Effect of Functional Groups on the I₂ Sorption Kinetics of Isostructural Metal–Organic Frameworks

Byeongchan Lee and Jinhee Park*

Department of Emerging Materials Science, Daegu Gyeongbuk Institute of Science and Technology (DGIST), Daegu 42988, South Korea. *E-mail: jinhee@dgist.ac.kr Received October 16, 2020, Accepted December 16, 2020, Published online January 19, 2021

In this work, the effect of functional groups on I₂ sorption kinetics is investigated using two different types of isostructural metal-organic frameworks, UiO-66-X series (X = H, Br, NO₂, NH₂, (OH)₂, and (COOH)₂) and M₂(*m*-DOBDC) series, (M = Co2+, Mg2+, and Ni2+; *m*-DOBDC⁴⁻ = 4,6-dioxo-1,3-benzenedicarboxylate). Among the UiO-66-X series, UiO-66-(COOH)₂ exhibits the fastest sorption kinetics and the highest sorption capacity due to dipole-induced dipole interactions between carboxylic acid groups and I₂ molecules. In addition, faster I₂ chemisorption is observed in M₂(*m*-DOBDC) because of electrophilic aromatic substitution of *m*-DOBDC⁴⁻ with I₂. The I₂ sorption mechanisms are further supported by fitting the I₂ adsorption kinetics data to pseudo-first-order and pseudo-second-order kinetic models.

Keywords: Metal-organic frameworks, Iodine capture, Functional group effects, Sorption kinetics

Effective utilization of nuclear energy is essential in order to meet the rapid increase in global energy demand. However, the radioactive nuclides generated from the fission of nuclear fuels are hazardous to human health and the environment, as witnessed in the 2011 Fukushima-Daiichi accident.¹ A major constituent of nuclear waste is radioactive iodine $(e.g., {}^{129}I \text{ and } {}^{131}I)$. The ${}^{129}I$ isotope is one of the longest-lived radioactive isotopes with a half-life of 1.57×10^7 years. Meanwhile, ¹³¹I, with a relatively short half-life (8.02 days), is generated in large amounts. These radioisotopes of iodine pose significant health hazards, such as hypothyroidism and thyroid cancer because of the emission of beta (β) and gamma (γ) radiation.² Thus, the secure sequestration of radioactive iodine is essential for safe nuclear waste management. Conventionally, iodine was sequestrated by filtration processes using wet scrubbers, sand bed filters, and metallic filters, which were followed by adsorption in porous sorbents.³ However, several drawbacks are associated with the use of traditional porous sorbents such as triethylenediamine-impregnated activated carbon and silver-exchanged zeolites. Activated carbon has a low ignition temperature and readily reacts with NO_x to form explosive compounds, because of which its use is restricted to mild sorption conditions such as low temperature and NO_x-free environment.⁴ In addition, silverexchanged zeolites have low sorption capacities because of their small accessible surface areas.⁵ Therefore, there is a need to investigate new kinds of I2 adsorbents that have high sorption capacity and strong affinity toward I₂.

Metal–organic frameworks (MOFs) are promising adsorbents for I_2 capture because of their large surface areas and easy structural tunability.^{6–11} Various MOFs such as

HKUST-1,¹² ZIF-8,¹³⁻¹⁶ UiO-66 series,¹⁷ MIL series,¹⁸ MFM-300 series,¹⁹ Tb-MOF,²⁰ and SBMOF²¹ have been evaluated for I2 capture. To design an ideal MOF sorbent, the interactions of the adsorbed I₂ molecules with the building blocks of MOFs must be enhanced. Nevertheless, there is a lack of in-depth research focusing on the effect of functional groups on the I₂ sorption of MOFs. Previous studies have reported the enhancement of the sorption capacities and kinetics by employing MOFs functionalized with electronrich and basic functional groups such as amine and pyridine, as these groups can form strong charge-transfer complexes with molecular I2.17,18 However, these reports might be misunderstood to suggest that basic functional groups are more effective in enhancing I₂ sorption than are acidic functional groups. Therefore, this study investigated the effect of functional groups on I₂ capture by examining the I₂ sorption kinetics of the UiO-66-X series containing various functional groups, including acidic and basic groups ($X = H, Br, NO_2$, NH₂, (OH)₂, and (COOH)₂) (Figure 1(a)). As another strategy to enhance the adsorption kinetics and interactions between the MOFs and the I₂ molecules, the use of a ligand consisting of a functional group that can react with I₂ was investigated. We previously reported the I2 adsorption of the isostructural MOFs, $Co_2(m$ -DOBDC) (m-DOBDC⁴⁻ = 4,6dioxo-1,3-benzenedicarboxylate) and Co₂(p-DOBDC) (p-DOBDC⁴⁻ = 2,5-dioxo-1,4-benzenedicarboxylate), and found that they followed different I₂ adsorption mechanisms, chemisorption and physisorption, respectively (Figure 1 (b)).²² While I₂ is adsorbed on the open Co^{2+} sites in $\text{Co}_2(p-$ DOBDC), I_2 adsorption by $Co_2(m$ -DOBDC) is facilitated by the electrophilic aromatic substitution (EAS) of m-DOBDC^{4–}. The adsorbed I₂ converts the aryl C5-H bond into an aryl



