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THERMODYNAMIC ASPECT OF REVERSIBLE STRUCTURAL CONVERSION INDUCED BY GUEST ADSORPTION/DESORPTION BASED ON INFINITE $Co(NCS)_2Py_4$ (*Py*=pyridine) SYSTEM

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Thermogravimetry (TG) and Me_2CO adsorption measurements for flexible porous crystalline coordination polymers with 2-dimensional (2-D) frameworks, $\{[Co(NCS)_2(3\text{-pia})_2]\cdot 4Me_2CO\}_n$ (**1**$\supset 4Me_2CO$, 3-pia=*N*-(3-pyridyl)isonicotinamide), were carried out. Taking advantages of capability of hydrogen bonding of amide groups for a dynamic properties, **1**$\supset 4Me_2CO$ show crystal (non-porous)-to-crystal (porous) structural rearrangement in Me_2CO adsorption/desorption processes. The activation energy for the Me_2CO desorption process of **1**$\supset 4Me_2CO$ was obtained using Flynn–Wall–Ozawa's (FWO) method. The Me_2CO adsorption isotherms on **1** have a threshold pressure (P_{th}) for abrupt accommodation of Me_2CO molecules, which is regarded as the equilibrium pressure for the inclusion reaction of Me_2CO.

Keywords: *adsorption, amides, coordination polymer, host-guest systems, hydrogen bonds, thermogravimetry*

Introduction

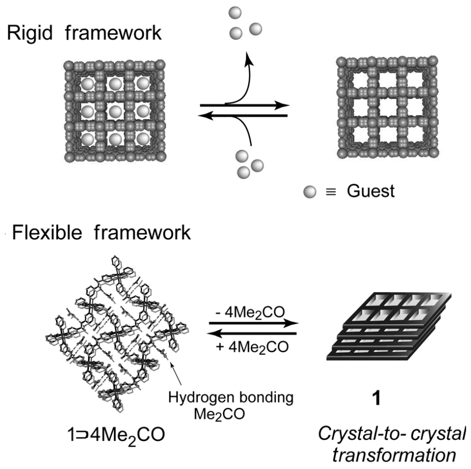
Recent extensive research into the design and synthesis of porous coordination polymers has provided a wide variety of structures and functionalities, leading to a new class of adsorbent [1–5]. These new porous materials are distinguished by two types of pore: Type I is a robust pore, as in zeolites [2], and Type II is a softer pore that is attained by structural conversion of the host in a gas adsorption process [6–8], Type I *H* and $H{\cdot}G_n$ pores have similar frameworks, while Type II pores have different frameworks, as Eq. (1);

$$H+nG \leftrightarrows HG_n\ (H\supset nG),\ \Delta H_{clath} \tag{1}$$

where *H* is the apohost, *G* is a guest molecule, *n* is the stoichiometry of the accommodated guest *vs.* that of the apohost, and ΔH_{clath} is the enthalpy of clathration. Soft pores (Type II) are characteristic of coordination polymers [9–14], and are expected to be useful for the separation of guest molecules and for magnetic modulation [15]. They are found in bistable frameworks where two states oscillate between two counter parts.

For robust pores (Type I), using a similar approach to that used for zeolites can make it easy to understand the adsorption mechanism, because the energy required for the adsorption/desorption process (ΔH_{clath}) can simply be ascribed to the heat of condensation of the guest molecule and the interaction between the guest molecule and the host. On the other hand, the adsorption mechanism of soft pores is complicated, and it remains relatively unexplored. Nevertheless, an estimation of ΔH_{clath} can lead to a better understanding of the nature of soft pores and the mechanism of structural conversion [16, 17].

Previously, we reported on an infinite $M(NCS)_2(Py)_4$ system, $\{[Co(NCS)_2(3\text{-pia})_2]\cdot 4Me_2CO\}_n$ (**1**$\supset 4Me_2CO$, 3-pia=*N*-3-pyridylisonicotinamide) that exhibits a reversible crystal-to-crystal transformation (**1**$\supset 4Me_2CO$ (open) ↔ **1**(closed)) accompanying Me_2CO adsorption/desorption [6]. In the **1**$\supset 4Me_2CO$ complex, the octahedral environment around the Co^{II} ion is similar to that in $M(NCS)_2(Py)_4$ [18], and each Co^{II} atom is bridged by four 3-pia ligands to form a 2-dimensional layer (Scheme 1). **1**$\supset 4Me_2CO$ entraps



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Me_2CO molecules by their forming a hydrogen bond with the amide moieties in the 3-pia ligands. Upon the removal of the Me_2CO molecules, the conversion of the initial hydrogen bonding mode to a complementary mode transforms the overall structure into an apohost, **1**. In this report, we introduce our preliminary thermodynamic analysis of flexible porous coordination polymers, and discuss the reversibility of structural transformations from an energetic point of view.

