ATOMISTIC LEVEL DESCRIPTION OF NEW GREENHOUSE GAS STORAGE MATERIALS USING CLATHRATE HYDRATE

クラスレートハイドレートを用いた新規温室効果ガス貯留材料の原子レベル記述

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ABSTRACT: The thermodynamic conditions for the formation and stability of clathrate hydrates with complex guest compositions were determined, with a special emphasis on the possibility of using hydrates as agents for storage of greenhouse gases. Over a wide pressure-temperature range, we performed atomistic-level theoretical modeling of structural, dynamical, and thermodynamic properties of various ices and hydrates with differing structures, using our original approach. The influence of the guest molecules on the host lattice of hydrates was examined. The possibility of maintaining self-preservation effects for gas clathrate hydrates were investigated.

RESULTS: (a) IMPLEMENTED TEORETICAL MODELS

In order to accurately estimate the thermodynamic properties of hydrogen hydrates, we developed an approach based on the solid solution theory of van der Waals and Platteeuw (vdW-P) with some modifications describing host lattice relaxation, guest-guest interactions and the quantum nature of guest behavior in clathrate hydrates. This approach is based on the lattice dynamics method that takes quantum effects into account in energy and the entropy calculations. For studying the binary clathrate hydrates proposed during this project, we derived all formulas for the possibility of single occupancy for type a guests and multiple occupancy for type b guests of both the small (S) and large (L) cavities. In this case, the expression for the free energy F can be written in the following form:

$$F = F_{1}(V,T,\{y\}) + kTN_{S}\left[\left(1 - y_{S}^{a} - \sum_{i=1}^{k_{S}} y_{S}^{ib}\right)\ln\left(1 - y_{S}^{a} - \sum_{i=1}^{k_{S}} y_{S}^{ib}\right) + y_{S}^{a}\ln y_{S}^{a} + \sum_{i=1}^{k_{S}} y_{S}^{ib}\ln\frac{y_{S}^{ib}}{i!}\right]$$

$$+ kTN_{L}\left[\left(1 - y_{L}^{a} - \sum_{i'=1}^{k_{L}} y_{L}^{i'b}\right)\ln\left(1 - y_{L}^{a} - \sum_{i'=1}^{k_{L}} y_{L}^{i'b}\right) + y_{L}^{a}\ln y_{L}^{a} + \sum_{i'=1}^{k_{L}} y_{L}^{i'b}\ln\frac{y_{L}^{i'b}}{i!}\right]$$

$$(1)$$

where F_I is the part of free energy at a given degree of filling for the *S* and *L* cavities. For a given arrangement $\{y\} = \{y_s^a, y_L^a, y_s^b, y_s^{k,s^b}, y_L^b, \dots, y_L^{k,L^b}\}$ of the guest molecules in the cavities the free energy $F_I(V,T, y_s^a, \dots, y_L^{k,L^b})$ of the crystal can be calculated within the framework of a lattice dynamics approach as

$$F_{1}(V,T, y^{a}s, \dots, y^{k_{L}b}L) = U + F_{vib}, \qquad (2)$$

where U is the potential energy and F_{vib} is the vibrational contribution:

$$F_{vib} = \frac{1}{2} \sum_{j\mathbf{q}} \hbar \omega_j(\mathbf{q}) + k_{\rm B} T \sum_{j\mathbf{q}} \ln \left(1 - \exp(-\hbar \omega_j(\mathbf{q}) k_{\rm B} T) \right), \qquad (3)$$

where $\omega_j(\mathbf{q})$ is the *j*-th frequency of crystal vibration and \mathbf{q} is the wave vector. If the free energy F is known then the equation of state and the Gibbs free energy $\Phi(P, T, \{y\})$ expressed in terms of the chemical potentials of the host and guest molecules can be found.

