

Synthesis of transition metal-doped MOF-5 and their application for adsorptive desulfurization*

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A series of transition metal-doped MOF-5 materials (M-MOF-5, M=Cu, Co or Mn) have been prepared by hydrothermal methodology. The structures of M-MOF-5 were confirmed by powder X-ray diffraction (XRD) and Fourier transform infrared (FT-IR). The adsorptive performance of thiophenic compounds (T, BT and DBT) with metal-doped MOF-5 materials was investigated using static adsorption method. Desulfurization capability of Cu-MOF-5 has been an appreciable increase in comparison with the MOF-5. The center metal of MOF-5 has an influence on their surface properties which causing an impact on the adsorption properties.

Keywords: MOF-5; Adsorptive Desulfurization; metal-doped.

1. Introduction

Deep desulfurization of fuel oil has attracted more attention due to adverse environmental effects of sulfur compounds present in fossil fuel[1]. And adsorption desulfurization is recognized as one of the most promising methods to break out the limitations with the traditional hydro-desulfurization process[2]. Metal-organic frameworks (MOFs) are a class of materials assembling both polydentate organic ligands and inorganic ions building blocks into a uniform framework by self-assembly[3]. They possess excellent adsorption properties for thiophenic compounds because of their huge variety of structures, large surface areas, ultrahigh porosity and high functionality. And MOF-5 is one of the most porous MOFs because of high specific prominent representatives of these 3D area and thermal stability[4]. However, the research about the adsorption thiophenic compounds by MOFs is still scarce.

In this work, we synthesized transition metal-doped MOF-5 (M-MOF-5, $Zn_{4-x}M_xO(BDC)_3$) for improving the adsorption capacity of MOF-5 by hydrothermal methodology during the crystallization process. The

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adsorptivedesulfurization properties of M-MOF-5 for the thiophene contaminants, including thiophene (T), benzothiophene (BT) and dibenzothiophene (DBT), were measured.

2. Experimental

2.1. Synthesis of MOF-5 and M-MOF-5 (M=Co, Cu, Zn)

Pure MOF-5 was prepared according to a previously reported method [5]. A mixture of 1,4-benzenedicarboxylic acid (H₂DBC, 0.33 g), Zn(NO₃)₂·6H₂O, (1.78 g) and DMF (50 mL) were added in a 100 mL teflon-lined steel autoclave at 130 °C for 8 h. After that, the reaction system cooled slowly to room temperature. And the synthesis of M-MOF-5 was synthesized by the manner similar to above, in which mixed Co(NO₃)₂·6H₂O, Cu(NO₃)₂·3H₂O or MnCl₂ and Zn(NO₃)₂·6H₂O (M:Zn (mol/mol)=1:9) took the place of pure Zn(NO₃)₂·6H₂O. And the resulting black products were filtered off, washed with DMF (50 mL×3). Then the remaining solid was washed three times with CH₂Cl₂. Finally, the product was activated at 150 °C for at least 8 h.

2.2. Characterization

X-ray diffraction (XRD) patterns were carried out using a Panalytical X'Pert PRO MPD diffractometer with Cu K α radiation. FT-IR spectra were recorded on a Nicolet NEXUS FT-IR at room temperature using KBr disks.

2.3. Adsorption Desulfurization Experiments

The model fuel containing 500 μ g/g sulfur was obtained by dissolving different thiophenic compounds (T, BT, DBT) in n-heptane. Adsorption desulfurization experiments of M-MOF-5 were evaluated with a static adsorption method at 30 °C under ambient conditions (adsorbent-oil ratio=1:20). The S-content of supernatant was analyzed by an ANTEK 9000 NS analyzer. The desulfurization capacity of adsorbent was calculated by the following formula: $Q_t = \rho V (C_0 - C_t) / 1000M$, where Q_t is the adsorption capacity of sulfur adsorbed on the adsorbent (mg/g), ρ is the density of the simulated fuel at room temperature (g/cm³), V is the volume of the simulated fuel (mL), M is the mass of the adsorbent (g), C_0 is the initial sulfur concentration of the simulated fuel (μ g/g), and C_t is the sulfur concentration of the simulated fuel (μ g/g) at any time t (h).