Experimental

Materials

Isonicotinic chloride hydrochloride and 3-aminopyridine were obtained from Tokyo Kasei Industrial. $Co(SCN)_2$ was obtained from Aldrich Co. **1**$\supset$4Me_2CO was synthesized according to [6].

Physical measurements

Thermogravimetry (TG) was carried out with a Rigaku Instrument TG8120 in a nitrogen atmosphere (50 mL min^{-1}) with sample (**1**$\supset$4Me_2CO) mass: 10.832 mg (2°C min^{-1}); 10.988 mg (3°C min^{-1}); 12.417 mg (5°C min^{-1}); 11.752 mg (7°C min^{-1}) and 11.500 mg (10°C min^{-1}).

Measurement of adsorption

The adsorption isotherms of gaseous Me_2CO were measured by using BELSORP18-Plus volumetric adsorption equipment from BEL JAPAN. In the sample chamber (~17.5 mL) maintained at T 298±0.03 K was placed the adsorbent sample (~50 mg), which had been prepared at 373 K and 10^{-1} Pa prior to measurement of the isotherms. The larger gas chamber (179.85 mL) with a pressure gauge was kept at (T+20)±0.1 K. The Me_2CO used to generate the vapor was degassed fully by repeated evacuation and vapor equilibration cycles of the liquid supply side of the vapor reservoir. Helium gas at a certain pressure was introduced in the gas chamber and was allowed to diffuse into the sample chamber by opening a valve. The change in pressure allowed an accurate determination of the volume of the total gas phase. The complexation was monitored in a similar manner by using a guest vapor in place of helium. The amount of guest adsorbed was calculated readily from pressure difference (P_{cal}–P_e), where P_{cal} is the calculated pressure with no guest adsorption, and P_e is the observed equilibrium pressure. All operations were computer-controlled and automatic.

Results and discussion

Thermogravimetry (TG)

1$\supset$4Me_2CO includes Me_2CO molecules as a guest. The Me_2CO desorption was monitored by TG. Figure 1a shows the TG curve **1**$\supset$4Me_2CO over the temperature range from 30 to 160°C with various heating rates. The observed mass loss of Me_2CO molecules is in agreement with that calculated for the corresponding crystal structure. The TG data for **1**$\supset$4Me_2CO indicates one stage for mass loss of the guest molecules; four Me_2CO molecules (observed 29.3%, calculated 28.8%). In desorption processes, '**1**$\supset$4Me_2CO→**1**', the activation energies for desorption (E_{de}) were estimated by recording TG curves at various heating rates (β) and by plotting logβ *vs.* 1/T at a given extent of desorption, according to the Flynn–Wall–Ozawa's (FWO) method as Eq. (2) [19, 20].

