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Metal–Organic Frameworks

Remarkable Adsorption Capacity of $CuCl_2$-Loaded Porous Vanadium Benzenedicarboxylate for Benzothiophene**

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Dedicated to Professor Young-Woo Kwak

There is a considerable demand to reduce the content of sulfur-containing compounds (S-compounds) such as thiophene (Th), benzothiophene (BT), and dimethyldibenzothiophene (DMDBT) in fuels like diesel and gasoline to a low level to prevent air pollution and deactivation of catalysts.[1,2] So far, various methods have been investigated for sulfur removal,[3] and adsorption has been regarded as one of the most competitive methods.[4] For efficient adsorption, not only adequate porosity/pore size but also specific adsorption sites are required.[3]

Remarkable progress on porous materials has been achieved because of the developments of metal–organic framework materials (MOFs) and coordination polymers (CPs).[5] The importance of MOF-type materials is due to the huge porosity, easy tunability of their pore size and shape,[5] and potential applications.[6] Recently, the MOF-type materials have also been investigated for the removal of harmful materials such as S-compounds,[1,2] dyes,[7] N-containing compounds,[8] and benzene[9] from liquids. Gaseous sulfur compounds have also been removed using MOFs.[1,10,11] A few important factors, such as open metal sites,[1] acid sites,[12] and pore functionality[11] have been suggested for the efficient removal of S-compounds. However, little has been understood for the high uptake of S-compounds with modified MOFs as adsorbents.

Herein, we have shown the remarkable adsorption capacity for BT over a modified MOF, $CuCl_2$-loaded MIL-47 (MIL = materials of the Institute Lavoisier). MIL-47 is a typical MOF composed of vanadium and benzenedicarboxylate (BDC).[13] The reduction of Cu^{II} to Cu^{I} has been observed in $CuCl_2$/MIL-47 compounds without high-temperature calcination for the partial reduction. Moreover, $CuCl_2$/MIL-47 compounds have been prepared by a simple process of loading $CuCl_2$ in the MIL-47 (purified at 70 °C) at room temperature.

To understand the contribution of loaded $CuCl_2$ to the adsorptive removal of BT, adsorption was done for various times over $CuCl_2$(0.05)/MIL-47 and MIL-47. Here, MIL-47 is the MIL-47 purified in *N*,*N*-dimethylformamide (DMF) at 70 °C (see the Supporting Information). $CuCl_2$(*n*)/MIL-47 denotes $CuCl_2$ loaded onto the purified MIL-47 and *n* is the Cu/V ratio (mol/mol). The amount of adsorbed BT over $CuCl_2$(0.05)/MIL-47 is much higher than that over MIL-47 without $CuCl_2$ at all adsorption times (Figure 1). However, the adsorption kinetic constants of the pseudo-second-order rate equation that are obtained with a nonlinear model[14] (see the Supporting Information) show that the adsorption rate may be decreased with any $CuCl_2$ loading ($k_2 = 7.68 \times 10^{-3}$ and $2.28 \times 10^{-2}\,g\,mg^{-1}\,h^{-1}$ for $CuCl_2$(0.05)/MIL-47 and MIL-47, respectively) probably because of steric effects of BT or the blocking of pores by the loaded $CuCl_2$.

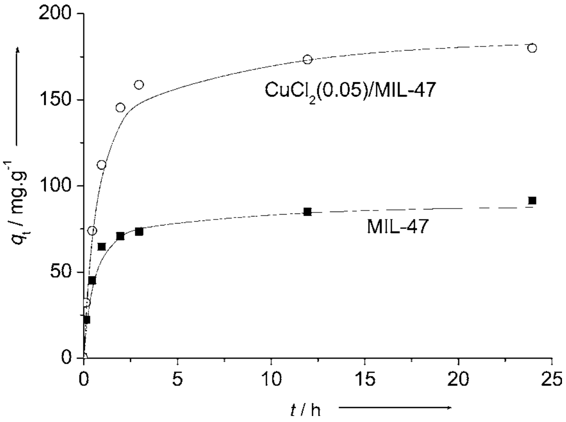

Figure 1. Effect of the contact time on the adsorption of BT over the two adsorbents at the initial BT concentration (c_i) of 1000 ppm. Symbols and solid lines show the experimental and calculated (with pseudo-second order nonlinear plot) results, respectively.

