AIChE Letter: Separations: Materials, Devices and Processes

MOF-Derived Porous Carbon for Adsorptive Desulfurization

Yawei Shi, Xiangwen Zhang, Li Wang, and Guozhu Liu
Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and
Technology, Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin University,
Tianjin 300072, China

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Significance

ZIF-8, a typical and popular type of MOFs, was synthesized and carbonized directly to produce highly porous carbon without washing or activation. The resulting carbon was found to be a promising candidate for adsorption desulfurization of DBT with a maximum adsorption capacity of 26.7 mgS/g in the concentration range below 174 ppmS, and the adsorption capacity decreased approximately 17% with the addition of 10% para-xylene. © 2014 American Institute of Chemical Engineers *AIChE J*, 60: 2747–2751, 2014

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Desulfurization of liquid hydrocarbon fuels has attracted increasing attention due to adverse environmental impacts of sulfur oxides present in engine exhaust emissions.[1,2] Adsorption desulfurization is considered to be one of the most promising methods to overcome the limitations with the traditional hydrodesulfurization process.[3–5] Various types of materials have been developed and investigated, including ion-exchanged zeolites,[3,6–8] carbon materials,[9–11] mesoporous aluminosilicates,[12,13] and metal oxides.[14–16] Besides, several meta-organic frameworks (MOFs) have been shown promising for adsorptive desulfurization,[17–21] but organic solvents were generally involved in the synthesis approaches, which were expensive, toxic, and flammable.[22] Recently, easy and cost-effective synthesis of zeolitic imidazolate framework-8 (ZIF-8), a typical and popular type of MOFs, has been achieved in aqueous solutions, showing great potential for large-scale production.[22,23] However, due to its small pore opening or unselective adsorption, ZIF-8 was shown to be ineffective for adsorption desulfurization.[24] Conversely, several MOFs have been demonstrated as promising precursors toward porous carbons, and the resulting carbon materials have been proved to be efficient in several adsorption processes such as hydrogen storage and CO_2 capture.[25,26] Thus, we infer that this kind of carbon may be promising for adsorptive desulfurization as well. In this Letter, highly porous carbon was synthesized by one-step carbonization of homemade ZIF-8, which was synthesized in an easy and cost-effective approach, without any additional carbon sources, and no further washing or activation was conducted. The resulting material was shown to be promising for the adsorption of dibenzothiophene (DBT) from its solution in *n*-hexane or *n*-hexane/para-xylene.

ZIF-8 was synthesized in a tenfold amount according to a previous report,[22] detailed in Supporting Information. It should be noted that ZIF-8 crystals were produced from stoichiometric precursors in aqueous ammonia solution without any other additives at room temperature in a short period of time (10min). As is shown in Figure 1a, the X-ray diffraction (XRD) pattern of the product was in accordance with the simulated sodalite (SOD)-type ZIF-8 structure,[22] confirming the successful crystallization of pure ZIF-8. Thermal gravimetric analysis (TGA) curve of the as-synthesized ZIF-8 conducted under air flow gave a total weight loss of approximately 64% (Figure 1b), in good agreement with the calculated value from $Zn(C_4H_5N_2)_2$ into ZnO. The Fourier-transform infrared spectroscopy (FT-IR) spectrum of the as-synthesized ZIF-8 (Figure 1c) is also in accordance with previous reports.[22]

By direct carbonization of the as-synthesized ZIF-8 at 950°C in nitrogen atmosphere, porous carbon was directly obtained. As observed by scanning electron microscope (SEM) (see Figure S1 in Supporting Information), the obtained nanoporous carbons retained a typical cubic morphology similar to that of the parent ZIF-8 (Figure 1d), suggesting that the carbon content of ZIF-8 is sufficient for the formation of carbon materials. XRD pattern of the

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Additional Supporting Information may be found in the online version of this article.

Correspondence concerning this article should be addressed to G. Liu at gliu@tju.edu.cn.

