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Metal–Organic Frameworks

Open Metal Sites within Isostructural Metal–Organic Frameworks for Differential Recognition of Acetylene and Extraordinarily High Acetylene Storage Capacity at Room Temperature**

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Open metal sites have played very important roles in synthetic assemblies and biological systems because of their specific recognition of small molecules and thus for their highly selective molecular transformations, transport, and storage.[1–4] Understanding the molecular recognition between the open metal sites and the substrate molecules at the molecular level will not only facilitate the discoveries of new catalysts, sensing, and storage materials, but will also provide a deep insight in the functions of the open metal sites in the biological systems and thus stimulate studies of modeling compounds to mimic biological functions. However, the highly reactive nature of such open metal sites has mainly limited our capacities to elucidate the metal–substrate recognition processes fundamentally and systematically within molecular assemblies. This situation changed recently with the emergence of porous metal–organic frameworks (MOFs) with sustained open metal sites, which provided the promise of elucidating the bonding nature of the open metal sites with small gas molecules at the molecular level.[5–7]

We realized that open Cu^{2+} sites within a porous HKUST-1 material have strong interactions with acetylene molecules (the adsorption enthalpy is $30.4\,kJ\,mol^{-1}$ at a coverage of $1\,mmol\,g^{-1}$) and thus contribute significantly to the high acetylene storage with a volumetric storage capacity of $177\,cm^3\,cm^{-3}$ at 295 K and 1 atm.[8] Because acetylene is a very important raw material for various industrial chemicals, fundamental studies on the metal site–acetylene interactions and their bonding nature will promote the discovery of new chemical transformations for the efficient usage of acetylene and new porous materials for high acetylene storage capacity.[9] The highly explosive nature of acetylene has limited the possible storage materials to fulfill high acetylene storage capacities at room temperature and at pressures of under 0.2 MPa (the compression limit for the safe storage of acetylene). It is thus particularly important to target systems having very strong interactions with acetylene to secure high acetylene storage capacities.[10–21] Herein, we report the differential interactions of the open metal sites with acetylene molecules within the isostructural CPO-27M or MOF-74 analogues $[M_2(DHTP)]$ ($M = Co^{2+}$, Mn^{2+}, Mg^{2+}, and Zn^{2+}; DHTP = 2,5-dihydroxyterephthalate), which have been exclusively established by the coordinated temperature-dependent adsorption isotherms, neutron diffraction studies, and first-principles calculation, featuring open Co^{2+} sites as the strongest sites for their interactions with acetylene molecules (adsorption enthalpy of $50.1\,kJ\,mol^{-1}$ at the low coverage) and $[Co_2(DHTP)]$ as the highest volumetric acetylene storage material ever reported with the capacity of $230\,cm^3\,cm^{-3}$ (standard temperature and pressure (STP): 295 K and 1 atm).

The temperature-dependent acetylene adsorption isotherms of these isostructural MOFs were examined to evaluate their adsorption enthalpies and thus their different interactions with acetylene molecules. The examined MOFs show repeatable adsorption isotherms.[22] The coverage-dependent adsorption enthalpies of the MOFs to acetylene were calculated based on a virial method, a well established and reliable methodology from fits of their adsorption isotherms at 273 and 295 K.[23] As shown in Figure 1, $[Co_2(DHTP)]$ exhibits much higher adsorption enthalpy of C_2H_2 ($50.1 \pm 0.9\,kJ\,mol^{-1}$) than does $[Mn_2(DHTP)]$ ($39.0 \pm 0.8\,kJ\,mol^{-1}$), $[Mg_2(DHTP)]$ ($34.0 \pm 0.8\,kJ\,mol^{-1}$), or $[Zn_2(DHTP)]$ ($24.0 \pm 0.7\,kJ\,mol^{-1}$) at low coverage. Such high adsorption enthalpies in $[Co_2(DHTP)]$ might enforce its full loading of one acetylene molecule per open Co^{2+} site even at room temperature and 1 atm, conditions in which $[Co_2(DHTP)]$ exhibits the highest volumetric acetylene storage capacity ever