In order to construct phase diagram of clathrate hydrates in high temperature region, the approach for calculating the chemical potential of water was realized. The *p*-*T* line of equilibrium between the hydrates and the liquid phase can be found from the equality condition of the chemical potentials of the H₂O molecules in the hydrates μ_Q and water μ_{wA_1} :

$$\mu_Q(P,T,\{y\}) = \mu_{wA_p} \tag{4}$$

The chemical potential of water, μ_{wA_q} , in the liquid state was taken from the model proposed earlier and is given by:

$$\mu_{wA_q} = \frac{T}{T_0} g_{w_0 L_{pre}} - \int_{T_0}^T \frac{dT'}{T} h_{wL_{Pure}} + \int_{P_0}^P v_{wL_{Pure}} dP'$$
(5)

where T_0 is the initial temperature and P_0 is the initial pressure. The following constants were also used: the Gibbs energy of formation $g_{w_0L_{pre}}$, the molar enthalpy of water $h_{wL_{pure}}$, and the water volume $v_{wL_{pure}}$, which refers to pure water. Instead of using the empirical value of $g_{w_0L_{pre}}$ we calculated this parameter directly by using the lattice dynamic method. This parameter can be evaluated from the chemical potential of water, μ_{wA_q} , which should be equal to μ_0^{Ih} of hexagonal ice calculated at the ice I_h melting point at standard pressure and temperature.

The validity of this approach was proved by estimating the p-T phase diagrams of the helium hydrates in different ices. The structural transitions between pure ice I_h and ice I_h -based helium hydrate as well as between ice II and ice II-based helium hydrate were found to be in agreement with the available experimental data [1].

In order to evaluate the parameters of weak interactions, a time-dependent densityfunctional formalism and local density (TDLDA) technique entirely in real space have been applied for calculations of van der Waals dispersion coefficients for atoms or molecules within the all-electron mixed-basis approach (TOMBO code). The frequency-dependent polarizabilities and vdW dispersion coefficients for atoms or molecules were calculated using the Casida method, in which TDLDA excitation energies Ω_I and oscillator strengths f_I can be derived from single-electron Kohn-Sham (KS) eigenvalues ε_k and eigenwave functions $\psi_k(\vec{r}')$ [2].

The true excitation energies, Ω_I , which correspond to the poles of the dynamic polarizability, can be obtained by solving the Casida equation:

$$QF_I = \Omega_I^2 F_I, \tag{6}$$

where matrices Q are given as:

$$Q_{ij,kl} = \delta_{i,k} \delta_{j,l} \omega_{kl}^2 + 2\sqrt{\lambda_{ij} \omega_{ij}} K_{ij,kl} \sqrt{\lambda_{kl} \omega_{kl}} , \qquad (7)$$

where $\lambda_{lk} = n_{\tau} - n_k$ is the difference between the occupation numbers, $\omega_{lk} = \varepsilon_k - \varepsilon_l$ is the difference between the eigenvalues of the l^{th} and k^{th} single-particle states, and $K_{ij,kl}$ is the adiabatic coupling matrix. The analytic expression for the adiabatic coupling matrix is written in the form:

$$K_{ij,kl} = \iint \psi_i^*(\vec{r})\psi_j(\vec{r}) \left(\frac{1}{\left|\vec{r} - \vec{r}'\right|} + \frac{\delta^2 E_{xc}[\rho]}{\delta\rho(\vec{r})\delta\rho(\vec{r}')} \right) \psi_k(\vec{r}')\psi_l^*(\vec{r}')d\vec{r}d\vec{r}' \quad (8)$$

The oscillator strengths, f_I , are given as

$$f_{I} = \frac{2}{3} \sum_{\beta=1}^{3} \left| B_{\beta}^{T} R^{1/2} F_{I} \right|^{2},$$
(9)

where F_I are the eigenvectors of the Casida equation (6) shown as

$$(B_{\beta})_{ij} = \int \Psi_i^*(\vec{r}) r_{\beta} \Psi_j(\vec{r}) d\vec{r} , \qquad (10)$$

where $\{r_1, r_2, r_3\} = \{x, y, z\}$. The single-electron KS eigenvalues, ε_k , and eigenwave functions $\psi_k(\vec{r}')$ obtained within the all-electron mixed-basis approach (TOMBO) were used to find the elements of the coupling matrix. For molecules, the Kohn-Sham wave functions are

$$\psi_{i}(\vec{r}) = \frac{1}{\sqrt{N}} \left[\sum_{G} c_{G}^{i} \frac{e^{iGr}}{\sqrt{\Omega_{0}}} + \sum_{jnlm} c_{jnlm}^{i} \Phi_{jnlm}(\vec{r} - \vec{R}_{j}) \right],$$
(11)

