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Motion of methanol adsorbed in porous coordination polymer with paramagnetic metal ions†

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Molecular motions of methanol adsorbed in 1D nanochannels of pillared-layer coordination polymer with paramagnetic metal ions have been studied by ^{2}H NMR together with X-ray crystallography.

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.[1] This feature is associated with their complete regularity, high porosity, and highly designable and dynamic frameworks, which, in certain cases, are beyond the scope of the zeolites and activated carbons.[2] 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.[3]

Herein, we have succeeded in observing solid state ^{2}H 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, $[Cu_2(pzdc)_2(pyz)]_n$ (**CPL-1**; pyz = pyrazine; pzdc = pyrazine-2,3-dicarboxylate),[4] 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 Å^2 along the *a* axis.[5] We have chosen the CH_3OH molecule (3.8×4.0 Å^2) 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 (CH_3) groups. **CPL-1** shows a high adsorption affinity for CH_3OH even at 298 K with type I isotherms.

To investigate the structural change of the framework before and after adsorption of CH_3OH, we performed *in-situ* high resolution synchrotron X-ray diffraction measurements at SPring-8, BL02B2 and Rietveld analysis.[6] 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·*n*H$_2$O** with only a slight structure distortion (Fig. 1(a)).[7]† The refinement also shows that the space group of **CPL-1·*n*CH$_3$OH** ($P2_1/c$) 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 CH_3OH 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 CH_3OH adsorbed in **CPL-1**, by measuring ^{2}H NMR spectra. Fig. 2(a) displays the observed ^{2}H NMR spectra for CD_3OH 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 CD_3OH. These asymmetric lineshapes are ascribed to the paramagnetic shifts due to the Cu^{2+} ions. Fig. 2(b) shows the simulated ^{2}H NMR spectra calculated by considering the dipole interaction between the ^{2}H nuclei of the guests and the paramagnetic Cu^{2+} ions in addition to the quadrupole interaction.[8] 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 ν_P†. The asymmetry parameter η is zero for all the spectra, and the ν_P value is small for each temperature, because the distance between the CD_3 group and Cu^{2+} ions of **CPL-1**, which is estimated from X-ray analysis, is longer than 5.0 Å.

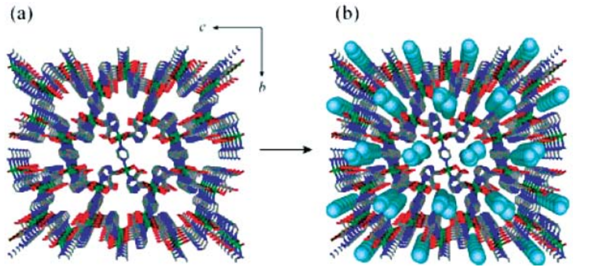

Fig. 1 X-ray crystallographic structures of **CPL-1** without (a) and with (b) methanol guest molecules projected down the *a* axis at 298 K. Methanol molecules are represented by a space filling model. Hydrogen atoms are omitted for clarity. Copper, oxygen, carbon, nitrogen atoms and guests are denoted with green, red, gray, blue and sky blue, respectively.

From the simulation, the adsorbed CD_3OH has only two kinds of motions for the entire temperature range. One is a fast rotation

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† Electronic supplementary information (ESI) available: refined powder diffraction data and simulated NMR lineshapes. See http://www.rsc.org/suppdata/cc/b4/b406883a/

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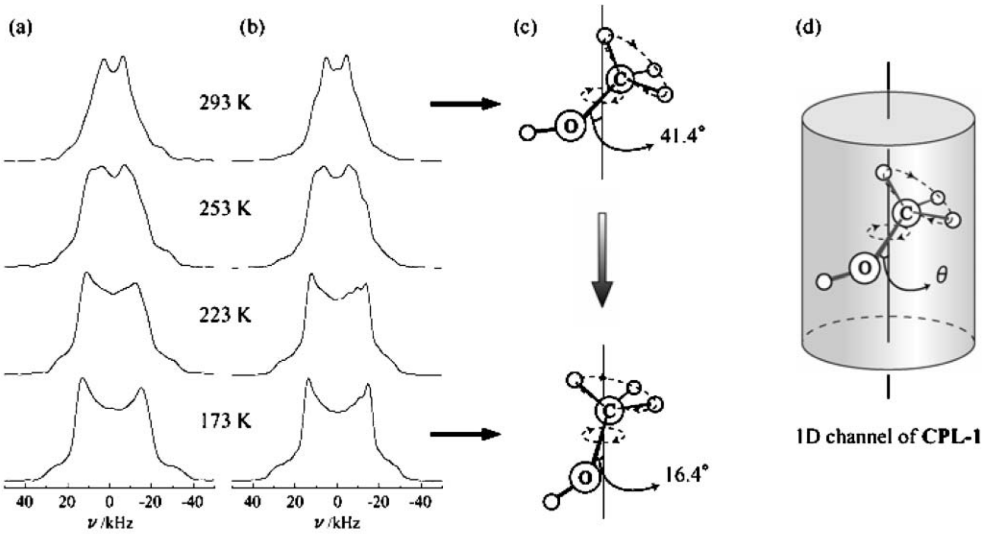

Fig. 2 Selected ^{2}H NMR spectra of (a) experimental, (b) simulation of the CD_3OH adsorbed in **CPL-1** in the range 173–293 K. (c) Schematic illustrations of motion for 293 and 173 K, respectively. (d) Model of the molecular motion of CD_3OH in **CPL-1**. The ^{2}H NMR spectra were measured with a Chemagnetics CMX-300 spectrometer operating at 46.825 MHz by using the shift-compensated quadrupole-echo sequence ($90_x - \tau/2 - 180_y - \tau/2 - 90_y - \tau/2 - 180_y - \tau/2 -$ acq) which refocuses the dephasing due to both the quadrupole interaction and the paramagnetic shift.[8] The 90 pulse-width and $\tau/2$ were 3 μs and 20 μs, respectively. Before the NMR measurement, **CPL-1** was dried at 393 K for 1 day, and then CD_3OH was adsorbed by vapor diffusion at 298 K for 1 day. The sample cell was set in a glass tube.

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 θ (Fig. 2(d)). Taking the wobbling motion into consideration, the effective quadrupole coupling constant Q_{eff} is given by equation 1

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

The value of Q_0 is the quadrupole constant of rigidly-bound CD_3 groups rotating rapidly only about the C_3 axis.[9]

Schematic illustrations of the adsorbed CD_3OH are represented in Fig. 2(c) for 293 and 173 K. The angle θ 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.[‖] 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 coordinatively 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 aluminophosphate ($AlPO_4$-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

[¶] Crystal data for **CPL-1·*n*CH₃OH**: $C_9H_4N_3O_5Cu$, *M*r = 297.69, monoclinic, $P2_1/c$, (No. 14), a = 4.7094(11) Å, b = 20.0417(2) Å, c = 11.0950(2) Å, β = 96.839(2)°, V = 1039.7(1) Å^3, Z = 4, T = 298 K. CCDC 244353. See http://www.rsc.org/suppdata/cc/b4/b406883a/ for crystallographic data in .cif or other electronic format.

[‖] The most dominant for the three Q_{eff} at each temperature (see ESI†) and Q_0 = 47 kHz are adopted, respectively.

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