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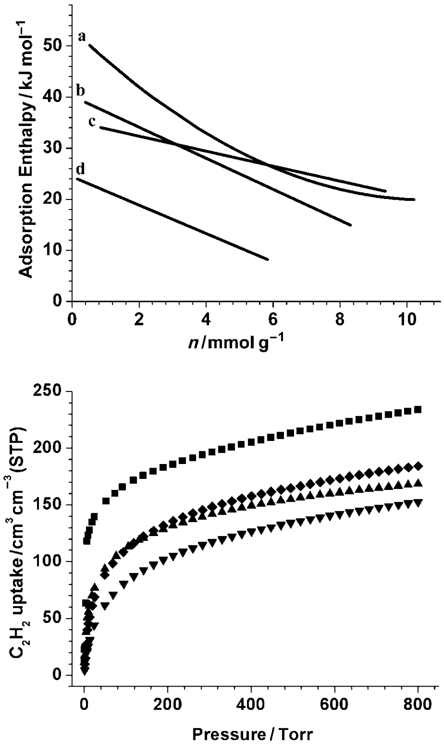

Figure 1. Top: Coverage dependencies of the adsorption enthalpies for C_2H_2 in MOFs calculated from fits of their 273 and 295 K isotherms a) [Co_2(DHTP]; b) [Mn_2(DHTP)]; c) [Mg_2(DHTP)]; d) [Zn_2(DHTP)]. Bottom: Acetylene adsorption isotherms of microporous MOFs at 295 K: [Co_2(DHTP)] (■); [Mn_2(DHTP)] (◆); [Mg_2(DHTP)] (▲); [Zn_2(DHTP)] (▼).

reported with a capacity of 230 $cm^3 cm^{-3}$ (STP) at 295 K and 1 atm, which is significantly higher than the previously reported highest value of 177 $cm^3 cm^{-3}$ (STP) in HKUST-1. Apparently, the stronger the interactions of open metal sites with acetylene, the higher acetylene uptake the MOF will have within this series of isostructural MOFs; accordingly, the acetylene storage capacities decrease in the order [Co_2(DHTP)] > [Mn_2(DHTP)] > [Mg_2(DHTP)] > [Zn_2(DHTP)]. A detailed comparison of several high acetylene storage capacity materials is given in Table 1.

The very strong interactions of open Co^{2+} sites with acetylene molecules certainly play very important roles for the extraordinarily high acetylene storage capacity of [Co_2(DHTP)]. Another crucial factor for [Co_2(DHTP)] to have very high acetylene storage capacity is the high open cobalt site density of 7.49 mmol Co^{2+} cm^{-3} in [Co_2(DHTP)], which is more than one and an half times higher than that of HKUST-1 (4.36 mmol Cu^{2+} cm^{-3}). Assuming that each open Co^{2+} site can bind one acetylene molecule, the open Co^{2+} sites can contribute to 168 $cm^3 cm^{-3}$ (STP) of total 230 $cm^3 cm^{-3}$ (STP) volumetric acetylene storage capacity because of the high open Co^{2+} sites density (7.49 mmol Co^{2+} cm^{-3}) in [Co_2(DHTP)] at 295 K and 1 atm. The remaining uptake of 62 $cm^3 cm^{-3}$ (STP) might be attributed from the pore space channel of 13.6 Å within [Co_2(DHTP)], which accounts for only 27 % of the total volumetric acetylene storage capacity, highlighting the crucial role of the high open Co^{2+} site density for the extraordinarily high volumetric acetylene storage capacity in [Co_2(DHTP)]. The potential contribution from the pore space within HKUST-1 for the volumetric acetylene storage capacity is expected to be more than 79 $cm^3 cm^{-3}$ (STP) (calculated from the total volumetric acetylene storage capacity (177 $cm^3 cm^{-3}$ (STP)) minus the volumetric acetylene storage capacity attributed from open Cu^{2+} sites (98 $cm^3 cm^{-3}$ (STP))), which is significantly higher than that in [Co_2(DHTP)] (62 $cm^3 cm^{-3}$ (STP)). The significant contribution from the high density open Co^{2+} sites for acetylene storage capacity of up to 168 $cm^3 cm^{-3}$ (STP) has featured the [Co_2(DHTP)] as the best volumetric acetylene storage material (230 $cm^3 cm^{-3}$ (STP)) with the highest safe acetylene storage density of adsorbed acetylene in bulk material (0.27 gcm^{-3} at 295 K and 1 atm, which is equivalent to the acetylene density at 25.1 MPa) ever reported.