where *i* is the index of a Kohn-Sham eigenstate, \vec{r} is a vector in direct space and $\vec{G} = l_1\vec{b}_1 + l_2\vec{b}_2 + l_3\vec{b}_3$ (l_i integers and $\vec{b}_1 = \frac{1}{L_0}(1,0,0)$, $\vec{b}_2 = \frac{1}{L_0}(0,1,0)$, $\vec{b}_3 = \frac{1}{L_0}(0,0,1)$ basis vectors of reciprocal space for crystal with cubic symmetry) is a vector in reciprocal space ($\Omega_0 = L_0^3$ is the volume of the unit cell, N – number of the unit cells, c_G^i , c_{jnlm}^i are the

expansion coefficients, j is an index designating atom in the molecule containing of J atoms (j=1,2,..J) and Φ denotes atomic orbital:

$$\Phi_{jnlm}(\vec{r}) = R_{jnl}(|\vec{r}|)Y_l^m(\theta,\varphi), \qquad (12)$$

where *Y* refers to a spherical harmonic.

The exact expression (Casimir-Polder integral) for the leading isotropic C_6 (*A*,*B*) term describing the vdW interaction between two atoms or molecules A and B.

$$C_6(A,B) = \frac{3}{\pi} \int_0^\infty \alpha_A(i\omega) \alpha_B(i\omega) d\omega , \qquad (13)$$

 $\alpha_{A/B}(i\omega)$ are the frequency-dependent polarizabilities of A and B evaluated at imaginary frequencies. The average dynamic polarizability of atoms or molecule is

$$\alpha(\omega) = \left\langle \alpha(\omega) \right\rangle = tr(\alpha_{\beta\gamma}(\omega)/3 = \sum_{I} f_{I}/(\Omega_{I}^{2} - \omega^{2}).$$
(14)

where Ω_I is true excitation energy and f_I is the oscillator strength determined from the Casida equations (6) and (9). Substituting $\alpha(\omega)$ into $C_6(A, B)$ and performing integration over ω , we obtain the coefficient $C_6(A, B)$ in the form:

$$C_{6}(A,B) = \frac{3}{\pi} \sum_{I_{A}} f_{I_{a}} \sum_{I_{B}} f_{I_{B}} \int_{0}^{\infty} \frac{d\omega}{(\Omega_{I_{A}}^{2} + \omega^{2})(\Omega_{I_{B}}^{2} + \omega^{2})} = \frac{3}{2} \sum_{I_{A}} f_{I_{a}} \sum_{I_{B}} f_{I_{a}} \sum_{I_{B}} f_{I_{B}} \frac{1}{\Omega_{I_{A}} \Omega_{I_{B}} (\Omega_{I_{A}} + \Omega_{I_{B}})}$$
(15)

(b) THEMODYNAMICS PROPERTIES OF GREENHOUSE GASES HYDRATES

The possibility to replace methane by carbon dioxide in clathrate hydrates has been investigated. First, in order to verify the validity of the calculated empirical potential for CO_2 and CH_4 , the thermal expansion of the CO_2 and CH_4 hydrates with cubic structure I (sI) has been estimated and shown in Figure 1.



Figure 1. Dependence of the thermal expansion of lattice for CO_2 (a) and CH_4 (b) hydrates using previous empirical parameters (CO_2 : N. M. Laurendeau, Statistical Thermodynamics: Fundamentals and Applications, Cambridge University Press, 2005; CH_4 : J.H. Van-der-Waals, J.C. Platteuw, Adv. Chem. Phys., **2** (1959) 1.) and parameters estimated from TOMBO results. The experimental data for CO_2 hydrate (x) is taken from E. D. Sloan, C. A. Koh, Clathrate Hydrates of Natural Gases, 3ed., Taylor & Francis Group, Boca Raton, 2008; and for CH_4 hydrate is taken from (x) A. G. Ogienko *et al.*, J. Phys. Chem. B, **110** (2006) 2840; and from (+) S. Takeya *et al.*, Chemical Engineering Science **61** (2006) 2670.

The calculated curves of the thermal expansion obtained using TOMBO program are practically similar to the curves calculated using the previous empirical parameters and agree with the available experimental data. Moreover, in the case of the CO_2 hydrates, better agreement with experiment has been achieved in low temperature region by using the

TOMBO parameters. The small discrepancy can be explained that in calculation only complete guest occupation in single form of all cavities has been considered. This ideal case may not be true for real situations in which some of cavities remain empty.

