

Highly efficient carbon monoxide trap by a transformable soft nanospace of porous crystal

Carbon monoxide (CO) is a central resource for carbon-based chemical products. Although industrial processes such as steel manufacturing produced vast quantities of CO in a mixed exhaust gas, most of it cannot be used as a carbon resource. Therefore, separating CO from a gas mixture has economic and environmental importance. To date, CO separation has been limited to processes using the strong chemisorption of CO, but a high temperature is required to release CO, which is energy consuming. The key to overcoming this problem is a synergistic system that uses a weak local interaction and a subsequent global structural change. This process has been achieved in the nanometer-sized space of a soft biosystem. Despite their crystalline form, porous coordination polymers (PCPs) can provide a nanometer-sized soft space, which can transform in response to guest accommodation or physical stimuli [1–4]; this feature has encouraged us to create a synergistic system in a PCP solid to achieve the ultimate separation of mixed gases. Herein we report a new PCP that has specific but weak CO adsorption/recognition sites and a reversibly transformable framework [5].

We prepared PCP **1** ($[\text{Cu}(\text{aip})(\text{H}_2\text{O})](\text{solvent})_n$), which is composed of 5-azidoisophthalate (aip) and divalent Cu^{2+} ions. In the as-synthesized crystal of PCP **1**, the Cu^{2+} and aip ligands form paddle-wheel-type dimeric Cu^{2+} clusters, forming an infinite kagomé-type two-dimensional (2D) sheet structure. The 2D sheets are stacked, creating two types of one-dimensional (1D) infinite channels with cross-section sizes of 9×9 (channel *L*; hexagonal larger channel) and 4×4 (channel *S*; triangular smaller channel) \AA^2 (Fig. 1). Guest molecules are easily removed by heating to give a dried PCP **2** ($[\text{Cu}(\text{aip})]_n$).

The crystal structure of dried PCP **2** was determined by Rietveld analysis using synchrotron powder X-ray diffraction data obtained at **BL44B2** beamline. Drying induces marked changes in the channel *S* shape;

channel *S* in dried PCP **2**, is squeezed at the neck, almost creating separate pores. This separation should greatly hinder the access of guest molecules.

The most competitive gas to CO is nitrogen (N_2), which is present in large amounts in industrial exhaust gas as an impurity. Typically it is difficult to distinguish and separate CO and N_2 in industrial processes due to their similar electronic structures, sizes, and physicochemical properties. After deducing that PCP **2** shows a contrasting sorption behavior for these two gases, we studied the sorption behaviors of CO and N_2 on PCP **2** and the structural changes upon sorption by *in situ* X-ray powder diffraction (XRPD)/sorption coincident measurements (Fig. 2). During the N_2 adsorption process, no appreciable positional changes in the peaks of the XRPD patterns were observed. However, pronounced changes in the XRPD patterns were observed upon CO adsorption and desorption. Although the XRPD pattern of PCP **2** did not change markedly in the initial CO adsorption, after point c in Figs. 2C and 2D, the original peaks of PCP **2** gradually decreased and new peaks appeared. These results clearly show that the steep uptake after point c was accompanied by a structural change. In addition, we successfully obtained the crystal structure of PCP **3** containing a Cu^{2+} –CO complex module. Structural analysis revealed that the coordination of CO induced a global structural change and created a suitable compartment for further accommodation of CO molecules in the center of channel *S*.

The mechanism for the stepwise sorption of CO can be explained as follows (Fig. 3). In the first step of the isotherm, CO molecules are physically and exclusively absorbed in the larger channel *L* without marked structural change to the framework due to poor accessibility of the highly constricted channel *S*. After filling channel *L*, CO molecules start to form Cu^{2+} –CO bonds, inducing a global structural transformation that expands the squeezed paths. This promotes additional CO adsorption in the center of channel *S*, which is the so-called self-accelerating gas adsorption. The adsorption event in channel *S* is reminiscent of a biosystem where a heme-protein efficiently traps oxygen molecules with a structural change, which is known as an allosteric effect.

