A Metal-Organic Framework with Immobilized Ag(I) for Highly Efficient Desulfurization of Liquid Fuels

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1.1. Materials

Monosodium 2-sulfoterephthalate (98%), dibenzothiophene (98%) and benzothiophene (98%) were purchased from TCI Co., Japan. n-Octane (98%) was provided by Alfa Aesar. Thiophene (99%) and chromium(III) nitrate nonahydrate (99.95%) were obtained from Aladdin Co., China. Silver nitrate (99.8%), hydrogen fluoride (HF, 37 wt%) and acetone (99.5%) were purchased from Sinopharm Chemical Reagent Co., China. Acetonitrile, toluene and methanol of chromatographic grade were provided by Merck Co., Germany. All the chemicals were commercially available and used without further purification.

1.2. Preparation of MOFs

**(Cr)-MIL-101-SO$_3$H.** (Cr)-MIL-101-SO$_3$H was synthesized and purified following the reported method. Monosodium 2-sulfoterephthalic acid (5.4 g, 20.15 mmol), Cr(NO$_3$)$_3$·9H$_2$O (4 g, 10 mmol), and aqueous HF solution (520 μL, 37 wt%) were dissolved in ultrapure water (60 mL), then transferred to a Teflon-lined stainless steel autoclave. This highly acidic solution was heated at 190 °C for 24 h. After that, the autoclave was slowly cooled down to ambient temperature. The produced dark green solid was centrifuged and washed with deionized water and then with methanol for three times. Then the solid was degassed under vacuum at 105 °C for 12 h and stored in a desiccator.

**(Cr)-MIL-101-SO$_3$Ag.** The evacuated MOFs (300 mg) were added into a solution of AgNO$_3$ (1 g) in 20 mL CH$_3$CN/H$_2$O (1:1, v/v) solution with continuous vigorous stirring at room temperature for 24 h, and then the solid was collected by centrifugation followed by washing with water. After three repeated exchange processes, (Cr)-MIL-101-SO$_3$Ag was dried under vacuum overnight. The whole process was performed carefully under dark environment. Energy-dispersive X-ray (EDX) analyses show that ~37% -SO$_3$H were transformed into -SO$_3$Ag based on the element analysis.

1.3. Batch adsorption experiments

The parent and modified MOFs were degassed under high vacuum pressure at 105 °C for
12 h in order to remove the solvated water molecules prior to adsorption. The stock model oils of S-compounds (0.03-2.0 mg/mL) were prepared with n-octane, which were used to obtain adsorption isotherms. For individual adsorption, a known amount of MOFs (~60mg) in the powder form was added to the vials containing stock model oils (20 mL). The vials were then sealed and shaken at 120 rpm in a temperature-controlled shaker for 14 h at 30 °C, being along with the same amount of the solution but without MOFs. After adsorption equilibrium, the solutions were separated from the adsorbents with a syringe filter (PTFE, hydrophobic, 0.25 μm), and the concentration was analyzed by a Waters 2695 high-performance liquid chromatography (HPLC) instrument equipped with a Waters 2489 UV-vis detector and a C\textsubscript{18} column (250 mm × 1. D. 4.6 mm, 5 μm). The mobile phase was the mixture of methanol and water (9:1, v/v) at flow rate of 0.8 mL/min. The detection wavelengths for TP, BT, and DBT were set at 231 nm, 227 nm, and 236 nm, respectively. The equilibrium adsorption amount ($q_e$) was then obtained using the following equation:

$$
q_e = (C_0 - C_e) \times \frac{V}{m}
$$

where $C_0$ and $C_e$ are the initial and equilibrium concentration of thiophene derivatives (mg/mL), respectively. $V$ is the volume of the model fuel (mL), and $m$ is the weight of MOFs used (g).

The adsorption isotherms obtained for TP, BT and DBT were shown in Figure S1 and Figure 1. The maximum adsorption capacity was calculated using Langmuir equation written as:

$$
\frac{c_e}{q_e} = \frac{c_e}{Q_0} + \frac{1}{Q_0b}
$$

where, $c_e$: equilibrium concentration of adsorbate (mg/mL), $q_e$: amount adsorbed at equilibrium (g S/kg MOFs), $Q_0$: Langmuir constant (maximum adsorption capacity) (g S/kg MOFs), $b$: Langmuir constant (mL/mg).

To study the effect of the introduced Ag(I) on the adsorption capacity, the adsorption kinetics experiments were carried out for all studied MOFs under varied time. Solutions with a fixed concentration of S-compounds (1.0 mg/mL) were used. During the period, the interval samples were analyzed the transient adsorption capacity at varied times. Adsorption kinetic
curves (Figure S2) were interpreted by the pseudo-second-order non-linear kinetic model, which is expressed by the following equation.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

(3)

where, $q_e$: amount adsorbed at equilibrium (g S/kg MOFs), $q_t$: amount adsorbed at time $t$ (g S/kg MOFs), $k_2$: pseudo-second-order kinetic constant (kg/g S/min).

The transient adsorption amount with time could be treated successfully with the pseudo-second-order kinetic model for favorably fitting between experimental and calculated values of $q_e$ ($R^2$ > 0.99) (Table S1).