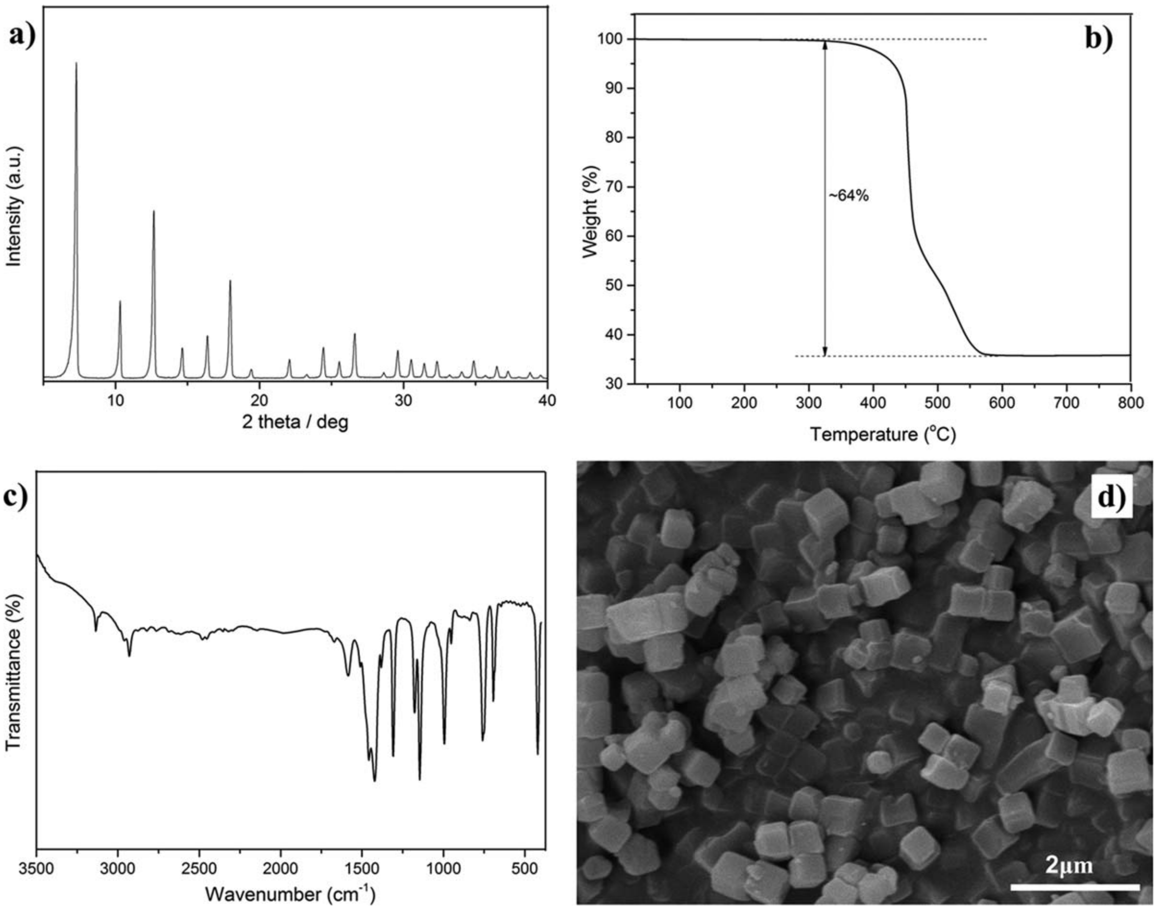

Figure 1. XRD pattern (a), TGA curve (b), FTIR spectrum (c), and SEM image (d) of as-synthesized ZIF-8.

synthesized carbon (Figure 2a) displayed two broad peaks at around 22° and 43°, suggesting the amorphous structure of the carbon.[27] Raman spectra of the obtained carbon is shown in Figure 2b, where D and G bands are located at 1328 and 1588 cm^{-1}, respectively arising from the disordered carbon structures and the vibration mode to the movement in opposite directions of two carbon atoms within a single graphene sheet.[25] The relative intensity ratio (I_D/I_G) is 1.04, suggesting that the graphene sheets were not well developed,[27] in accordance with the XRD pattern. Besides, no diffraction peaks of Zn impurities could be observed in the XRD pattern. During the carbonization process, ZnO was produced initially and further reduced to Zn by carbon.[27] The reduced Zn might act as a template to support the formation of porous carbon and, then, would be evaporated at the temperature above the boiling point of Zn (908°C).[25,27] It was estimated that almost 99% zinc was removed based on EDS (see Supporting Information Figure S2b) and ICP measurements (see details in Supporting Information).