We tested its CO separation ability using CO and N_2 mixtures with various compositions. Exposing dried PCP **2** to mixtures of CO and N_2 at 100 kPa, results in an equilibrium state upon gradually decreasing the temperature from 300 to 81 K. The adsorbed gas ratios were examined by gas chromatography. For example,

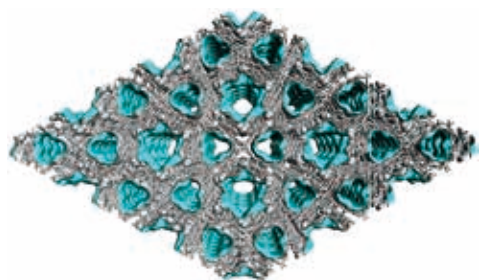


Fig. 1. Crystal structure of PCP **1**. Guest molecules are omitted for clarity.

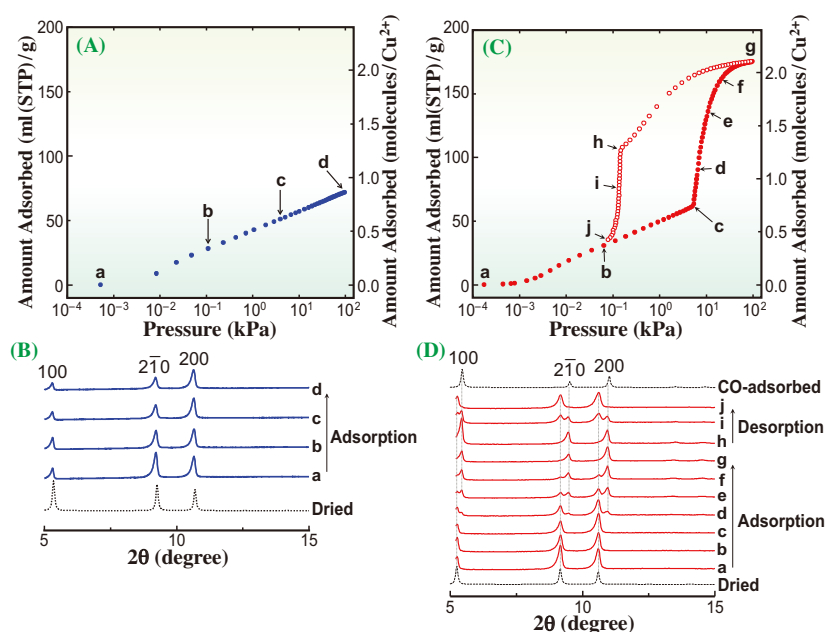


Fig. 2. Coincident XRPD/sorption measurements of PCP 2. (A) N₂ sorption isotherm at 120 K. (B) XRPD patterns measured at each point shown in the N₂ sorption isotherms. (C) CO sorption isotherms at 120 K. (D) XRPD patterns measured at each point in the CO sorption isotherms.

a surprising enrichment of CO of 94% was achieved after the second cycles starting from a 1:1 mixture of CO and N₂. Because of the size restrictions, neither CO nor N₂ can diffuse into channel S without expansion of the narrow path. However, CO can expand the path and realize CO diffusion into the channel when it breaks the coordination bond between Cu and O and subsequently forms a coordination bond with Cu. On the other hand, the weak coordination ability prevents N₂ from expanding the path. Even after CO expands the path, N₂ cannot diffuse into the channel because the paths are surrounded by the three coordinated CO molecules, which sterically inhibit N₂.

In conclusion, our newly synthesized nanoporous crystalline material can realize a highly effective separation of CO from a competitive gas mixture. The self-accelerating sorption system, which is triggered by a weak coordination interaction, is reminiscent of that in soft biological systems such as hemoglobin. In this sense, our artificial soft porous crystalline is the first system to exhibit a highly efficient molecular trapping and releasing ability similar to a biological system. We believe that this new concept of “self-accelerating sorption in a soft nanoporous crystal” will lead to a new approach to separate and store valuable gases without consuming large amounts of energy.

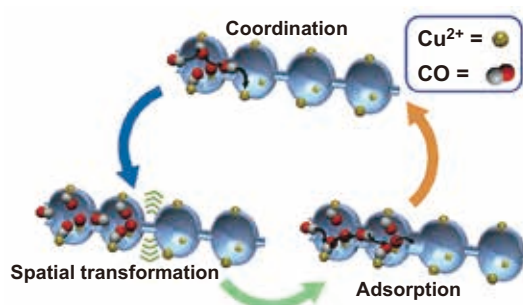


Fig. 3. Schematic representation of the self-accelerating CO adsorption mechanism in PCP 2.

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