To understand the effect of the $CuCl_2$ content on the adsorption capacity, the adsorption isotherms were obtained after adsorption for a sufficient time of 24 h, and the results are compared in Figure 2a. The adsorption isotherms have been plotted (Figure 2b) to follow the Langmuir equation[15] (see the Supporting Information), and the maximum adsorption capacities Q_0 for all of the samples are summarized in Table 1. Q_0 increases with increasing $CuCl_2$ loading up to a specific content (Cu/V = 0.05 mol/mol) and decreases with further increase in the $CuCl_2$ content, showing that there is an

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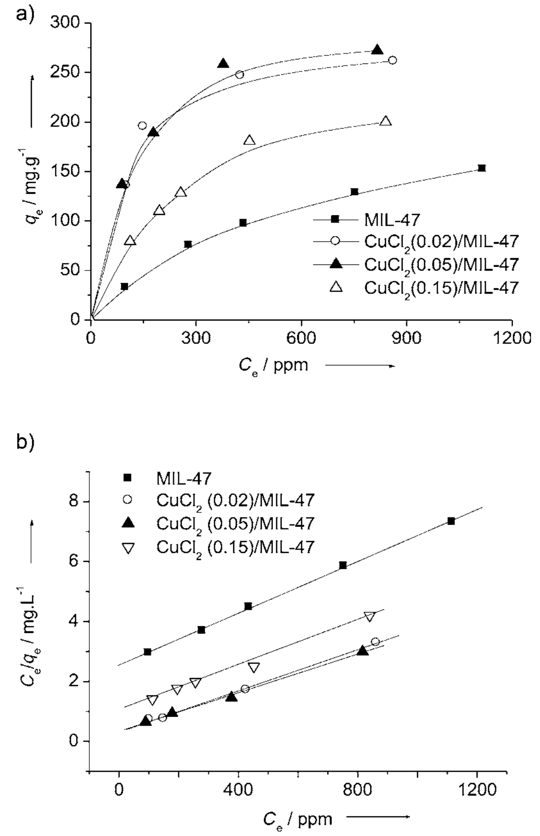

Figure 2. a) Adsorption isotherms and b) Langmuir plots of the isotherms for MIL-47 and $CuCl_2$/MIL-47 compounds.

Table 1: The textural properties and maximum adsorption capacities (Q_0) of BT over MIL-47 and $CuCl_2$/MIL-47 compounds.

Adsorbent	S_{BET} [$m^2 g^{-1}$]	PV(total) [$cm^3 g^{-1}$]	PV(micro) [$cm^3 g^{-1}$]	Q_0 [$mg g^{-1}$]	Q_0 [$cm^3 g^{-1}$]
MIL-47	890	0.48	0.41	231	0.20
$CuCl_2$(0.02)/MIL-47	681	0.38	0.30	291	0.25
$CuCl_2$(0.05)/MIL-47	599	0.35	0.26	310	0.27
$CuCl_2$(0.08)/MIL-47	546	0.31	0.24	276	0.24
$CuCl_2$(0.15)/MIL-47	480	0.28	0.22	266	0.23

optimum $CuCl_2$ concentration. This is due to the contribution of both the porosity/acidity of MIL-47[16] and a Cu^I site derived from $CuCl_2$.

As shown in Table 1, the adsorption capacity of $CuCl_2$(0.05)/MIL-47 for BT is 310 mg g^{-1} at 25 °C. So far many adsorbents have been evaluated as candidates for the removal of BT and their adsorption capacities have varied widely from 1.21 to 254 mg of BT per gram of adsorbent.[17] To the best of our knowledge, the adsorption capacity of $CuCl_2$(0.05)/MIL-47 is the highest (310 mg g^{-1}) and much higher than that of Cu^I-Y zeolite (254 mg g^{-1}) that showed the highest capacity so far.[17]

It is not easy to explain why the $CuCl_2$(0.05)/MIL-47 shows the best performance for adsorption of BT. So far, the adsorptive removal of S-compounds has been explained with high porosity[18] and specific interactions like acid–base interactions[12,19] and π-complexation.[20] Because of the low porosity (Table 1) of $CuCl_2$(0.05)/MIL-47 (compared with MIL-47), the porosity is not an important factor in this study. The increase of Q_0 with increasing $CuCl_2$ content up to a Cu/V ratio of 0.05, even with the decrease of porosity (Table 1), suggests that there are very favorable interactions between BT and the loaded $CuCl_2$. However, further increase of the $CuCl_2$ content does not increase the adsorption capacity because of the decreased porosity (Table 1). Actually the adsorption capacity (based on the volume) of $CuCl_2$(0.05)/MIL-47 is similar to the micropore or total pore volume of the adsorbent (Table 1). Therefore, the $CuCl_2$/MIL-47 compounds having a higher $CuCl_2$ content will hardly adsorb more BT than $CuCl_2$(0.05)/MIL-47.