Table 1: Acetylene uptake in the examined metal–organic frameworks at 295 K and 1 atm.

MOF	C_2H_2 uptake		Density of adsorbed C_2H_2[a] [gcm^{-3}]	P[b] [MPa]
	[$cm^3 cm^{-3}$ (STP)]	wt%		
[Co_2(DHTP)]	230	22.9	0.27	25.1
[Mn_2(DHTP)]	182	19.5	0.21	19.8
[Mg_2(DHTP)]	167	21.4	0.19	18.2
[Zn_2(DHTP)]	150	14.2	0.17	16.4
HKUST-1	177	23.4	0.21	19.3

[a] Calculated density of adsorbed acetylene in bulk material. [b] Pressure of acetylene at 295 K corresponding to the calculated density of adsorbed acetylene in bulk material.

The amount of acetylene gas adsorbed at room temperature reaches to 230 $cm^3 cm^{-3}$ (STP) at 295 K and 1 atm in [Co_2(DHTP)], which corresponds to 1.40 C_2H_2 molecules per Co^{2+} site. To verify the preferential adsorption sites experimentally and thus confirm our speculation that the high open Co^{2+} site density in [Co_2(DHTP)] is the determining role for the extraordinarily high acetylene storage capacity, we measured the 0.54 C_2D_2 per Co loaded [Co_2(DHTP)] with the high-resolution neutron powder diffractometer BT1 at the National Institute of Standards and Technology Center for Neutron Research (NCNR). The data were analyzed using the program EXPGUI with Rietveld refinement.

From the Rietveld refinement results ($\chi^2 = 0.9280$), acetylene is only adsorbed at one site at 0.54 C_2D_2 per Co loading, that is, all acetylene gas molecules are adsorbed at open Co^{2+} sites. The experimental pattern and the calculated curves using the Rietveld method are shown in Figure S2 a. The refinement results indicate that 0.54 C_2D_2 molecules per Co site are loaded inside the sample, which is in good agreement with the amount of gas loaded into the material. The distance between a C_2D_2 molecule and the closest Co atom is about 2.65 Å, which is comparable to that observed between a C_2D_2 molecule and the closest Cu atom in HKUST-1. Figure S2 b shows the Fourier difference map of acetylene adsorbed in [Co_2(DHTP)]. The pink blobs are the locations indicating additional new neutron scattering length density after introduction of acetylene molecules into the sample. High-resolution neutron powder diffraction studies on the

$0.54\,C_2D_2$ per Co loaded [Co_2(DHTP)] sample exclusively confirm that the open Co^{2+} sites are the first preferential acetylene storage sites that make the major contribution to the high volumetric acetylene storage capacity.

Unlike the well-separated adsorbed C_2D_2 molecules in C_2D_2-loaded HKUST-1, the C_2D_2 molecules aligned along the *c* axis as pseudo-one-dimensional arrays with intermolecular C_2D_2 distance of about 4 Å in C_2D_2-loaded [Co_2(DHTP)] (Figure 2). The high density of adsorbed acetylene molecules is also clearly shown in that each 1D pore channel of 13.6 Å in diameter can encapsulate six such pseudo-1D C_2D_2 arrays (one C_2D_2 molecule per open Co^{2+} site).

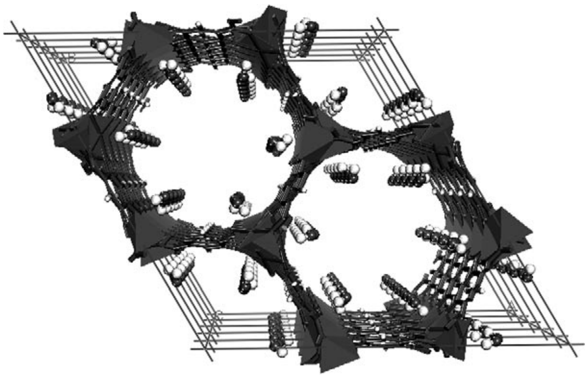

Figure 2. Crystal structure of [Co_2(DHTP)] with loading of $0.54\,C_2D_2$ per Co viewed along the *c* axis, exhibiting the high density of adsorbed acetylene molecules in pseudo-one-dimensional arrays.

