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Microporous Magnesium and Manganese Formates for Acetylene Storage and Separation

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Abstract: Acetylene sorption of microporous metal formates $M(HCOO)_2$ ($M = Mg$ and Mn) was investigated. Measurements of acetylene sorption at 196, 275, and 298 K showed a Type I isotherm with quick saturation at low pressures, and 50–75 $cm^3 g^{-1}$ uptake at 1.0 atm. The single-crystal X-ray structure analysis of the acetylene-adsorbed metal formates revealed that acetylene molecules occupy two independent positions in the zigzag channels of the frameworks with a stoichiometry of $M(HCOO)_2 \cdot {}^1\!/_3 C_2H_2$, which is consistent with the gas sorption experiments. No specific interaction except van der Waals interactions between the adsorbed acetylene molecules and the walls of the frameworks was found. Sorption properties of other gases, including CO_2, CH_4, N_2, O_2, and H_2, were also investigated. When the temperature was increased to 298 K, the amount of adsorbed acetylene was still above 60 $cm^3 g^{-1}$ for $Mg(HCOO)_2$ and 50 $cm^3 g^{-1}$ for $Mn(HCOO)_2$, whereas the uptake of other gases decreased substantially. The microporous metal formates may thus be useful not only for the storage of acetylene but also its separation from other gases at room or slightly higher temperatures.

Keywords: acetylene · adsorption · magnesium · manganese · microporous materials

Introduction

Acetylene is a key starting material for the synthesis of various organic compounds, such as 1,4-butanediol, which is widely used in the preparation of polyurethane and polyester plastics. One issue associated with acetylene is its storage. Unlike other gases, acetylene cannot be stored in a steel cylinder under high pressure because it becomes highly explosive when compressed to over 0.2 MPa at room temperature, even in the absence of oxygen. The current method of storing acetylene involves dissolution of the gas in acetone placed in a steel cylinder along with an absorbent to prevent polymerization.[1] Another issue in acetylene production and use is its separation from other gases, which include CO_2, a commonly present impurity in many industrial processes. Zeolites[2] and other materials[3] are known to have a high capacity for acetylene sorption, but they usually show little selectivity over CO_2 as these adsorbates have similar size, shape, and physical properties. Therefore, finding low-cost, efficient materials to store acetylene with high selectivity is important for its production, transportation, and delivery.

Recently, metal–organic porous materials have attracted much attention for gas storage,[4] particularly hydrogen storage.[5] Although metal–organic porous materials with narrow channels may be useful for the storage and separation of acetylene, only one report concerning the use of metal–organic porous materials for this purpose has been published so far. Kitagawa and co-workers recently reported that $[Cu_2(pzdc)_2(pyz)]$ (pzdc = pyrazine-2,3-dicarboxylate, pyz = pyrazine) shows selective adsorption of acetylene over carbon dioxide with a C_2H_2 uptake of 42 $cm^3 g^{-1}$ at saturation.[6] Powder X-ray diffraction studies of acetylene-adsorbed

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$[Cu_2(pzdc)_2(pyz)]$ revealed that the acetylene molecules reside in the straight channels while forming hydrogen bonding with the carboxylate oxygen atoms of the framework walls.

Microporous manganese[7] and magnesium[8] formates are cheap, easily prepared metal–organic porous materials that contain one-dimensional zigzag channels with a pore opening of 4.9 and 4.7 Å, respectively.[9] The channels can include various organic and inorganic molecules such as 1,4-dioxane, tetrahydrofuran (THF), benzene, and I_2.[7,8] We have already demonstrated that microporous manganese formate has permanent porosity and selectively adsorbs gases of small size, such as H_2 and CO_2.[7a] As the metal formates may be useful for acetylene storage and separation, we decided to extend this work to acetylene sorption. Herein we report the acetylene sorption of microporous manganese and magnesium formates and the single-crystal X-ray crystal structures of the acetylene-adsorbed metal formates determined with synchrotron radiation. They show not only a high capacity for acetylene sorption but also remarkable selectivity over CO_2, CH_4, N_2, O_2, and H_2 at room temperature.