To shed light on the remarkable adsorption of BT over $CuCl_2$(0.05)/MIL-47, the adsorbents including MIL-47-AS (as-synthesized MIL-47 before purification) and purified MIL-47 (treated with DMF at 70 °C) were analyzed with X-ray photoelectron spectroscopy (XPS) and XRD. To our surprise, XPS spectra of the Cu region (Figure 3 a) show the presence of Cu^I ions in $CuCl_2$(0.05)/MIL-47 rather than Cu^{II} ions. The presence of CuCl is also supported by XPS of the Cl region (Figure 3 b) as the XPS spectrum is similar to that of CuCl and not to that of $CuCl_2$. Moreover, the presence of CuCl (and negligible $CuCl_2$) after $CuCl_2$ loading is confirmed by XRD even though the XRD intensity is low (Figure 4). It has been reported that metal ions like Cu^I (such as in CuCl), Ag^I, Pd^{II}, and Pt^{II} have an adsorption capability for S-compounds through formation of π-complexes.[20,21] However, Cu^{II} ions such as in $CuCl_2$ do not show a noticeable adsorption capacity.[21] Therefore, it may be concluded that the remarkable adsorption capacity of $CuCl_2$/MIL-47 compounds is mainly due to a synergy between reduced Cu^I ions (for π-complexation) and MIL-47.[16]

It is also not easy to understand why the reduction of Cu^{II} to Cu^I occurs easily at relatively low temperatures (drying at room temperature and evacuation at 100 °C) without calcination and partial reduction at high temperatures.[20,21] The XPS spectra of vanadium (Figure 3 c) show that the MIL-47-AS and MIL-47 (purified at 70 °C) have similar binding energies. Moreover, the binding energies of the two MIL-47 compounds are lower than that of $VOSO_4$ composed of V^{IV}. Therefore, it can be concluded that the oxidation state of the purified MIL-47 is not four but similar to three like in MIL-47-AS.[13] These are unexpected results because MIL-47-AS and traditionally purified MIL-47 (purified by calcination at high temperatures) are composed of V^{III} and V^{IV}, respectively.[13] This might be due to low-temperature purification in the presence of DMF,[22] preventing the oxidation of V^{III} to V^{IV} that is observed in high-temperature calcination (in the presence of air) for purification.[13] The binding energy of V in $CuCl_2$/MIL-47 is a bit higher than that in MIL-47 showing an increase in the oxidation state of vanadium upon $CuCl_2$

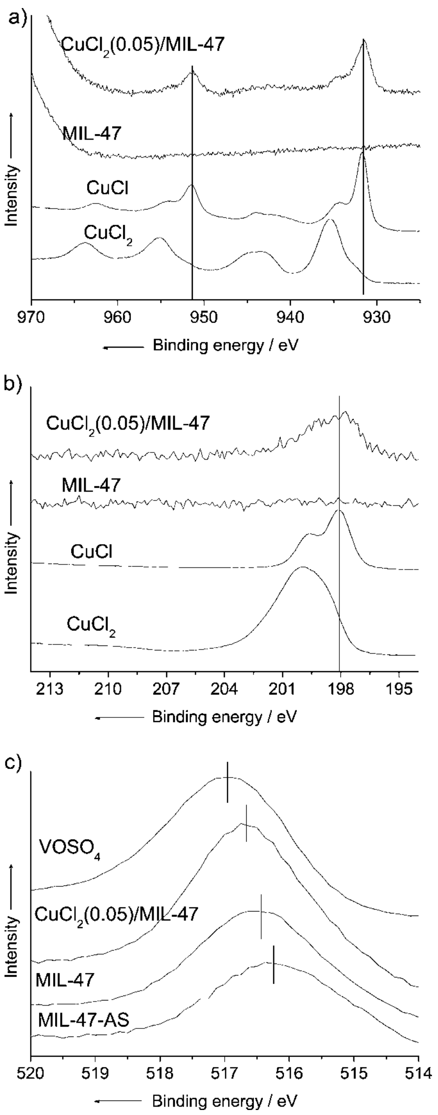

Figure 3. XPS spectra of MIL-47 compounds and CuCl$_2$(0.05)/MIL-47 in a) copper; b) chlorine and c) vanadium regions. The XPS spectra of some authentic samples are also included.