To understand the interaction of C_2H_2 with different open metal sites within the four [M_2(DHTP)] frameworks ($M = Co^{2+}, Mn^{2+}, Mg^{2+}$, and Zn^{2+}), we performed first-principles total-energy calculations. The static binding energies derived from density-functional theory calculations are summarized in Table 2, along with the C≡C bond lengths and C≡C−H bond angles of the adsorbed C_2H_2 molecules. As expected, the local-density approximation (LDA) overestimates the binding strength, whereas the generalized gradient approximation (GGA) underestimates it. Nevertheless, the relative binding strengths of various metals derived from the two approaches are consistent. Among the various metals investigated, Co^{2+} stands out for its highest affinity to C_2H_2.

Table 2: Data derived from our calculations, including the static binding energies of C_2H_2 on the open metal sites in the MOFs, the C≡C bond lengths, and C≡C−H bond angles of the adsorbed C_2H_2 molecules.

	E_B, LDA/GGA [kJ mol^{-1}]	C≡C−H bond angle, LDA/GGA [°]	C≡C bond length LDA/GGA [Å]
free C_2H_2	/	180.0/180.0	1.200/1.208
C_2H_2 on open Co^{2+} ([Co_2(DHTP)])	71.4/18.5	167.5/166.7	1.228/1.232
C_2H_2 on open Mn^{2+} ([Mn_2(DHTP)])	55.0/17.3	177.2/176.9	1.208/1.213
C_2H_2 on open Mg^{2+} ([Mg_2(DHTP)])	53.0/16.9	179.2/178.8	1.204/1.210
C_2H_2 on open Zn^{2+} ([Zn_2(DHTP)])	51.5/16.5	179.3/179.0	1.206/1.211

The calculated static C_2H_2 binding energies on Co^{2+} are 71.4 kJ mol^{-1} and 18.5 kJ mol^{-1} (corresponding to LDA and GGA results, respectively), which are significantly larger than those found for the Mn, Mg, and Zn analogues. The overall trends of the calculated binding energies agree well with the experimentally derived adsorption enthalpies. The calculated C≡C−H bond angle is approximately 167° (in contrast to the value of 177–179.8° for adsorbed C_2H_2 on other open metals), suggesting a significant polarization of the adsorbed C_2H_2 molecule by the open Co^{2+} site. The C≡C bond lengths also suggest a high degree of bond activation by the Co ion. As we have shown before, the major contribution to the overall binding between C_2H_2 and the open metal ion is the Coulombic interaction between the adsorbed C_2H_2 dipole moment and the open metal charge density.[8] It is thus the strong ability of open Co^{2+} to polarize and distort C_2H_2 molecule that leads to high affinity of C_2H_2 on Co^{2+}.

In summary, a series of isostructural [M_2(DHTP)] MOFs ($M = Co^{2+}, Mn^{2+}, Mg^{2+}$, and Zn^{2+}) with open metal sites were examined for their differential recognition of acetylene molecules and realized as high acetylene storage materials. The open metal sites within this series of isostructural MOFs exhibit differential interactions with acetylene molecules in which Co^{2+} has the strongest interactions with acetylene and a very high adsorption enthalpy of 50.1 kJ mol^{-1} at the low coverage. Such a strong interaction makes [Co_2(DHTP)] the highest volumetric acetylene storage material reported so far, with a capacity of up to 230 cm^{3}cm^{-3} (STP) at 295 K and 1 atm. This high capacity maximizes the safe acetylene storage density of adsorbed acetylene in bulk material (up to 0.27 g cm^{-3}). The strong interaction of open Co^{2+} sites with acetylene was further confirmed by high-resolution neutron powder diffraction studies on acetylene-loaded [Co_2(DHTP)] and by first-principles calculations. The exceptionally high volumetric acetylene storage capacities make such microporous MOFs as very practical acetylene storage media. As acetylene is a very important raw material for various industrial chemicals, consumer products, and oxyacetylene cutting in metal fabrication, the realization of such safe and high-density acetylene storage media will facilitate the safe transportation and wider usage of acetylene in the future.[24,25]

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