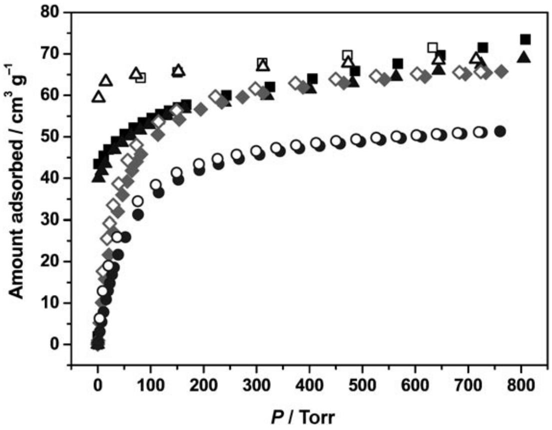

Figure 1. Acetylene sorption isotherm for $M(HCOO)_2$: M = Mg, 196 K (squares), M = Mg, 298 K (diamonds), M = Mn, 196 K (triangles), and M = Mn, 298 K (circles). Solid symbols = adsorption, open symbols = desorption.

Table 1. Acetylene sorption of magnesium and manganese formates.

Material	BET surface area $[m^2 g^{-1}]$	V_p $[cm^3 g^{-1}]$ ($[cm^3 cm^{-3}]$)	C_2H_2 uptake[c] $[cm^3 g^{-1}]$ ($[cm^3 cm^{-3}]$)		
			196 K	275 K	298 K
$Mg(HCOO)_2$	284[a]	0.14	72.5	69.4	65.7
		(0.20)[a]	(101)	(96.5)	(91.3)
$Mn(HCOO)_2$	297[b]	0.13	68.2	57.7	51.2
		(0.21)[b]	(112)	(95.2)	(84.5)

[a] Calculated from the N_2 sorption isotherm recorded at 78 K (see Supporting Information). [b] Calculated from the CO_2 sorption isotherm recorded at 196 K.[7a] [c] V_{ads} (STP) at 1.0 atm.

Results and Discussion

Properties of Acetylene Sorption

Acetylene sorption isotherms of microporous $M(HCOO)_2$ (M = Mg, Mn) measured at 298, 275, and 196 K show a Type I isotherm with quick saturation at low pressures (Figure 1). The C_2H_2 sorption data are given in Table 1. The amounts of adsorbed acetylene at 298 K, 1.0 atm are 65.7 and 51.2 $cm^3 g^{-1}$ for Mg and Mn formate, respectively, which correspond to 0.33 mol per formula unit for both metal formates. The acetylene uptakes at 298 K, 1 atm are substantially higher than those for the metal–organic porous material $[Cu_2(pzdc)_2(pyz)]$ (42 $cm^3 g^{-1}$),[6a] the organic material *p-tert*-butylcalix[4]arene (18 $cm^3 g^{-1}$),[10] carbon molecular sieves (45 $cm^3 g^{-1}$),[3a] and mesoporous silica SBA-15 (36 $cm^3 g^{-1}$)[3b] (Table 2). The storage density of acetylene in the bulk sample is 0.10 and 0.11 $g cm^{-3}$ (at STP) for Mg and Mn formate, respectively, which is equivalent to the density of acetylene at 9.5 and 10.0 MPa, respectively, at room tem-

Abstract in Korean:

마이크로 다공성 마그네슘 포메이트 ($Mg(HCOO)_2$) 와 망간 포메이트 ($Mn(HCOO)_2$) 의 아세틸렌 흡착성질을 연구하였다. 196 K, 275 K, 298 K 에서 측정한 아세틸렌 등온흡착곡선은 낮은 압력에서 빠르게 포화되는 Type I 의 형태를 보이며 1 기압에서 흡착용량은 50–70 $cm^3 g^{-1}$ 이었다. 아세틸렌이 흡착된 금속 포메이트의 결정구조를 단결정 X-선 회절법으로 규명한 결과 $M(HCOO)_2 \cdot ⅓C_2H_2$ 의 조성을 갖고 있으며 이는 기체흡착 실험 결과와 잘 일치한다. 아세틸렌은 다공성 물질의 꾸불꾸불한 채널 속에 2 개의 서로 다른 위치를 차지하고 있다는 것을 알 수 있었다. 흡착된 아세틸렌 분자와 다공성 물질의 벽 사이에는 반데르발스 인력을 제외하고는 특정한 인력이 없었다. 아세틸렌 외에 CO_2, CH_4, N_2, O_2, H_2 와 같은 기체의 흡착성질도 연구하였다. 온도가 298 K 까지 증가하면 마그네슘 포메이트와 망간 포메이트에 흡착된 아세틸렌의 양은 여전히 각각 60 $cm^3 g^{-1}$ 와 50 $cm^3 g^{-1}$ 인 반면 다른 기체의 흡착양은 현저히 감소한다. 그러므로 이 마이크로 다공성 금속 포메이트는 아세틸렌의 저장뿐만 아니라, 상온 또는 그 이상의 온도에서 아세틸렌을 다른 기체로부터 분리하는데 유용하게 사용될 수 있을 것이다.

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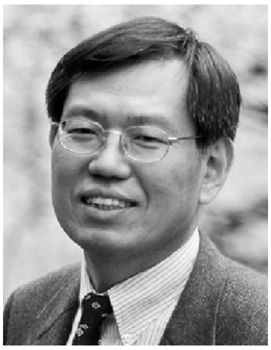

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"I believe that Chemistry—An Asian Journal *will become one of the major forums for chemists of the world in the 21st century, the century of Asia."*

Table 2. Comparison of acetylene uptake in metal–organic or organic porous materials.

Material	C_2H_2 uptake[a] [$cm^3 g^{-1}$] ([$cm^3 cm^{-3}$])	C_2H_2 density[b] (in V_p[c]) [$g cm^{-3}$]	P[d] [MPa]	Reference
$Mg(HCOO)_2$	66 (91)	0.10 (0.55)	9.5	this work
$Mn(HCOO)_2$	51 (85)	0.11 (0.46)	10	this work
$[Cu_2(pzdc)_2(pyz)]$	42 (74)	0.09 (0.32)	8.6	[6a]
p-tert-butyl-calix[4]arene	18 (19)	0.02 (0.18)	2.0	[10]

[a] V_{ads} (STP) at 1.0 atm, 298 K. [b] Calculated density of adsorbed C_2H_2 at STP in bulk material. [c] Calculated density of adsorbed C_2H_2 at STP in pore volume V_p. [d] Pressure of C_2H_2 at 298 K corresponding to the calculated density of adsorbed C_2H_2 in bulk material.

perature. These values are almost 50 times the compression limit for the safe storage of acetylene (0.2 MPa). The slightly higher storage density of acetylene in Mn formate than in Mg formate is due to the higher bulk density of Mn formate.

The uptake of acetylene increases with decreasing temperature for both metal formates: the amounts of adsorbed acetylene at 196 K, 1.0 atm are 72.7 and 68.2 $cm^3 g^{-1}$, or 0.37 and 0.43 mol per formula unit for Mg and Mn formate, respectively. Interestingly, the acetylene adsorption–desorption isotherms at 196 K for both metal formates show large hysteresis at low pressures in contrast to those at 275 and 298 K. Upon depressurization, most of the acetylene sorbed at 1.0 atm by the metal formates is still retained even at 20 Torr, which may be due to the slow desorption kinetics of acetylene at low temperatures. Undoubtedly, the small window of the pore is responsible for the impeded desorption of acetylene.[11] This behavior suggests that acetylene may be loaded at higher pressures and stored at low pressures without significant loss in the metal–organic porous materials.[11]

The enthalpy of adsorption of acetylene for the metal formates was estimated from the adsorption isotherms measured at 275 and 298 K by using the Clausius–Clapeyron equation. The enthalpy of adsorption at 0.2 C_2H_2 molecules adsorbed per unit pore was approximately 38.5 $kJ mol^{-1}$ for both metal formates, which is somewhat smaller than that for $[Cu_2(pzdc)_2(pyz)]$ (42.5 $kJ mol^{-1}$).[6a] The higher enthalpy of acetylene adsorption for $[Cu_2(pzdc)_2(pyz)]$ is presumably due to hydrogen bonding between the acidic H atoms of C_2H_2 and the carboxylate oxygen atoms of the framework walls. The enthalpy of adsorption of acetylene for both metal formates decreases as the amount of adsorbed acetylene increases; however, Mg formate shows a more-rapid decrease than Mn formate.