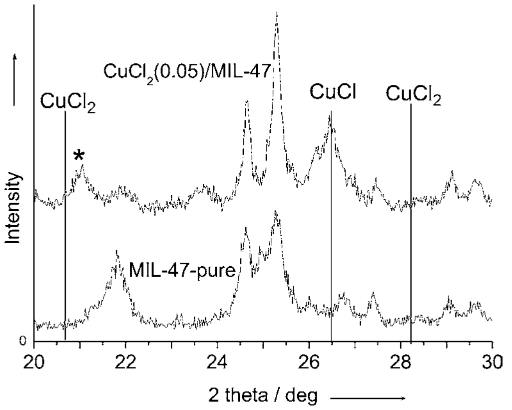

Figure 4. XRD patterns of MIL-47 (lower) and CuCl$_2$(0.05)/MIL-47 (upper). A diffraction peak (*) of MIL-47-AS (containing terephthalic acid) originates from incomplete purification or partial destruction of MIL-47 under acidic conditions for the CuCl$_2$ loading.

loading. This shift in binding energy may be explained by the following redox process [Eq. (1)]:

$$V^{III} + Cu^{II}Cl_2 \rightarrow V^{IV} - Cl + Cu^{I}Cl \qquad (1)$$

Even though the reduction of Cu^{II} to Cu^{I} is confirmed by XPS analysis and by the presence of CuCl (by XRD and XPS), the shift in binding energy of V is relatively small probably because of a low Cu/V ratio of 0.05. Further work to confirm the oxidation states of V and Cu with sophisticated techniques like extended X-ray absorption fine structure (EXAFS) analysis will be necessary.

In conclusion, MIL-47, purified at low temperature, shows an unexpected reduction ability to form Cu^{I} ions from loaded Cu^{II} ions probably because of V^{III} in MIL-47. The obtained Cu^{I} ions show a beneficial effect on the adsorption of BT probably through π-complexation. The highest BT adsorption capacity over CuCl$_2$(0.05)/MIL-47 (122% of Cu^{I}-Y that had the highest capacity so far) shows potential applications of the modified MOF-type materials for adsorptive removal of harmful materials like S-compounds. Moreover, the adsorbent can be readily prepared without calcination and reduction at high temperature.

Experimental Section

The MOF MIL-47 was synthesized similarly to a reported method[13,16] and purified[22] with DMF under ultrasound at 70°C (see the Supporting Information). The loading of CuCl$_2$ was done by mixing MIL-47 and an ethanolic solution of CuCl$_2$ at Cu/V molar ratios of 0.02, 0.05, 0.08, and 0.15. The mixture was stirred for 10 min and allowed to dry in air at room temperature. The phases of purified MIL-47[22] and CuCl$_2$-loaded MIL-47 were identified by X-ray diffraction (see Figure S1 for XRD patterns in the Supporting Information). The porosity of the adsorbents was confirmed by nitrogen adsorption (see Figure S2 for isotherms in the Supporting information and Table 1). XPS analysis was done with a Quantera SXM X-ray photoelectron spectrometer (ULVAC-PHI) with a dual beam charge neutralizer for the adsorbents and authentic samples like VOSO$_4$, CuCl$_2$, and CuCl under the same conditions. The binding energies were compared with reported values[23] of authentic samples. A BT solution was made by dissolving BT in *n*-octane. Before adsorption, the adsorbents were evacuated at 100°C. The adsorbent was added to the BT solutions, and the BT concentration was measured by a gas chromatograph equipped with a flame ionization detector. The adsorption capacity was calculated using the Langmuir equation.[15] The kinetic constants for the adsorption were calculated with a nonlinear model of the pseudo-second-order rate equation.[14]

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