3. Results and Discussion

3.1. XRD characterization of MOFs

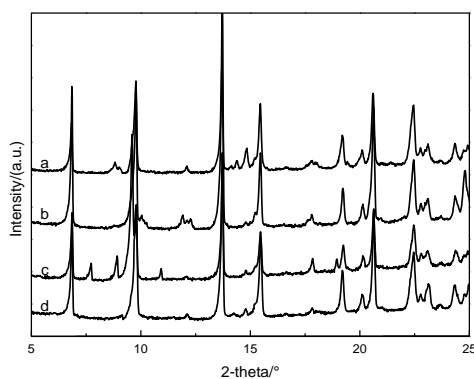


Fig. 1. XRD patterns of (a) Cu-MOF-5, (b) Mn-MOF-5, (c) Co-MOF-5, (d) MOF-5 samples.

The XRD patterns of metal-doped MOF-5 and undoped MOF-5 are plotted in Figure 1. The sharp peaks of all samples at 2θ values of 6.8° , 9.7° , 13.4° , 15.7° indicate that the textures of M-MOF-5 are in accord with MOF-5. This proves the successful synthesis procedure. And the topology construction of MOF-5 is not corrupted by metal cation exchange.

3.2. FT-IR characterization of MOFs

The FT-IR spectra of the undoped and metal-doped MOF-5 are plotted in Figure 2, further confirming the structure of MOF-5. The spectra confirm that the metal-doped MOF-5 materials still have all functional groups and MOF-5 bonds forming in both the samples.

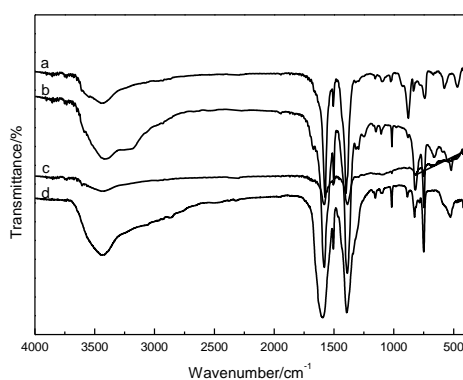


Fig. 2. FT-IR spectra of (a) Cu-MOF-5, (b) Mn-MOF-5, (c) Co-MOF-5, (d) MOF-5 samples.

3.3. Adsorption desulfurization performance of MOFs

The Table 1 shows the desulfurization performance of MOF-5 and functionalized M-doped MOF-5 samples at 4 hours. The desulfurization performance for thiophene decreases in the order Cu-MOF-5 > Co-MOF-5 > Mn-MOF-5 > MOF-5, while the sulfur adsorption capacity for BT, DBT decreases is similar. It indicates that the center metal of MOF-5 plays a vital role in the removal of thiophenic compounds. The thiophene uptake capacity of Cu-MOF-5 has been an appreciable increase in comparison with the MOF-5, which is attributed to the accessible active Cu (II) sites to form π -complexation.

Table 1. Desulfurization capacity of thiophenic compounds with M-MOF-5 and undoped MOF-5.

desulfurization capacity/(mg·S·g ⁻¹)	MOF-5	Cu-MOF-5	Co-MOF-5	Mn-MOF-5
T	1.25	1.80	1.48	1.40
BT	1.03	1.60	1.35	1.18
DBT	0.52	0.92	0.74	0.75

4. Conclusions

Transition metal- doped MOF-5 adsorbents were prepared by direct hydrothermal synthesis for the removal of thiophenic compounds in model fuel. The structure of products verified from the XRD and FT-IR. It was finally found that center metal has an influence on the adsorption performance of MOF-5. And the Cu-MOF-5 showed the excellent adsorption capacity under the same experimental conditions. Improvement of adsorption capacity of MOF-5 by optimizing the pore texture and exchanging center metal should be a promising prospect.

References

1. G. Chen and S. Tan, Metal Organic Frameworks for Selective Adsorption of t-Butyl Mercaptan from Natural Gas. *Energy&Fuels***29**, 5 (2015).
2. Y. Shi and X. Zhang, MOF-Derived Porous Carbon for Adsorptive Desulfurization. *AIChE J.* **60**, 8 (2014).
3. I. Ahmed and S. H. Jhung, Adsorptive desulfurization and denitrogenation using metal-organic Frameworks. *J. Hazard. Mater.***301**, 259 (2016).
4. W. Zhen and B. Li, Enhancing catalytic activity and stability for CO₂methanation on Ni@MOF-5 via control of activespecies dispersion.*Chem. Commun.***51**,1728(2015).
5. U. Mueller and M. Schubert, Metal-organic frameworks-prospective industrial applications. *J. Mater. Chem.***16**, 626(2006).