X-ray Crystal-Structure Analysis

To understand the nature of the interaction between C_2H_2 and the framework wall, the structures of acetylene-adsorbed $M(HCOO)_2$ (M = Mg and Mn) were investigated by using single-crystal X-ray crystallography. Single crystals of the metal formates were prepared by solvothermal reaction of magnesium perchlorate or manganese chloride with formic acid in a mixture of *N*,*N*-diethylformamide (DEF) and THF as solvent. The resulting crystals of $M(HCOO)_2\cdot{}^1/_3THF$ (M = Mg, Mn) were heated under dynamic vacuum to remove the guest THF molecules. The guest-free $M(HCOO)_2$ crystals were placed in thick-walled glass capillaries, which were then evacuated, filled with acetylene gas, and sealed while immersed in a liquid-nitrogen bath.

X-ray diffraction data of acetylene-adsorbed Mg formate (**1**) and Mn formate (**2**) were collected at 90 K with synchrotron radiation. The crystal-structure analysis showed that 1) the framework structures of **1** and **2**, which are isomorphous to each other, are essentially the same as those of the corresponding guest-free frameworks, and 2) the acetylene molecules occupy two independent positions (A and B) in the zigzag channels of the frameworks with a stoichiometry of $M(HCOO)_2\cdot{}^1/_3C_2H_2$ or four molecules per unit cell for both **1** and **2** (Figure 2). The stoichiometry is consistent with that found by the above-mentioned sorption experiments. The A and B positions, which are too close to each other to be fully occupied at the same time, are occupied in a 75:25 ratio for **1** and a 63:37 ratio for **2**. The more-balanced distribution of acetylene molecules in **2** may be explained by the slightly larger unit-cell volume (see Supporting Information) and, therefore, wider channels in **2**. Notably, these are the first single-crystal X-ray structures of acetylene trapped in metal–organic porous materials.

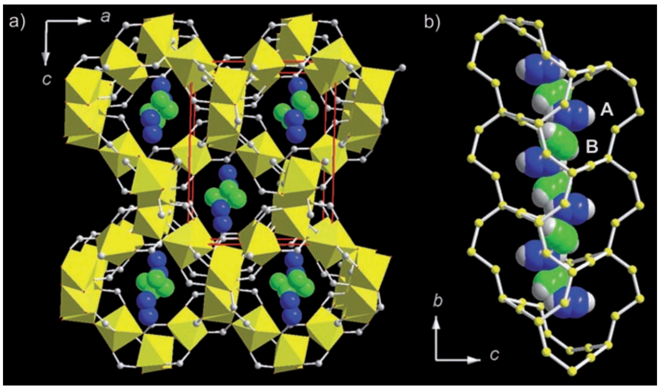

Figure 2. X-ray crystal structure showing acetylene molecules adsorbed in the 1D zigzag channels of **1**. a) View down the *b* axis. b) Two sorption sites (A and B) for acetylene in the channel. The structures of **1** and **2** are isomorphous.

The C–C bond lengths of the guest acetylene molecules (average 1.157(15) Å) (Table 3) are in good agreement with

Table 3. Bond distances, site-occupancy factors (SOFs), and isotropic displacement parameters (U_{iso}) of acetylene molecules in **1** and **2**.

Compound	Position	d(C–C) [Å]	SOF	U_{iso} of C atoms [$Å^2$]
1	A	1.166(7)	0.754(5)	0.057(1), 0.074(1)
	B	1.149(18)	0.246(5)	0.050(3), 0.059(3)
2	A	1.174(12)	0.628(6)	0.078(2), 0.095(3)
	B	1.154(14)	0.372(6)	0.054(2), 0.060(2)

the values (1.097–1.191 Å, average 1.163 Å) found in the Cambridge Structural Database.[12] Interestingly, the C−C bond length of acetylene in A is about 0.02 Å longer than that in B for both **1** and **2**. The thermal parameters of the carbon atoms of acetylene were slightly larger than those for the framework atoms, which is not unusual for guest molecules.

