

Chemisorption of Organic Iodide by Aryl C-H Bond Activation in MOFs

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1. Introduction

Currently, nuclear energy generates more than 10% of world's electricity offering a low cost and low greenhouse-gas emissions compared to fossil fuel.^[1] However, during the handling of nuclear fuel in nuclear power plants, various radioactive nuclides are generated. Therefore, the stable long-term storage of radioactive nuclides from nuclear power plants is important for their safe operation.^[2] Among these radionuclides, a radioactive iodine molecules and organic iodides (ROIs, e.g., methyl iodide, ethyl iodide, and propyl iodide) are the important nuclides due to their volatility and the significant radiological effects on the human metabolic system through diseases such as thyroid cancer. Compared to iodine, ROIs are known to be remarkably difficult to capture.^[3]

Triethylenediamine (TED) impregnated activated carbon and silver-exchanged zeolites have been used as conventional organic iodide adsorbents. However, activated carbon exhibit low chemical and thermal stabilities, and silver-exchanged zeolites have disadvantages of low sorption capacities because of low surface areas.^[4] In comparison, metal-organic frameworks (MOFs) are promising materials for ROIs adsorption due to their high surface area, high chemical and thermal stabilities and tailorability of nanopores.

Herein, $\text{Co}_2(m\text{-DOBDC})$ ($m\text{-DOBDC}^{4-} = 4,6\text{-dioxo-1,3-benzenedicarboxylate}$) and $\text{Co}_2(p\text{-DOBDC})$ ($p\text{-DOBDC}^{4-} = 2,5\text{-dioxo-1,4-benzenedicarboxylate}$, Co-MOF-74) were chosen as organic iodide adsorbents.^{[5],[6]} Because the two MOFs possess high chemical and thermal stability and highly unsaturated open-metal-site densities that point toward these 1-D hexagonal channels. We previously studied to iodine adsorption on $\text{Co}_2(m\text{-DOBDC})$ and $\text{Co}_2(p\text{-DOBDC})$, but interestingly both MOFs revealed significantly different adsorption mechanisms. Whereas a $\text{Co}_2(p\text{-DOBDC})$ exhibited physisorption for molecular iodine, a $\text{Co}_2(m\text{-DOBDC})$ indicated chemisorption via electrophilic aromatic substitution owing to electron rich C5 carbon of $m\text{-DOBDC}$ ligand and then the formations of iodide (I^-) and triiodide (I_3^-).

In this study, we focused on ROIs adsorption by electrophilic aromatic substitution of the $\text{Co}_2(m\text{-DOBDC})$ and then compared the sorption mechanism with $\text{Co}_2(p\text{-DOBDC})$ which does not have an electron-rich carbon in the aromatic group. The detailed analyses of both MOFs were performed by powder X-ray diffraction (PXRD), nuclear magnetic resonance (NMR),

thermogravimetric analysis (TGA), Brunauer-Emmett-Teller (BET) analysis, UV-Vis spectroscopy and X-ray photoelectron spectroscopy (XPS). Furthermore, the single crystal X-ray diffraction (SXRD) analysis of ROI@MOFs enables to understand the adsorption mechanism of ROIs.

2. Result and Discussion

The ROIs adsorption experiment was performed to measure sorption capacities (wt%) of $\text{Co}_2(m\text{-DOBDC})$ and $\text{Co}_2(p\text{-DOBDC})$ through gravimetric measurements. The vial containing the activated MOFs was inserted into a large vial containing a small amount of ROIs (2.5mg/mL). The sealed vials were heated for 6 - 48h at 100 °C; in a result, the sublimated ROIs adsorbed into the activated MOFs.

2.1 Analysis of the SXRD of ROI@MOFs

Generally, the SXRD analysis of guest-incorporated MOFs such as ROI@MOFs is easy to be failed because the activation and adsorption processes lower the stability of MOFs. Herein, for the first time, the chemisorption of ROIs via the C-C bond formation of an aromatic ring is reported.

We speculate the electron rich carbon undergoes electrophilic aromatic substitution resulting in the aryl C-H bond activation in a $\text{Co}_2(m\text{-DOBDC})$. The structures of the resulting ROI@ $\text{Co}_2(m\text{-DOBDC})$ were crystallographically visualized by SXRD (Figure 1).

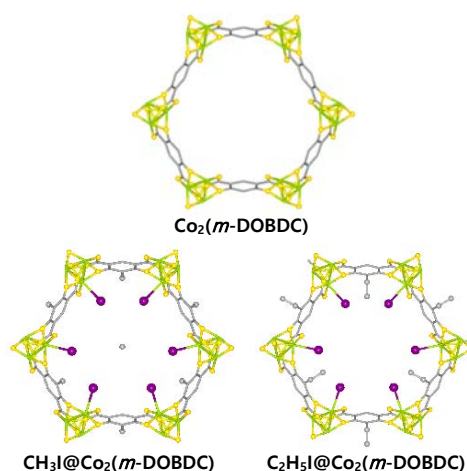


Fig. 1. Crystal structure of $\text{Co}_2(m\text{-DOBDC})$, $\text{CH}_3\text{I}@Co_2(m\text{-DOBDC})$ and $\text{C}_2\text{H}_5\text{I}@Co_2(m\text{-DOBDC})$.