The nitrogen-sorption isotherm for the as-synthesize carbon is shown in Figure 2c. The sample showed typical Type I isotherms with a sharp uptake at low relative pressure ($P/P_0 < 0.15$), demonstrating that the sample has a microporous structure. The Brunauer–Emmett–Teller (BET) surface area and total pore volume were calculated to be 1913 m^2/g and 0.84 cm^3/g, respectively. Generally, to develop the pore network in carbon materials, physical or chemical activation is often required.[28] During the carbonization process of ZIF-8, ZnO was reduced by carbon, resulting in Zn and carbon oxides. The release of these species might be responsible for generating the pore network.[25] The pore size distribution of the sample (Figure 2d) was evaluated by nonlocal density functional theory (NL-DFT) method. As reported previously,[9] the sulfur capacity of carbon materials depends strongly on the volume of pores smaller than 1 nm. This value of the ZIF-8 derived carbon was found to be 0.40 cm^3/g (see Figure S3 in Supporting Information), which is a relatively high one compared to previous reports.[9,29] This indicates that the carbon may be a potential candidate for adsorptive desulfurization of transportation fuels. Elemental analysis (see Table S1 in Supporting Information) showed that the carbon contained a small amount of nitrogen, which may be beneficial for the adsorption of DBT due to the enhancement of polar–polar interactions.[30]

The isotherms of the carbon for the adsorption of DBT using different solvents (*n*-hexane or *n*-hexane/para-xylene = 90%/10%) were measured at 25°C in the concentration range below 174 mgS/kg. Kinetic studies were performed in advance to decide an appropriate contact time (Figure S4 and Table S2 in Supporting Information). The adsorption isotherms were plotted to follow Langmuir and Freundlich equation (Figure 3 and see details in Supporting

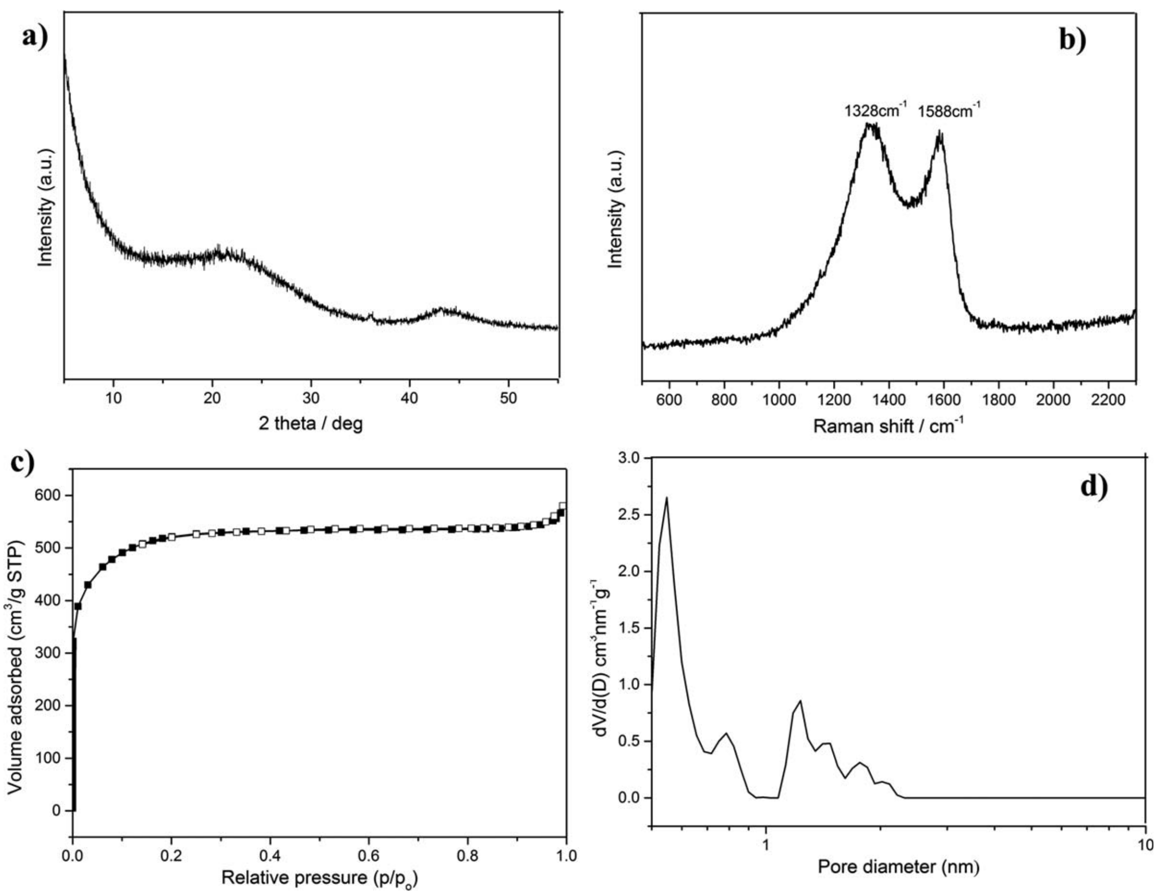

Figure 2. XRD pattern (a), Raman spectrum (b), nitrogen-sorption isotherm (c), and the corresponding NL-DFT pore size distribution (d) of ZIF-8 derived carbon.