In contrast to the situation in [$Cu_2(pzdc)_2(pyz)$],[6] no specific interaction except for van der Waals interactions between adsorbed acetylene molecules and the framework wall was apparent. The shortest distances between the H atoms of C_2H_2 and the O atoms of the frameworks are in the range of 2.51–2.66 Å (average 2.58(5) Å), which is close to the sum of the van der Waals radii of H and O atoms (2.6 Å). Nevertheless, the acetylene molecules are effectively held in the twisted narrow channels of Mg and Mn formates as a result of extensive van der Waals interactions between the guest molecules and the framework wall.

Selective Adsorption of Acetylene

To demonstrate the potential application of $M(HCOO)_2$ for the separation of acetylene from other gases, CO_2, CH_4, N_2, O_2, and H_2 adsorption isotherms of $M(HCOO)_2$ (M = Mg, Mn) were recorded at 275 (see Supporting Information) and 298 K (Figure 3). As the temperature was increased from 196 to 298 K, the amount of adsorbed acetylene was still above 60 $cm^3 g^{-1}$ for $Mg(HCOO)_2$ and 50 $cm^3 g^{-1}$ for $Mn(HCOO)_2$, whereas the uptake of the other gases decreased substantially. At 298 K, essentially no (N_2, O_2, and H_2) or only a small amount (CH_4) of gas adsorption was observed. In the case of CO_2, the amount of adsorbed gas at 298 K was significant, particularly at high pressures, but was far smaller than that of acetylene, especially at low pressures. The sorption properties of the metal formates correlate well with the size, boiling point, and critical temperature of the adsorbates (see Table S2 in the Supporting Information). Interestingly, the metal formates discriminated acetylene and CO_2 despite their similar size (5.5 vs. 5.3 Å), sublimation point (189.2 vs. 194.7 K), and critical temperature (308.2 vs. 304.2 K), and the discrimination against CO_2 is expected to be even more pronounced as the temperature is increased further. Such discrimination is presumably due to the slightly larger size of acetylene relative to carbon dioxide, which provides the former with more-effective van der Waals interactions with the framework walls. This observation suggests that the microporous metal formates may be useful in the separation of acetylene from carbon dioxide.

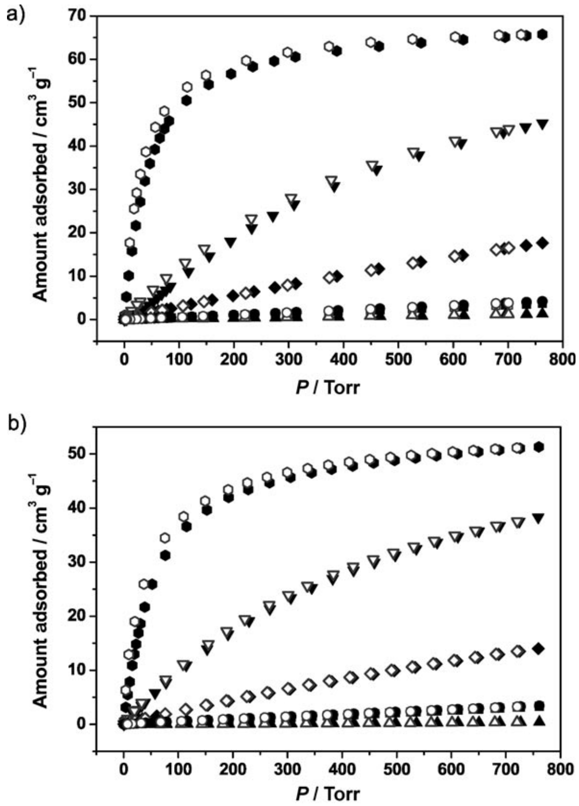

Figure 3. Acetylene (hexagons), carbon dioxide (inverted triangles), methane (diamonds), nitrogen (squares), oxygen (circles), and hydrogen (upright triangles) sorption isotherms for a) $Mg(HCOO)_2$ and b) $Mn(HCOO)_2$ at 298 K. Solid symbols = adsorption, open symbols = desorption.