Interestingly, the remaining iodides after the substitution reaction were coordinated to the open Co sites. The post-synthetic modifications of MOF surfaces through the formation of a C-C bond has been rarely reported. On the other hand, $\text{Co}_2(p\text{-DOBDC})$ is adsorbed ROIs at the open Co sites by physisorption.

2.2 Analysis of NMR and XPS

The NMR analysis was employed to evaluate the formation of the alkyl-substituted $m\text{-DOBDC}$ ligands. The ratios of the peak area of the NMR signal corresponding to the proton on C5 to the one of the proton on C2 gradually decreased during the conversion of $m\text{-DOBDC}$ into alkyl- $m\text{-DOBDC}$ by the ROIs adsorption of $\text{Co}_2(m\text{-DOBDC})$ (Figure 2). Furthermore, XPS analysis explicitly exhibit that Co^{2+} was not oxidized to Co^{3+} .

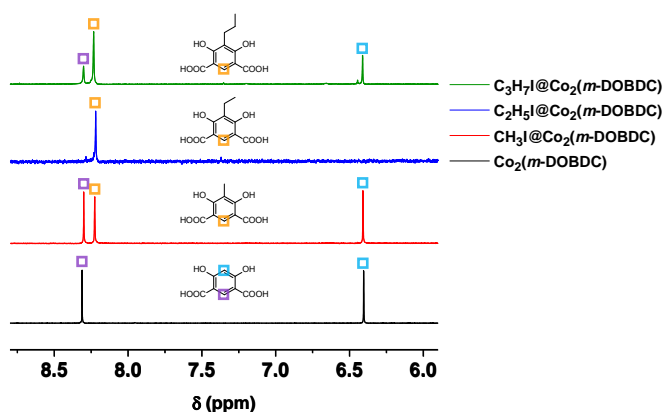


Fig. 2. ^1H -NMR spectra of H45-alkyl- $m\text{-DOBDC}$ from gas-phase ROI adsorbed $\text{CH}_3\text{I}@Co_2(m\text{-DOBDC})$, $\text{C}_2\text{H}_5\text{I}@Co_2(m\text{-DOBDC})$ and $\text{C}_3\text{H}_7\text{I}@Co_2(m\text{-DOBDC})$.

2.3 Sensing Property

Surprisingly, the significant color change of the $\text{Co}_2(m\text{-DOBDC})$ was observed during the adsorption of ROIs (Figure 3). The adsorption of iodide on the open Co site presumably alters the $d-d$ transition of Co^{2+} . This color change was not observed at $\text{Co}_2(p\text{-DOBDC})$ because of ROI physisorption. Moreover, the $\text{ROI}@Co_2(m\text{-DOBDC})$ exhibited the remarkable color change by exposure of H_2O . Because Co-I bond interaction affected by hydrogen bonding between H_2O and iodide at the Co site. Interestingly, the color of the $\text{ROI}@Co_2(m\text{-DOBDC})$ is easily recovered by the vacuum treatment of H_2O exposed $\text{ROI}@Co_2(m\text{-DOBDC})$ at room temperature. Furthermore, the colors of $\text{ROI}@Co_2(m\text{-DOBDC})$ depend on the substituted alkyl group. Based on this color change property of the $\text{Co}_2(m\text{-DOBDC})$ can be applied in sensing various molecules such as ROIs and H_2O .

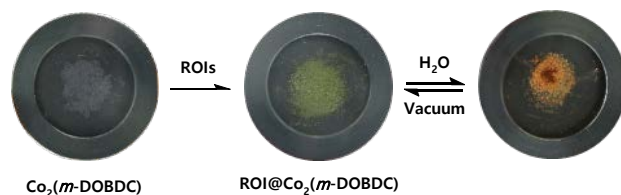


Fig. 3. Color changes observed for $\text{Co}_2(m\text{-DOBDC})$ by adsorption of ROIs and H_2O .

3. Conclusions

We studied the adsorption mechanism of ROIs in $\text{Co}_2(m\text{-DOBDC})$ and $\text{Co}_2(p\text{-DOBDC})$. Whereas $\text{Co}_2(p\text{-DOBDC})$ exhibited the physisorption of ROIs, $\text{Co}_2(m\text{-DOBDC})$ exhibited chemisorption by the formation of the C-C bond resulted from the electrophilic aromatic substitution of aryl C-H bond in $m\text{-DOBDC}$. As a consequence, $\text{Co}_2(m\text{-DOBDC})$ exhibited a stable and effective adsorption property for ROIs than $\text{Co}_2(p\text{-DOBDC})$. In addition, $\text{ROI}@Co_2(m\text{-DOBDC})$ possessed excellent sensing property for H_2O and NH_3 through hydrogen bonding of iodide on the Co site. We anticipate that the $\text{Co}_2(m\text{-DOBDC})$ can be a novel material for the effective capture of ROIs and sensing for NH_3 and H_2O .

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