Information). The calculated parameters using nonlinear fitting together with the related regression coefficient (R^2) values are summarized in Supporting Information Table S3. The calculated maximum adsorption capacity ($q_{\max}$) for ZIF-8 derived carbon in pure *n*-hexane was 26.70 mgS/g. In the presence of 10% para-xylene (in hexane), $q_{\max}$ decreased by 17.0% to 22.17 mgS/g. This was attributed to the competitive adsorption of DBT and para-xylene.[18] For comparison, Table 1 summarizes the capacity of several carbon adsorbents and some noncarbonaceous materials toward DBT. Note that the adsorption measurements were conducted in

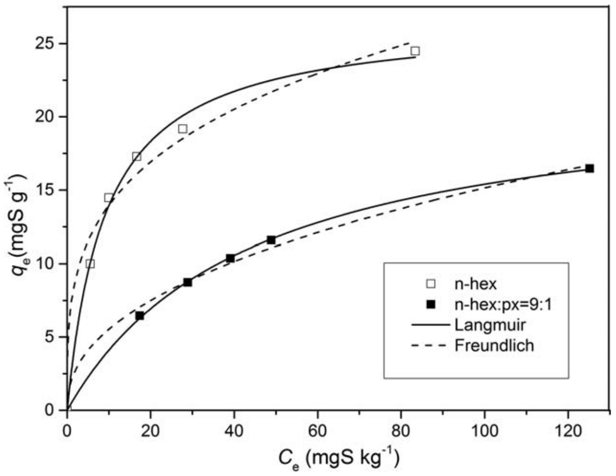

Figure 3. Adsorption isotherms of DBT in *n*-hexane or *n*-hexane: para-xylene = 9:1 at 25°C on ZIF-8 derived carbon.

Table 1. Comparison of DBT Adsorption Capacity

Adsorbent	Solvent	C_0 (mgS/kg)/ System	$q_{\max}$[d]	Ref.
MIL-101	*n*-octane	<2000/batch	28.9	18
MOF-5	*iso*-octane	300/fixed bed	12.7	20
MOF-5	*iso*-oct:tol[b] (85:15)	300/fixed bed	9.1	20
MOF-505	*iso*-octane	300/fixed bed	20.5	20
MOF-505	*iso*-oct:tol[b] (85:15)	300/fixed bed	14.9	20
Activated Al_2O_3	*n*-hexane	<174/batch	21.0	14
CMK-3	*n*-hexane	<261/batch	10.9	11
CMK-5	*n*-hexane	<261/batch	21.7	11
Carbon aerogel	*n*-hexadecane	<696/batch	15.1	31
AC[a]	*n*-octane	300/batch	28.9	32
AC spheres	*n*-octane	<124/batch	17.6	33
Cu(I)-Y zeolite	*n*-octane	~690/batch	32.6	34
Co-Y zeolite	*n*-octane	~690/batch	29.4	34
Ce/Ni-Y zeolite	*n*-octane	~124/batch	22.2	35
ZIF-8-derived	*n*-hexane	<160/batch	26.7	This
ZIF-8-derived	*n*-hex:para[c] (9:1)	<174/batch	22.2	This

[a] Activated carbon.
[b] Toluene.
[c] Para-xylene.
[d] mgS/g.

different concentration ranges. Typically, the higher solution concentration, the higher adsorption capacity.[11] Also, saturation has not been reached for the isotherm, indicating that the carbon has the potential for higher adsorption amounts.[19] Meanwhile, the carbon used here is the unmodified form. Previous works have demonstrated that incorporation of metals[29,36–38] or functional groups[1] could enhance the interactions between the carbon framework and sulfur compounds and, thus, cause an increase in the capacity and selectivity for adsorption. Thus, the adsorption capacity may be further enhanced after modification.

In brief, ZIF-8 was synthesized and carbonized directly to produce highly porous carbon ($S_{\mathrm{BET}} = 1913$ $\mathrm{m^2/g}$) without washing or activation. The whole synthesis process is easy and cost-effective. The resulting carbon was found to be a promising candidate for adsorption desulfurization with a maximum DBT adsorption capacity of 26.7 mgS/g in the concentration range below 174 ppmS, and the adsorption capacity decreased approximately 17% with the addition of 10% para-xylene.

Acknowledgments

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