Conclusions

We have studied the acetylene sorption of microporous magnesium and manganese formates. The acetylene sorption measurements showed a Type I isotherm with quick saturation at low pressures and more than 50 $cm^3 g^{-1}$ of C_2H_2 uptake at 1.0 atm, 298 K. The acetylene adsorption–desorption isotherms at 196 K for both metal formates showed large hysteresis, which suggests that acetylene may be loaded at higher pressures and stored at low pressures without significant loss in these metal–organic porous materials. The X-ray crystal structure of acetylene-adsorbed metal formates revealed that acetylene molecules are held in the zigzag channels of the frameworks through van der Waals interactions. A set of different gas sorption measurements showed remarkable selectivity of acetylene adsorption over CO_2, CH_4, N_2, O_2, and H_2. Thus, microporous Mg and Mn formates may be useful not only for the storage of acetylene but also for its separation from other gases at room or slightly higher temperatures.

Experimental Section

General

All solvents and reagents were purchased and used without further purification. Solvothermal reactions were carried out in sealed glass tubes under autogenous pressure. Gas sorption isotherms were recorded volumetrically with an Autosorb 1MP instrument in the temperature range 77–298 K and in the pressure range 10^{-5}–1.1 atm. A sample was considered to have reached equilibrium when the pressure change was less than 0.0008 atm for 3 min. Highly pure gases (99.95 % for C_2H_2, 99.9995 % for O_2 and CH_4, 99.9999 % for N_2, H_2, and CO_2) were used for the measurements. The BET surface area of $Mg(HCOO)_2$ was calculated from the N_2 isotherm in the range $0.02 \leq P/P_0 \leq 0.10$.

Syntheses

$M(HCOO)_2$ (M = Mg, Mn): $Mn(HCOO)_2\cdot{}^1/_3$dioxane was synthesized by our procedure published previously.[7a] $Mg(HCOO)_2\cdot{}^1/_3$dioxane was synthesized by the same method with $Mg(ClO_4)_2\cdot 6H_2O$ as a magnesium source. Samples for gas sorption measurements were prepared by heating $M(HCOO)_2\cdot{}^1/_3$dioxane at 200 and 150 °C for magnesium and manganese formates, respectively, for 48 h under dynamic vacuum.

Single crystals of C_2H_2-adsorbed $M(HCOO)_2$ (M = Mg (**1**), Mn (**2**)): Single crystals of $M(HCOO)_2\cdot{}^1/_3$THF (M = Mn, Mg) were synthesized by the same procedure as above except with a mixture of DEF/THF as solvent. To prepare guest-free crystals, the crystals were heated at 120 °C under dynamic vacuum for 2 days. After cooling, a crystal of guest-free $M(HCOO)_2$ was placed in a thick-walled (0.1 mm) glass capillary, which was attached to a vacuum manifold and evacuated. After acetylene gas was introduced, the capillary was sealed with flame while its bottom half was immersed in a liquid-nitrogen bath.

X-ray Crystal-Structure Determination

X-ray diffraction data of **1** and **2** were collected at 90 K with an ADSC Quantum 210 charge-coupled device (CCD) diffractometer by using synchrotron radiation ($\lambda = 0.70000$ Å) at the Macromolecular Crystallography Wiggler Beamline 4A, Pohang Accelerator Laboratory (PAL), Pohang, Korea. Data reduction and adsorption correction were performed with the HKL2000 package.[13] The structures were solved by direct methods and refined by full-matrix least squares with the SHELXTL package.[14] Acetylene molecules were found to occupy two independent positions A and B in the channels of the frameworks, which are too close to each other to be fully occupied at the same time. Accordingly, the SOFs of A and B were refined with their sum fixed at 1, which resulted in one acetylene molecule per unit pore. The diffraction data collected at a temperature higher than 90 K did not result in satisfactory refinement of adsorbed acetylene molecules inside the channel because of their high thermal motion. Crystal data and results of the structure refinements are summarized in Table S1 in the Supporting Information. CCDC-627936 and -627937 (**1** and **2**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk./data_request/cif.

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