The calculated curves for the phase transformation between hexagonal ice and CO_2 and CH_4 hydrates as well as water in the liquid phase and CH_4 and CO_2 hydrate agree well with the available experimental data as shown in Figure 2. The calculated results verify the validity of the present approach in which the proposed formula for calculating the chemical potential of water in liquid state was used.



Figure 2. The *p*-*T* – diagram of phase equilibria "hydrate – gas – ice (water)" for pure carbon dioxide (a) and methane (b) hydrates. The results of calculations are shown by filled squares, experimental data [E. D. Sloan, C. A. Koh, Clathrate Hydrates of Natural Gases, 3ed., Taylor & Francis Group, Boca Raton, 2008] by open triangles ∇ and \circ circles.

It is known that both carbon dioxide and methane clathrate hydrate first stabilizes in the form of the sI structure and the structural transformation to the hydrate with cubic structure II (sII) may occur at higher pressure. Moreover, the CO₂ hydrate is more thermodynamically stable than CH₄ hydrates and the present calculation results are also shown the same tendency (see Figure 2). It is experimentally known that the increasing the formation pressure of carbon dioxide hydrate can be achieved in binary hydrates by adding the second guest component, such as nitrogen molecules. Thus, the thermodynamic stability of binary N₂+CO₂ sI hydrate has been investigated at various nitrogen concentrations in the gas phase. The formation pressure of the binary N₂+CO₂ sI hydrate depend on nitrogen concentration in the gas phase and with increasing concentration were found to be higher in comparison with the pressure of pure carbon dioxide hydrate formation for the sI structure as shown in Figures 3a.



Figure 3. Phase diagram of CO_2 , CO_2 - N_2 and CH_4 hydrates at different N_2 concentration (a) and at 70%-80% N_2 concentration (b) in gas phase.

It has been found that at high nitrogen concentration (70-80%) in the case of CO_2/N_2 gas mixture carbon dioxide can replace methane in the hydrate phase at temperatures and pressures typical for the permafrost regions or below the seafloor since the phase stability of CO_2/N_2 hydrate is similar to pure CH₄ hydrate (see Figure 3b). Figure 4a shows the pressure dependence of the small and large cavities degree of filling at T=273 K and 80% nitrogen concentrations in the gas phase. The filling of the small cages by nitrogen molecules increases with increasing pressure. The continuous growth of a number of small cavities occupied by methane is observed and reaches a value of 50% at a pressure of 200 atm as shown in Figure 4a. At this nitrogen concentration the large cavities are mainly filled by carbon dioxide molecules and reach about 80% at formation pressure (30 atm) for binary N₂+CO₂ hydrates (see Figure 4a). The small occupation of large cavities by nitrogen molecules can be explained by weaker guest-host interactions due to relative sizes of nitrogen and the large cavity in the sI structure.

Figure 4b shows the carbon dioxide storage capacity of the mixed N_2+CO_2 sI hydrate at various nitrogen concentrations at 273 K. It has been found that the amount of stored carbon dioxide depends on the nitrogen concentration in the gas phase as well as the thermodynamic conditions of hydrate formation. Thus, at concentrations 80% the mass percentage of carbon dioxide in the $CO_2-N_2-H_2O$ system is 2/3 of amount for pure CO_2 hydrate at T=273 K and p=30 atm. The amount of carbon dioxide storage will not significantly decrease even at high pressures as can be seen in Figure 4b. Thus the 20% - 80% gas ratio of CO_2/N_2 gas mixture seems to be promising from the practical point of view.



Figure 4. (a) Degree of filling of the small and large cavities of the N_2+CO_2 sI and (b) sII hydrate at a nitrogen concentration of 80 % in the gas phase at T=273K; (b) Carbon dioxide storage capacity of the N_2+CO_4 hydrate as a function of pressure for various nitrogen concentrations at T=273 K.

