c) is the same as that of CPL-1 (Fig. 1(b)).§ The b lattice parameter slightly increases about 1.0% on the sorption, but the initial porous framework undergoes a little change even after adsorption. The CH₃OH molecules in 1D channels in Fig. 1(b) have relatively high atomic displacement parameters, making the determination of their precise position difficult. This indicates that guest molecules are under a highly dislocating motion, or that the unit space does not allow guests to be lined up in a commensurate fashion. In this situation, to date we have not been able to obtain any more detailed information on the methanol molecules, but we succeeded in gaining their dynamic aspect, detailed mobility of CH₃OH adsorbed in CPL-1, by measuring 1H NMR spectra. Fig. 2(a) displays the observed 1H NMR spectra for CD₃OH adsorbed in CPL-1 from 173 to 293 K. The conditions of NMR measurement and the procedure for sample preparation are also described in Fig. 2. Over the whole temperature range, the observed spectra show the distorted Pake doublet patterns, indicative of the anisotropic motions of the adsorbed CD₃OH. These asymmetric line shapes are ascribed to the paramagnetic shifts due to the Cu²⁺ ions. Fig. 2(b) shows the simulated 1H NMR spectra calculated by considering the dipole interaction between the 1H nuclei of the guests and the paramagnetic Cu²⁺ ions in addition to the quadrupole interaction.§ As a result, observed spectra for the whole temperature range can be reproduced by the superposition of three theoretical Pake doublet spectra, those of which have different values of the parameters: the quadrupole coupling constant Q, the angle β between the principal axis of the quadrupolar tensor and that of the dipole tensor, and the paramagnetic shift parameter νµ.§ The asymmetry parameter η is zero for all the spectra, and the νµ value is small for each temperature, because the distance between the D₀ group and Cu²⁺ ions of CPL-1, which is estimated from X-ray analysis, is longer than 5.0 Å. From the simulation, the adsorbed CD₃OH has only two kinds of motions for the entire temperature range. One is a fast rotation
of the CD$_3$ group about the C$_3$ axis, and the additional one is a wobbling motion of the C–O axis, which is defined to be a cone angle $\theta$ (Fig. 2(d)). Taking the wobbling motion into consideration, the effective quadrupole coupling constant $Q_{\text{eff}}$ is given by equation 1

$$Q_{\text{eff}} = Q_0 \frac{3 \cos^2 \theta - 1}{2}$$

The value of $Q_0$ is the quadrupole constant of rigidly-bound CD$_3$ groups rotating rapidly only about the C$_3$ axis.\(^8\)

Schematic illustrations of the adsorbed CD$_3$OH are represented in Fig. 2(c) for 293 and 173 K. The angle $\theta$ at 293 K is calculated as 41.4° from equation 1 while at the lower temperature, the guests are thermally deactivated, resulting in $\theta = 16.4°$ at 173 K.\(^9\) The two anisotropic motions are maintained for the whole temperature range.

In contrast to zeolites, CPL-1 has no acidic site in the channels because the copper ions are coordinately saturated and, therefore, confinement effects on guest molecules are associated with van der Waals type forces. For example, methanol adsorbed in the micropores of several zeolites, with pore sizes similar to that of CPL-1, is tightly bound to Brønsted acid sites, so-called chemical sorption where rotation about the C$_3$ axis is the only effective motion even at room temperature.\(^10\) On the other hand, methanol in aluminiumophosphate (AlPO$_4$-5), which has no acidic site and whose 1D channel diameter is 7.3 Å, is rapidly isotropic.\(^11\) In contrast to these adsorbents, CPL-1 affords the regular low-dimensional nanospace, effective for physisorbed confinement of methanol molecules even at room temperature.

Here, we successfully obtained information on guest methanol in a restricted pore space; the high crystallinity of CPL-1 allowed the methanol to undergo only two motions, rotation and wobbling, whose aspects, to our knowledge, have not been reported in zeolites previously. The results obtained here provide a hint for the design of a metal–organic channel for confining a guest molecule with a certain orientation and motion. The $^2$H NMR method is useful for characterizing the motions of the guests in porous coordination polymers even with paramagnetic metal ions.

Notes and references

4. CPL-1 itself is an apohost, that is a host without included guests.