Figure 1. (a) Crystal structure of the UiO-66-X series and interactions of various organic linkers with I₂. (b) I₂ adsorption mechanisms of Co₂(*p*-DOBDC) and M₂(*m*-DOBDC) (Mg²⁺, Co²⁺, and Ni²⁺). I₂ removal efficiencies (%) of (c) UiO-66-X series and (d) M₂(*m*-DOBDC) series and Co₂(*p*-DOBDC) as functions of exposure time. ¹H-NMR spectra of H₄*m*-DOBDC and H₄5-I-*m*-DOBDC derived from (e) I₂@Ni₂(*m*-DOBDC) and (f) I₂@Mg₂(*m*-DOBDC). Color code: light blue, M (Mg²⁺, Co²⁺, Ni²⁺, and Zr⁴⁺); gray, C; yellow, O; blue, N; white, H; and purple, I.

C5—I bond, while generating an iodide ion (I⁻), which binds to an open Co²⁺ site. Upon increasing the I₂ loading, a triiodide ion (I₃⁻) is formed by the interaction of an I₂ molecule with an I⁻ ion. In this study, these findings were extended to examine the I₂ sorption by an isostructural M₂(*m*-DOBDC) series (M = Mg²⁺ and Ni²⁺).

The UiO-66-X series, which is built up with thermally and chemically stable 12-connected Zr_6 clusters, was

readily prepared from substituted terephthalates (BDC-X, X = H, Br, NO₂, NH₂, (OH)₂, (COOH)₂) by following previously reported procedures with slight modifications (Figure 1(a)).^{23–26} The synthetic feasibility of this MOF series makes it useful for examining the effects of acidic and basic functional groups on the I₂ sorption. The formation of these MOFs was confirmed by powder X-ray diffraction (PXRD) (Figure S2). The porosities of the

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	Pseudo-first-order		Pseudo-second-order	
	k_{I} (h ⁻¹)	R^2	$k_2 (g \cdot mg^{-1} \cdot h^{-1})$	R^2
UiO-66-H	0.021 (±0.001)	0.975	0.0000067 (±0.0000036)	0.034
UiO-66-Br	0.018 (±0.001)	0.962	0.00030 (±0.00017)	0.913
UiO-66-NO ₂	0.017 (±0.002)	0.935	0.00027 (±0.00017)	0.865
UiO-66-NH ₂	0.016 (±0.001)	0.984	0.000026 (±0.000014)	0.860
UiO-66-(OH)2	0.022 (±0.001)	0.954	0.000032 (±0.000021)	0.809
UiO-66-(COOH) ₂	0.024 (±0.001)	0.999	0.000019 (±0.000002)	0.990
Co ₂ (<i>p</i> -DOBDC)	0.016 (±0.001)	0.984	0.000022 (±0.000010)	0.876
Co ₂ (<i>m</i> -DOBDC)	0.15 (±0.02)	0.919	0.0021 (±0.0001)	0.999
Mg ₂ (<i>m</i> -DOBDC)	0.089 (±0.022)	0.792	0.0015 (±0.0007)	0.999
Ni ₂ (<i>m</i> -DOBDC)	0.045 (±0.002)	0.981	0.00024 (±0.00002)	0.999

Table 1. I₂ adsorption kinetic studies of the UiO-66-X, Co₂(*p*-DOBDC), and M₂(*m*-DOBDC) series.

solvent-evacuated samples were revealed by N₂ adsorption– desorption isotherms, which were comparable to previously reported isotherms (Figure S4).^{23–27} As expected, the introduction of functional groups into the pores decreased the N₂ uptake and the surface areas (Table S1). Thus, UiO-66-(COOH)₂, the MOF containing two bulky COOH groups, exhibited the lowest N₂ uptake (151.4 cm³/g at 0.99 *P*/*P*₀) and surface area (492.3 m²/g).

The I₂ sorption kinetics were examined by immersing the desolvated MOFs into a solution of I₂ in cyclohexane. UV–vis spectroscopy was used to determine the concentration of the I₂ solution and to examine the I₂ uptake of the UiO-66-X series as a function of exposure time (Figure 1 (c) and Figure S6).