The phase equilibrium in the "hydrate – gas mixture – ice (water)" ternary system with the methane and carbon dioxide gas mixture has been also studied at different gas phase compositions, pressures and temperatures. The calculations of hydrate formation conditions have been performed in wide pressure and temperature ranges. The formation pressures of the sI CO_2+CH_4 hydrate also depend on methane concentration in the gas phase and with increasing concentration were found to be higher in comparison with the pressure of pure CO_2

hydrate formation for the sI structure. Moreover, the formation pressure of this binary hydrate was appeared to be a linear function of the guest content in the hydrate phase. Figure 5 shows that the amount of carbon dioxide in hydrate form exceeded content of CO_2 in the gas mixture. The present results have shown that even at 25% carbon dioxide concentration in the gas phase the hydrate can accumulate 50% of the hydrate cavities (see Figure 5a) at low temperatures. However, at temperatures exceeding the melting temperature of ice, the carbon dioxide occupies more than 50% of the cavities only when its proportion in the gas phase reach 40% (see Figure 5b).



Figure 5. Guest molecules fractions in binary CO_2+CH_4 hydrate as a function of various guest concentrations at temperatures (a) T=273 K and (b) T = 288 K.

The CO₂ molecules occupy 78 % of large cages and CH₄ about 21%, while in small cages the occupancies are 52 % and 27 %, respectively. In the case of the large cage, the ratio of occupancies by CO₂ and CH₄ is 3.7:1 and in the case of the small cage the ratio is 1.9:1. The obtained results agree with the available experimental data. It can be indicated that the replacement of methane by carbon dioxide in hydrate is preferable at the low temperatures. The solubility of carbon dioxide in water is relatively high and it can reach the value of 1 mol/L under the conditions of hydrate formation (12.4 atm and at T = 273 K). At the same conditions, the solubility of methane is significantly lower and does not exceed 3 • 10⁻² mol/L. It can be assumed that even at low concentrations of carbon dioxide, the amount of CO₂ may exceeded in the reaction medium and it can facilitate the replacement of methane molecules from hydrate phase.

Figure 6 shows the phase equilibrium in the "hydrate – gas mixture – ice (water)" ternary system with the methane and carbon dioxide gas mixture with different gas phase compositions and pressures at selected temperatures. The formation pressure of binary hydrate increases with increasing the methane concentration in the gas phase and at higher temperature. For temperature T=277 K that corresponds to water temperature near the bottom of oceans, the methane hydrates can form and exist in thermodynamic equilibrium with water and gas at the pressure 42 atm that corresponds to the depth 410 meters (depths of continental slope) while the



Figure 6. The calculated curves of "guest gas $-CO_2+CH_4$ hydrate - ice I_h (water)" equilibrium at various methane concentrations in the gas phase.

formation pressure of the pure carbon dioxide hydrate is lower (12 atm). At lower temperatures (T=273 K and T=258 K) the reduction of the formation pressure of binary hydrate is more smoothly by adding carbon dioxide in gas mixture.

(c) SELF-PRESERVATION EFFECT IN ICE/GAS HYDRATES SYSTEMS

The one of the important features of clathrate hydrates is self-preservation effect. This feature is associated with a drastic reduction of hydrate dissociation speed at temperatures higher than the equilibrium temperature and below the ice melting point (T=273 K) at atmospheric pressure. As example, in the case of methane hydrate and at temperature range from 240 K to 273 K the dissociation rate is several orders in magnitude lower than expected value for these conditions and methane hydrate can be stored even for a days.

In the macroscopic model hydrate phase having volume V_{hyd} was located inside ice phase having volume V ice at temperature T_0 and pressure P_0 . For calculation of pressure of hydrate phase immersed in the ice I_h phase the approximation of the coordinated compression was used, i.e. relative change of volume was considered identical to ice and hydrate. Pressure in hydrate at heating ice from T_0 up to some temperature T ice at pressure P_0 was taken from a condition of equality of relative change of equilibrium volume of ice and hydrate:

$$\frac{V_{hyd}(T,P)}{V_{hyd}(T_0,P_0)} = \frac{V_{ice}(T,P_0)}{V_{ice}(T_0,P_0)}.$$
(16)

For the calculation of the thermal expansion for different hydrates as well as for different ices the statistical thermodynamics model with some modifications describing host lattice relaxation, guest-guest interactions and the quantum nature of guest behavior in clathrate hydrates was applied. Figure 7a shows the relative thermal expansion, i.e. ratio of volume at temperature T and pressure P₀ to volume at T₀, P₀, of different structures. As reference points the temperature and pressure were selected as T₀ = 140 K and P₀ = 0.1 MPa, respectively. The ice I_h and empty sI and sII hydrate lattices have similar thermal expansion coefficient. The CH₄ and H₂ hydrates have considerable larger thermal expansion coefficient. According our assumption the relative thermal expansion of ice I_h phase and immersed in ice hydrate phase should be equal. Therefore, such calculated difference of thermal expansion should lead to self-preservation effect because of appearing additional pressure.