$$\log\beta = -0.4567E_{de}/RT + \text{const.} \qquad (2)$$

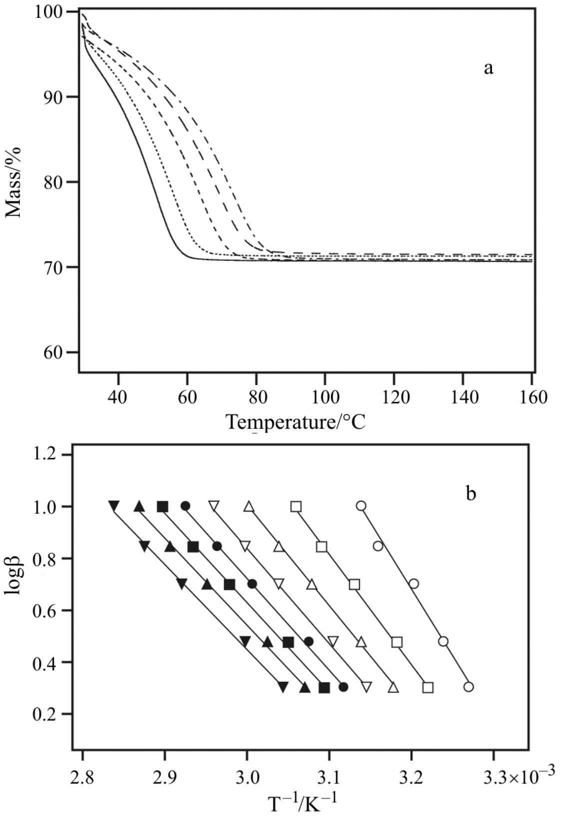

Fig. 1 a – The TG curves of **1**$\supset$4Me_2CO plotted *vs.* the absolute temperature. Heating rate: 2, 3, 5, 7 and 10°C min^{-1}; b – The plots of logarithms of heating rate (β) *vs.* the conversions of absolute temperature of 20 (open circle), 30 (open square), 40 (open triangle), 50 (open reverse triangle), 60 (filled circle), 70 (filled square), 80 (filled triangle), 90% (filled reverse triangle) desorption for **1**$\supset$4Me_2CO

Table 1 Estimation for activation energies (E_{de}) based on FWO method with various degree of Me_2CO desorption

Degree of desorption/%	E_{de}/kJ mol^{-1}
20	93.6(11)
30	77.7(4)
40	71.0(3)
50	67.0(3)
60	64.6(3)
70	62.9(4)
80	61.3(4)
90	59.8(4)

The results of the thermogravimetry at various heating rates are plotted *vs.* the absolute temperature in Fig. 1b. In all measurements, straight lines are obtained and the method of the least squares affords the activation energies determined. Table 1 shows the values of E_{de} obtained from the slopes of the curves in Fig. 1b. In the case of '**1**$\supset 4Me_2CO \rightarrow$**1**', the values of E_{de} become smaller as increasing the degree of conversion. According to the classification for solid-state dehydration [21], '**1**$\supset 4Me_2CO \rightarrow$**1**' is regarded as type WET-2 (*WET*='water evolution type'), where Me_2CO molecules diffuse across and adherent and coherent barrier layer of product. In such a desorption process, the multiple steps which have different activation energies in the degree of desorption are involved [22], and in this stage it is difficult to further discuss about the smaller E_{de} as increasing the degree of conversion.

Adsorption measurements and estimation of ΔH_{clath}

Since **1** shows a structural regeneration when exposed to Me_2CO vapor, Me_2CO adsorption experiments were carried out on **1**. Figure 2 shows the adsorption isotherms for Me_2CO over the relative pressure range from 0–0.9 at T=268–338 K. All the adsorption isotherms show an abrupt rise at the threshold pressure (P_{th}). When the concentration of a suitable guest molecule increases to a given threshold concentration, closed-to-open reconstruction takes place, indicating the conversion of crystalline **1** to crystalline **1**$\supset 4Me_2CO$ [7, 23]. The P_{th} values decreased with decreasing temperature: 4.9 kPa at 268 K, 8.9 kPa at 278 K, 10.0 kPa at 288 K, 14.8 kPa at 298 K, 25.9 kPa at 308 K, 45.9 kPa at 318 K, 55.9 kPa at 328 K, and 85.9 kPa at 338 K. Since the P_{th} value can be regarded as the equilibrium pressure for the inclusion reaction of Me_2CO, the temperature dependence of P_{th} allows us to evaluate the associated enthalpy change on Me_2CO adsorption based on the following equation

