Focus Issue Paper

Carbonization and oxidation of metal–organic frameworks based on 1,4-naphthalene dicarboxylates

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Abstract
Three new isostructural metal–organic frameworks (MOFs), [V(OH)(NDC)] (1), [Cr(OH)(NDC)] (2), and [Ga(OH)(NDC)] (3) have been synthesized hydrothermally using 1,4-naphthalene dicarboxylate (NDC) as the linker. These MOFs (1, 2 and 3) have been used as a template for the synthesis of metal-oxide-inserted nanoporous carbon materials. The newly synthesized MOFs and the resulting porous carbon hybrid functional materials have been characterized using powder x-ray diffraction, scanning electron microscopy, transmission electron microscopy, and energy dispersive x-ray spectroscopic analysis. Results show that compounds 2 and 3 form their respective metal oxide nanoparticles on the surface of the carbon materials during carbonization at 800 °C. The gas sorption properties of the new MOFs and their corresponding carbon frameworks have been reported.

Keywords: nanoporous carbon, metal oxide nanoparticle, metal–organic frameworks

1. Introduction
Metal–organic frameworks (MOFs) have seen a rapid growth in the past decade because of their interesting structural properties and potential applications in different fields [1–7]. Among the strategies applied for the synthesis of MOFs, the isoreticular concepts provide many advantages for the structural design and functional applications of MOFs [8, 9].

On the other hand, since porous carbon materials have a high surface area, tunable porous structure, high thermal stability, chemical stability, and adsorption ability, they are widely used in a variety of applications such as adsorbents [10], separation membranes [11], super capacitors [12], sensors [13], and so on. Porous carbon materials can be prepared in many ways, such as activation, carbonization of polymers, and template synthesis [14–17]. In this regard, inorganic porous materials, such as mesoporous silica and zeolites, have been successfully used as templates for the synthesis of porous carbon functional materials in recent years [15, 16]. Each method has its own merits for the formation of carbon frameworks with controlled pore size and/or enhanced surface.
Since the metal centers and organic bridging linkers are well organized in MOFs, they were recently shown to be suitable precursors for constructing porous carbon frameworks [10]. Further, due to the confinement effect of MOFs, the regular arranged metal centers can be transformed into metal/metal oxide nanoparticles during the carbonization process, while the organic bridging linkers tend to form fine porous carbon frameworks [20]. So, this in situ approach leads to dispersion of the metal/metal oxide nanoparticles throughout the carbon frameworks. It is interesting to note that the resulting carbon frameworks have prevented the metal/metal oxide nanoparticles from aggregating [20].

Although many carbon nanocomposite materials have already been synthesized using MOFs as precursors in recent years [10, 12, 13], the design and construction of carbon frameworks from MOF precursors are still in a developing stage. Also, the direct synthesis of carbon–metal oxide hybrid materials from a MOF as a single precursor is still rare [20, 21]. With this background in mind, we have synthesized three new isostructural MOFs ([M(OH)(NDC)] (1–3), where $M = V$, Cr, and Ga respectively) having the same organic linker (1,4-naphthalene dicarboxylate, NDC) but different metal cations ($V^{3+}$, $Cr^{3+}$, $Ga^{3+}$), and utilized them as precursors for the synthesis of a nanoporous carbon matrix through a simple one-step thermal conversion without using any additional carbon source.

2. Experimental section

All reagents were commercially available and used as received without further purification. The hydrothermal reactions were carried out by heating the reaction mixtures in 23 mL Teflon-lined digestion bombs to the desired temperature under autogenous pressure, followed by slow cooling at the rate of $6^\circ\text{C} \text{h}^{-1}$ to room temperature. The phase purity of all the compounds was examined by powder x-ray diffraction (PXRD) using a Bruker D2 PHASER instrument. Elemental analyses were carried out using an Elemental vario EL III Heraeus CHNOS Rapid F002 instrument. Thermal gravimetric analyses (TGA) using a DuPont TA Q50 analyser were performed on powder samples under flowing $N_2$ with a heating rate of $10^\circ\text{C} \text{min}^{-1}$. The gas sorption isotherms were measured at 77 K for $N_2$, and 273 and 298 K for CO$_2$ using an ASAP 2020 system of Micromeritics. Ultrahigh purity grade CO$_2$, $N_2$, and He were used as received. Before the gas sorption measurements, the sample was initially dehydrated at 423 K for 24 h under vacuum. Scanning electron microscopy (SEM, using a JEOL JEM-7600F instrument) and transmission electron microscopy (TEM, using a JEM-2010 instrument) were employed to characterize the morphology.