**Table S1.** The pseudo-second order kinetic constants ($k_2$) with correlation coefficients ($R^2$) of the adsorbates

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>$q_e$ (g S/kg MOFs)</th>
<th>$k_2$ (kg/g S/min)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>thiophene</td>
<td>12.11</td>
<td>0.080</td>
<td>0.994</td>
</tr>
<tr>
<td>BT</td>
<td>20.7</td>
<td>0.094</td>
<td>0.995</td>
</tr>
<tr>
<td>DBT</td>
<td>23.8</td>
<td>0.099</td>
<td>0.991</td>
</tr>
</tbody>
</table>
Figure S1. Adsorption isotherms for thiophene (top) and benzothiophene (bottom) over (Cr)-MIL-101-SO$_3$Ag (olive) and (Cr)-MIL-101-SO$_3$H (pink) from $n$-octane solutions. The curves represent the fit to Langmuir equation.
Figure S2. Effect of contact time on the adsorption of TP (top), BT (middle) and DBT (bottom) over (Cr)-MIL-101-SO\textsubscript{3}Ag (olive) and (Cr)-MIL-101-SO\textsubscript{3}H (pink) at the initial concentration of 1.0 mg/mL of thiophene derivatives in \textit{n}-octane. The curves represent the calculated (with pseudo-second order nonlinear plot) results.
After adsorption, (Cr)-MIL-101-SO$_3$Ag was regenerated by washing with acetone or methanol. The filtered MOFs were immersed in the solvent and under sonication for 1 h. The obtained MOFs by centrifugation were treated with the above regeneration process again. Then the powder was dried overnight under high vacuum pressure at 105 °C and the adsorption operations were carried out as previously described method. The adsorption-regeneration experiments were conducted successively for five cycles (Figure S3).

![Graph](image)

**Figure S3.** Effect of regeneration on adsorptive removal of DBT over regenerated (Cr)-MIL-101-SO$_3$Ag by washing with ethanol (red) or acetone (blue). The adsorption was performed using 1.8 mg/mL DBT for 14 h at 30 °C.
1.4. Packed bed breakthrough experiments

Breakthrough adsorption experiments were performed by packing a stainless steel column (5 mL × 4.6 mm I.D.) with MOFs crystallites at room temperature. MOFs were dispersed evenly in moderate n-octane under sonication, and then were packed by column packing machine under high pressure. The packed bed was first equilibrated with n-octane at a flow rate of 0.4 mL/min using a Waters 515 HPLC pump, and then a solution of 0.4 mg/mL DBT was delivered through the adsorbent bed at a flow rate of 0.4 mL/min. Every 0.8 mL of sample was taken at the column outlet and measured by HPLC using a UV-vis detector (Waters 2489). The recorded concentration profiles of thiophene derivatives were presented in Figure 2 and Figure S4.

After breakthrough experiments, the adsorbent bed was regenerated by flowing room-temperature acetone at a flow rate of 0.4 mL/min until no DBT eluted from the bed (as evidenced by UV-vis spectroscopy). Elution curves of (Cr)-MIL-101-SO$_3$Ag by 0.4 mL/min acetone was shown in Figure S5. Then, the breakthrough experiment was repeated and breakthrough curve was shown in Figure S6.
Figure S4. Breakthrough curves for 0.4 mg/mL thiophene (top) and benzothiophene (bottom) in n-octane for (Cr)-MIL-101-SO$_3$Ag (olive) and (Cr)-MIL-101-SO$_3$H (pink) at room temperature.
Figure S5. Elution curve for DBT from (Cr)-MIL-101-SO₃Ag with acetone at flow-rate of 0.4 mL/min and room temperature.
**Figure S6.** Breakthrough curves for adsorption DBT from \( n \)-octane on (Cr)-MIL-101-SO\(_3\)Ag before and after regeneration. Run 1 (blue) is the initial breakthrough curve. Run 2 (pink) is after regeneration with room-temperature acetone.
1.5. IR characterizations of interactions between MOFs and thiophene derivatives

The samples for IR experiments were typically prepared as follows. A known amount of MOFs (~60mg) was added to the n-octane solution containing individual thiophene derivative (20 mL). The vials were then sealed and shaken at 120 rpm for 14 h at 30 °C. The solid was collected by centrifugation and then dried at 35 °C under vacuum for 6 h. The IR spectra were recorded on a Nicolet iS50 FT-IR spectrometer (Thermo Scientific).

As shown in Fig. S7 and Fig. S8, absorbance peaks observed at 1184 (or 1176 for MIL-101-SO$_3$Ag) and 1225 cm$^{-1}$ correspond to the O=S=O symmetric and asymmetric stretching vibrations, respectively. The bending vibrations of O=S=O may ascribe to the peaks at 769 and 661 cm$^{-1}$. For the parent MIL-101-SO$_3$H, the spectra after guest loading did not differ significantly from each other because of weak interaction between framework and thiophene derivatives except for a slight shoulder peak occurred at 746 cm$^{-1}$ in case of dibenzothiophene loading, indicating relatively stronger adsorption of dibenzothiophene on MIL-101-SO$_3$H compared to thiophene and benzothiophene. However, for Ag(I)-doped framework after adsorbing dibenzothiophene, it can be clearly seen from Fig. S8 that the strongest shoulder absorbance is observed at 746 cm$^{-1}$. Moreover, the absorbance peak at 661 cm$^{-1}$ were enhanced significantly in the increased order thiophene < benzothiophene < dibenzothiophene. These observations might be due to the strongest interaction between Ag(I) ions and dibenzothiophene.
Figure S7. FTIR spectra of MIL-101-SO$_3$H (black) framework compared to that of MIL-101-SO$_3$H after adsorbing different compounds from $n$-octane solutions: thiophene (blue), benzo thiophene (olive), dibenzo thiophene (magenta) and blank (red).

Figure S8. FTIR spectra of MIL-101-SO$_3$Ag (black) framework compared to that of MIL-101-SO$_3$Ag after adsorbing different compounds from $n$-octane solutions: thiophene (blue), benzo thiophene (olive), dibenzo thiophene (magenta) and blank (red).
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