$$d\ln P_{th}/d(1/T)=\Delta H_{clath}/R \qquad (3)$$

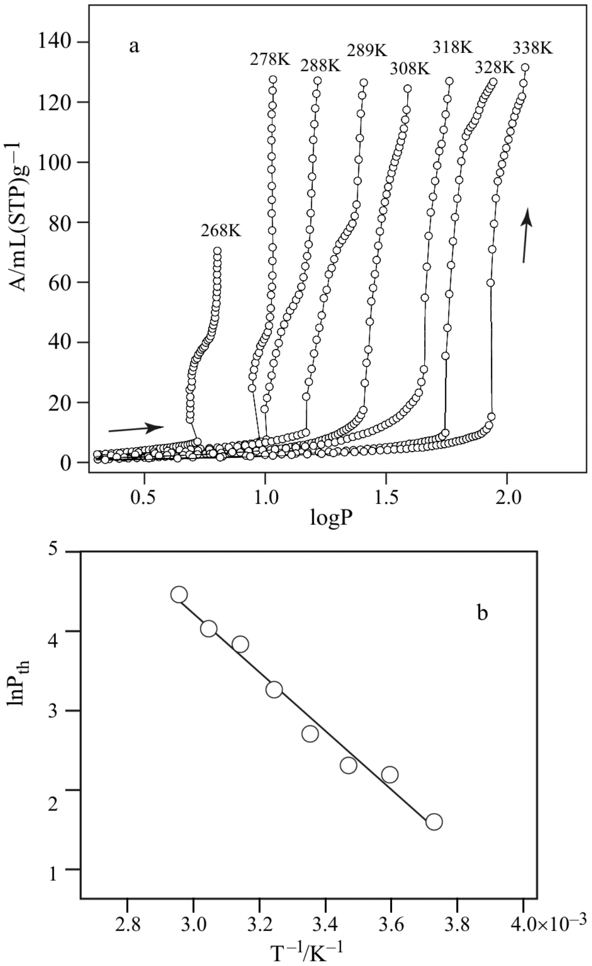

Fig. 2 a – Isotherm for Me_2CO vapor adsorption at 268, 278, 288, 298, 308, 318, 328 and 338 K of **1**. Saturated vapor pressure of Me_2CO: 7.195 (268), 12.123 (278), 19.610 (288), 30.593 (298), 46.211 (308), 67.818 (318), 96.976 (328) and 135.466 kPa (338 K); b – Plot of $\ln P_{th}$ *vs.* T^{-1}

where R denotes the universal gas constant. From Eq. (3), a plot of $\ln P_{th}$ *vs.* $1/T$ yields a straight line (Fig. 2b), whose gradient gives ΔH_{clath}= –30.8(2) kJ mol^{-1} for the inclusion of Me_2CO. Furthermore, clathration entropy, ΔS_{clath}=127(2) J mol^{-1} K^{-1}, is obtained according to the equation, $\ln P_{th}=\Delta H_{clath}/RT+\Delta S_{clath}/R$.

In the case of a discrete system, $[Ni(NCS)_2(4\text{-}MePy)_4]$ adsorbs toluene, ethylbenzene, *p*-xylene, and *p*-dichlorobenzene, with ΔH_{clath}= –29.72, –32.35, –30.1 and –35.1 kJ mol^{-1}, respectively [24, 25]. The closed-to-open phase transformation enthalpy of the host $[Ni(NCS)_2(4\text{-}MePy)_4]$ (ΔH_{trans}) is 6.6 kJ mol^{-1}, only involving van der Waals forces among the molecules [25, 26]. Although the accurate comparison between $[Ni(NCS)_2(4\text{-}MePy)_4]$ and **1** is impossible in different kinds of guest system, the value of ΔH_{clath} in **1**$\rightarrow$**1**$\supset 4Me_2CO$ is not so far different from those observed in $[Ni(NCS)_2(4\text{-}MePy)_4]$. In $\mathbf{1}\rightarrow\mathbf{1}\supset4Me_2CO$, an input energy is required to dissociate the complementary hydrogen bonds formed among the amide moieties in **1**, which adds to the subsequent exothermic heat of formation of amide-Me_2CO hydrogen bonds in $\mathbf{1}\supset4Me_2CO$. Thus, the initial endothermic heat is canceled out by the ensuing exothermic heat. This is the reason for the relatively small value for ΔH_{clath} in $\mathbf{1}\rightarrow\mathbf{1}\supset4Me_2CO$, even if multiple hydrogen bonds are related in the network **1**.

Conclusions

This work demonstrates TG and Me_2CO adsorption measurements for flexible porous frameworks, $\mathbf{1}\supset4Me_2CO$. The existence of the P_{th} for Me_2CO adsorption on **1** was confirmed, and ΔH_{clath} ($-30.8(2)$ kJ mol^{-1}) was obtained based on the temperature dependence of P_{th}. The value of ΔH_{clath} is not so far different from ones of discrete system, implying that this infinite $Co(NCS)_2Py_4$ system is often much more dynamic as well as the discrete system.

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