In a typical synthesis of the MOFs, the mixture of VCl$_3$ (0.154 g, 1.0 mmol), $H_2$NDC (0.108 g, 0.5 mmol), and $H_2$O (10 mL) was placed in a 23 mL Teflon autoclave and then heated at 180 $^\circ\text{C}$ for 1 day. A light-green powder of 1 was obtained (yield: 0.115 g). Elemental analysis, found calculated: C, 47.96/48.02; H, 3.11/3.02% for $1\cdotH_2$O. MOF 2 was synthesized by same procedure with CrCl$_3$·6H$_2$O (0.266 g, 1.0 mmol), $H_2$NDC (0.108 g, 0.5 mmol), and $H_2$O (5 mL) at 220 $^\circ\text{C}$ for 3 days. A pale-green powder of 2 was obtained (yield: 0.142 g). Elemental analysis, found/calculated: C, 38.07/38.61; H, 4.00/4.60% for $2\cdot5H_2$O. A similar reaction mixture ratio and conditions as those used for the synthesis of 1 were used for the synthesis of 3 except that of Ga(NO$_3$)$_3$·xH$_2$O instead of VCl$_3$. A white powder of 3 was obtained (yield: 0.126 g). Elemental analysis, found/calculated: C, 40.60/40.60; H, 3.19/3.69% for $3\cdot3H_2$O.

The synthesis of porous carbon framework materials involves simple one-step direct carbonization using the synthesized MOFs as precursors. The MOFs (0.200 g) were taken in a silica boat and then placed in a tube furnace and heated from room temperature to 800 $^\circ\text{C}$ under $N_2$ gas with a heating rate of 5 $^\circ\text{C} \text{min}^{-1}$ to carbonize the MOFs. After reaching the target temperature (800 $^\circ\text{C}$), the temperature was maintained at 800 $^\circ\text{C}$ for 5 h, after that cooled down to room temperature with a cooling rate of 1 $^\circ\text{C} \text{min}^{-1}$. The final black colored powder products were further characterized.

3. Results and discussion

The simple hydrothermal reactions of $H_2$NDC (0.5 mmol) with the corresponding metal salts (1.0 mmol) yielded the new MOFs. The new MOFs have initially been characterized by elemental analysis which agreed well with theoretical values. The phase purity of the bulk materials was independently confirmed by PXRD measurements (figure 1). On comparing the PXRD patterns of 1–3 with one another showed that the three new MOFs are isostructural to each other. Further comparison of these PXRD patterns with calculated PXRD patterns of reported aluminum naphthalene dicarboxylate (Al-NDC) MOF material [22] confirms that these new MOFs (1–3) have the same type of structural architecture as Al-NDC (isostructural).
The TGA measurements for the compounds were performed under N2 atmosphere and the results are shown in figure S1. The slight weight loss observed initially (up to 80 °C) for compounds 2 and 3 may be due to the presence of small lattice water molecules in it. TGA studies indicated that all the compounds are stable up to 300 °C. This was further confirmed through in situ PXRD measurements at various temperatures for all the compounds (figures 2–4). Further, the compounds were heated at various temperatures for one hour, and the corresponding images are given in figures S2–S4. The compounds showed a stable color up to 300 °C owing to their high thermal stability. The calcined products of 1–3 at 600 °C were characterized using PXRD measurements and compared with calculated PXRD patterns of their corresponding metal oxides (figures S5–S7). The results indicated that the compounds 1, 2 and 3 were converted to their corresponding metal oxides (V2O5, Cr2O3 and Ga2O3 respectively) during calcination at 600 °C for one hour.

The porosity of the new MOFs has been analyzed using N2 gas sorption measurements at 77 K (figure 5) and the results are shown in table 1. The results indicated that compound 1 has a better pore structure than 2 and 3 (which showed a non-porous nature and adsorption takes place at the external surface). However, the CO2 gas sorption measurements showed that compounds 2 and 3 have a porous nature.

The CO2 gas sorption isotherms for compounds 1–3 at 273 and 298 K are given in figures 6–8. Compounds 1–3 showed CO2 adsorption of 1.65 mmol g⁻¹, 3.07 mmol g⁻¹, and 1.86 mmol g⁻¹, respectively, at 273 K, 1 atm; whereas 0.89 mmol g⁻¹, 1.60 mmol g⁻¹, and 1.00 mmol g⁻¹ of CO2

| MOFs | BET surface area (m² g⁻¹) | Langmuir surface area (m² g⁻¹) | Total pore volume (cm³ g⁻¹) |
|------|--------------------------|-------------------------------|----------------------------|
| 1    | 107                      | 292                           | 0.53                       |
| 2    | 33                       | 48                            | 0.02                       |
| 3    | 31                       | 45                            | 0.03                       |

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![Figure 2. PXRD patterns of 1 at various temperatures.](image)

![Figure 3. PXRD patterns of 2 at various temperatures.](image)

![Figure 4. PXRD patterns of 3 at various temperatures.](image)

![Figure 5. The N2 gas adsorption isotherms for 1–3 at 77 K.](image)

![Figure 6. The CO2 gas sorption isotherms for 1 at 273 K and 298 K.](image)
adsorption have been observed for compounds 1–3, respectively, at 298 K and 1 atm.