Figure 7. Dependence of the relative thermal expansion (V/V_0) on temperature for (a) empty sI and sII hydrates, ice I_h, sI CH₄ hydrate and sII H₂ hydrate; (b) Ice I_h and sII hydrogen hydrate.



Figure 8. Dependence of the relative volume of H_2 hydrate and empty sII hydrate on pressure at T= 250 K.

The appearing of additional pressure effect is presented in Figure 7b. This shows the relative thermal expansion of ice I_h and hydrogen hydrate expansion at $P_0 = 10$ MPa, 20 MPa, 50 MPa, and 100 MPa. Points of thermal expansion crossing determine the equal relative temperature of thermal expansion. In other words with increasing temperature the additional pressure on immersed hydrate is increase too. Therefore hydrogen hydrate can be preserved by the covering ice shell. Dependence of the relative volume of a hydrogen hydrate in comparison with empty sII hydrate on pressure at fixed temperature (T = 250 K) presented in Figure 8. Unlike empty hydrate lattice, hydrogen hydrate relative volume dependence is

complicated. Such behavior caused by the presence of the guest molecules. From thermodynamic point of view, with pressure increasing it is more favorably to capture hydrogen into the cavity that causes a lattice parameter expansion. After structure saturation by gas molecules the isothermal compressibility starts to govern this process. Overall format of this dependence does not depend on temperature.

In order to describe the interface between methane hydrate – ice I_h systems the structure in which methane hydrate sphere surrounded by ice I_h was optimized using the MD simulations. Methane hydrate was modeled as a supercell containing 63 molecules of methane and 6224 water molecules. Radius of the hydrate sphere on the average was about 1.25 nm. The periodic boundary conditions were applied that corresponds to an infinite ice matrix with hydrate clusters included as shown in Figure 9a.



Figure 9. (a) Initial structure of methane sI hydrate sphere immersed in ice I_h ; (b) Surface layer of optimized ice/gas hydrate system.

The resulting surface layer was shown in Figure 9b. This layer was selected in such a way that the presented water molecules are belonged to both hydrate and ice and this layer contained 479 molecules. After MD optimization, lengths of the hydrogen bonds in this layer

become equal to 1.7 - 1.8 Å. Thus, the network of hydrogen bonds tends to self-reconstruction, even at rough mechanical destruction.

(d) THEORETICAL STUDY OF GAS SEPARATION USING MOF STRUCTURES

A new soft nanoporous metal-organic material (MOF) that selectively adsorbs CO with adaptable pores has been studied using first-principles calculations in collaboration with experimentalists [3]. Eleven different CO/N_2 gas compositions were considered for gas adsorption in the CO-coordinated MOF structure. Despite the small values of interactions indicating physical adsorption between MOF framework and adsorbed non-coordinated gas molecules, the results of calculations showed a remarkable distinction in adsorption properties of CO-coordinated MOF towards CO and N₂ separation. The presence of CO molecules in the center of channel *S* allows for the thermodynamic favorable adsorption of any gas compositions in channel *L* and the value of adsorption energy grows by increasing CO concentration in gas mixture. The difference between N₂ and CO adsorptions in PCP can be analyzed from the analysis of the charge density isosurface related to host-guest interaction.



Figure 10. Charge density distribution for CO-coordinated MOF with (a) CO and (b) N_2 in small channels. Red represents an excess and blue a depletion of electrons.

For the adsorption of the CO molecule in the small channel it was found that the excess charge localized on adsorbed molecules, and electron depletion observed on CO-coordinated MOF framework indicated the favorable attraction between the guest molecule and the host structure (Figure 10a). As shown in Figure 10b, electron depletion localized on both N₂ and CO-coordinated MOF. This shows the repulsion between nitrogen molecules and the MOF framework. This is in agreement with the energy calculations that showed a large difference in absorption energies between these two cases. Thus, the high selectivity has been achieved by the synergetic effect of the local interaction between CO and accessible Cu^{2+} metal sites and a global transformation of the framework. This transformable crystalline material realized the separation of CO from a mixture with nitrogen, a gas that is the most competitive to CO.

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