Despite having the largest surface area, UiO-66-H showed the lowest I₂ removal efficiency in the series, *i.e.*, 22.4% in 150 h. The introduction of Br and NO₂ groups in the MOFs did not considerably affect the I₂ uptake, implying that the halogen bonding and dipole-induced dipole interactions between these functional groups and I₂ were insignificant. The I₂ removal efficiency of UiO-66-NH₂ was 70.1% in 150 h, which was much higher than that of UiO-66-H, in accordance with the previous reports. In particular, although UiO-66-(OH)₂ contains two hydroxyl groups, its sorption kinetics and removal efficiency were comparable to those of UiO-66-NH₂. This result suggests that the amine group, which is a better electron donor than the hydroxyl group, formed a more stable charge-transfer complex with the I₂ molecule.

Interestingly, despite having the smallest surface area, UiO-66-(COOH)₂ showed the fastest sorption kinetics and the highest I₂ removal efficiency, which reached 82.0% in 150 h. Presumably, the I₂ molecule was easily polarized into the $[I^{\delta+}I^{\delta-}]$ state because of its large electron cloud,²⁸ which enabled it to simultaneously interact with the electron-rich oxygen atom (carbonyloxygen) and the acidic hydrogen of the carboxylic acid group via double dipole-induced dipole interactions. However, the hydroxyl or amine group can only form single dipole-induced dipole interactions with polarized I₂. As a result, UiO-66-(COOH)₂ possessed superior I₂ sorption properties.

To explore the effect of ligand reactivity on I_2 capture, four isostructural MOFs, Co₂(*p*-DOBDC), $Co_2(m-$ DOBDC), Mg₂(m-DOBDC), and Ni₂(m-DOBDC), were synthesized by following previously reported procedures.^{29,30} N₂ adsorption-desorption isotherms of the prepared samples revealed that the MOFs had comparable surface areas (Figure S5 and Table S1). While the I₂ removal efficiency of Co2(p-DOBDC) slowly reached 23.2% in 30 h, Co₂(m-DOBDC), Mg₂(m-DOBDC), and $Ni_2(m$ -DOBDC) rapidly removed I_2 in 30 h with 78.1%, 76.1%, and 76.9% efficiencies, respectively (Figure 1(d)). After the decomposition of I_2 -adsorbed $M_2(m$ -DOBDC), NMR spectroscopy was performed, which revealed the formation of the iodo-substituted ligand via the conversion of the C5-H bond into the C5-I bond (Figure 1(b)). The intensity ratio of the peaks corresponding to the C5 proton, 6.4 ppm, and the C2 proton, 8.3 ppm, of H_4m -DOBDC was lower in I_2 -adsorbed $M_2(m$ -DOBDC) than in the pristine MOFs (Figures 1(e)-(f)). These results indicate that the functionalization of organic linkers is a useful strategy to enhance the affinity of MOFs toward the I₂ molecules.

To obtain further information on the adsorption kinetics, the I₂ adsorption data were fitted to Lagergren's pseudofirst-order and pseudo-second-order kinetic models (Table 1).^{31,32} The data for the UiO-66-X series were better fitted to the pseudo-first-order model than to the pseudosecond-order model, implying that the rate-determining step was the physisorption of I₂ (Figures S7-S18). As mentioned above, the addition of functional groups on the linkers affected the I2 sorption kinetics; among the UiO-66-X series, UiO-66-(COOH)₂ exhibited the highest rate constant $(0.024 h^{-1})$ owing to the high affinity provided by the dipole induced-dipole interactions between the carboxylic acid groups and the polarizable I2 molecules. In addition, unlike Co₂(*p*-DOBDC), whose adsorption kinetic data were fitted to the pseudo-first-order model, the I2 adsorption kinetic data of the $M_2(m$ -DOBDC) series were better fitted to the pseudo-second-order model (Figures S19-S26). This indicates that in M₂(m-DOBDC), adsorption occurred via the chemisorption of I2, which was facilitated by the EAS

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of the electron-rich aryl C—H bond with I_2 . This result is consistent with the proposed sorption mechanism.

In summary, the effect of functional groups on I₂ adsorption was investigated using MOFs, which were functionalized with acidic and basic functional groups, as well as the substituent aryl C—H group. Among the UiO-66-X series, UiO-66-(COOH)₂ exhibited the highest I₂ removal efficiency owing to the dipole-induced dipole interactions between the carboxylic acid group and I₂ molecules. Moreover, UiO-66-(COOH)₂ will be beneficial for practical applications as it can be derived from the reasonably priced pyromellitic acid.³³ In addition, the M₂(*m*-DOBDC) series showed rapid sorption kinetics and high removal efficiency because of the chemisorption of I₂, which was facilitated by the EAS of *m*-DOBDC^{4—}. Thus, it is crucial to consider the effect of functional groups while designing MOFs for effective I₂ adsorption.

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Supporting Information. Additional supporting information may be found online in the Supporting Information section at the end of the article.

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