In order to study the application possibilities of compounds 1–3, they were used as templates to synthesise nanoporous carbon materials. In a typical carbonization procedure, MOFs (1–3) were calcined at 800 °C under nitrogen gas flow for 5 h. The final products were characterized with the aid of various techniques. The carbonized products from 1, 2 and 3 are designated as 1c, 2c and 3c respectively. Compounds 1c–3c were initially characterized using PXRD measurements which indicated that 1c has a disordered-oriented graphitic type structure (figure 9). At the same time, the PXRD patterns matching 2c with Cr2O3 (figure 10) and 3c with Ga2O3 (figure 11) suggested the presence of their corresponding metal oxide particles in the synthesized carbon hybrid materials.

The comparison SEM images of 1, 2 and 3 with 1c, 2c and 3c respectively (figure 12) suggested that the obtained nanoporous carbons retained a typical crystal morphology similar to that of the parent MOFs. Further, the SEM images of 2c and 3c revealed that the surface of nanoporous carbon samples embedded with their corresponding metal oxide nanoparticles. The SEM observations were confirmed by TEM images of the carbon materials (figures 12(C), (F) and (I)). The compositions of the carbon matrix and the metal oxide nanoparticles were confirmed by energy dispersive x-ray spectroscopy (EDS) analysis and the results are given in figures S8–S10.

Further investigation of the local structure of the synthesized carbon materials was achieved by Raman spectroscopy. Raman spectra of the obtained carbon samples are shown in figure 13, exhibiting D and G bands centered around 1320 cm⁻¹ and 1600 cm⁻¹, respectively, which may be due the disordered carbon structures and the stretching vibrations.
in opposite directions of two carbon atoms in a graphene sheet. The relative ratios of the G band to the D band \( \left( \frac{I_G}{I_D} \right) \) were found to be 1.15, 1.08, and 1.03 for 1c, 2c and 3c, respectively, suggesting that the graphene sheets were not well developed in all samples and the local carbon structures contained both graphitic and disordered carbon atoms [12].

The nitrogen gas adsorption analysis was used to further characterize the nanoporous structure of 1c, 2c and 3c (figure 14). The shape of the isotherms indicated the existence of both micropores and mesopores. The steep increase at low relative pressure indicates the presence of micropores. The isotherms showed a small hysteresis which is typical for the presence of spherical mesopores randomly connected with weak microporosity. The analyzed pore characteristics of the carbon materials are summarized in table 2. Further, the pore size distribution results for 1c–3c obtained using the density
Figure 14. The N$_2$ gas adsorption isotherms for 1c–3c at 77 K.

Table 2. Pore characteristics of the obtained nanoporous carbons.

| Materials | BET surface area (m$^2$ g$^{-1}$) | Langmuir surface area (m$^2$ g$^{-1}$) | Total pore volume (cm$^3$ g$^{-1}$) | P/P$_o$ $\sim$ 0.99 |
|-----------|----------------------------------|----------------------------------------|-----------------------------------|----------------------|
| 1c        | 43                               | 75                                     | 0.14                              |                      |
| 2c        | 435                              | 620                                    | 0.36                              |                      |
| 3c        | 274                              | 373                                    | 0.19                              |                      |

A functional theory (DFT) method are shown in figure S11. The results indicated that 1c mostly shows a mesoporous nature, which may be due to the lower stability of the microporous structure of 1 during carbonization, whereas compounds 2c and 3c showed some kind of microporosity along with their mesoporous nature. There are a large number of pores of different sizes (2 $\sim$ 20 nm) observed for all three compounds. Overall, it is interesting to note that the pore structures of the carbon materials are better than those of their parent MOF materials, but are not necessarily better than those reported in the literature. Since the pore structure and surface area of the resultant carbon materials can be tuned simply by changing the calcination temperature, the experimental carbonization temperature (800 °C) may not be the ideal one to make the best porous carbon materials from our new MOFs. Hence, although compound 1 has the highest surface area among these new MOFs, its derived carbon material 1c has a lower surface area than the other carbon materials (see tables 1 and 2).

4. Conclusions

In summary, three new isostructural MOFs based on an NDC linker have been prepared and characterized. Using these MOFs as precursor materials, metal oxide nanoparticle inserted nanoporous carbons were prepared by simple direct carbonization without using any additional carbon sources. The PXRD, SEM, TEM, EDS and nitrogen sorption measurements confirm the dispersion of metal oxide nanoparticles on the resulting nanoporous carbon materials. Further application studies of these metal oxide nanoparticle inserted porous carbon hybrid functional materials are in progress.

Acknowledgments

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