DOI: 10.1002/ejic.200901064

Effect of Water Concentration and Acidity on the Synthesis of Porous Chromium Benzenedicarboxylates

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Keywords: Metal–organic frameworks / Hydrothermal synthesis / Chromium benzenedicarboxylates / Acidity / Water

In the present work, two metal–organic frameworks (MOFs), chromium benzenedicarboxylates MIL-53 and MIL-101, have been synthesized. A wide range of reaction conditions were explored in order to understand the effects of water concentration and acidity. It was found that MIL-101 is preferentially obtained when the water content is high and the acidity is low. On the contrary, concentrated reactants and high acidity lead to the formation of MIL-53. The steady conversion of MIL-101 into MIL-53 during the reaction, due to the difference in relative stability, was also confirmed. The effect of water may therefore be explained by the increase in reaction rate with increasing concentration of reactants. The MIL-53 is selectively obtained at low water content, because the MIL-101, a transient phase, even if formed initially, may be converted into MIL-53 because of the high reaction rate. Relatively low acidity (a pH of about 3) is beneficial to the synthesis of MIL-101 even though increased MIL-53 yield was expected at low acidity due to the accelerated deprotonation of terephthalic acid. The selective formation of MIL-101 at low acidity is probably because the concentration of a chromium trimer (the chromium species that is essential for the MIL-101 structure) increases with increasing pH. The concentration of the Cr trimer is more important than the concentration of benzenedicarboxylate for the synthesis of MIL-101.

Introduction

The number of materials exhibiting permanent nanoporosity have expanded rapidly in recent years, due in large part to the discovery of organic–inorganic hybrid materials including metal–organic frameworks (MOFs) and coordination polymers.[1] The major applications currently being considered for these compounds involve gas storage/adsorption,[2] catalysis,[3] separations,[4] drug delivery,[5] and their use as carriers for nanomaterial/nanoparticle thin films.[6] Two chromium benzenedicarboxylates (Cr-BDCs), MIL-53[7] and MIL-101,[8] having high surface area and pore volume, were synthesized from chromium nitrate and terephthalic acid (TPA) or 1,4-benzenedicarboxylic acid (H_2-BDC) under autogenous pressure at high temperature. MIL-53, $Cr(OH)[C_6H_4(CO_2)_2]$, has an orthorhombic structure and a pore volume of 0.6 cm^3/g.[7] MIL-101, $Cr_3O(F/OH)(H_2O)_2[C_6H_4(CO_2)_2]$, has a cubic structure and large pore volume.[8] The pore sizes of MIL-53 and MIL-101 are about 0.85 and 2.9–3.4 nm, respectively.[7,8] MIL-53 is very interesting because of the breathing effect,[9] and it has been widely studied for adsorption[10] and drug delivery.[11] MIL-101 is a very important material, because of its mesoporous structure and large porosity, and it is widely studied for adsorption,[12] catalysis,[13] and drug delivery.[11]

However, the majority of research on MOFs has been focused mainly on the synthesis of new structures and structure determination, even though reproducible synthesis, through an understanding of the effect of process parameters, is very important not only for commercial applications but also in terms of increasing our fundamental knowledge of these systems. To the best of our knowledge, there are few reports on the effect of reaction conditions on the structure, yield, stability, and kinetics of MOF synthesis. Forster et al. reported the effect of reaction temperature on the synthesis of hybrid organic–inorganic materials (cobalt succinates).[14] They also systematically studied the effect of pH, temperature, and concentration on the synthesis of similar cobalt succinates by using high-throughput methods and could discover two additional structures.[15] The effect of synthesis parameters (such as precursors, solvents, temperature) on the preparation of Cu-BTC, MOF-5, and MIL-101-NDC has also been studied.[16] Very recently, Mahata et al. synthesized MOFs under a wide range of reaction conditions and suggested that thermodynamics is more important than kinetics in synthesis.[17] However, there has been no study on the effects of synthesis conditions on the preparation of important and interesting MOF materials including chromium BDCs. It is very interesting to study the syntheses of Cr-BDCs such as MIL-101 and MIL-53 in detail, because two well-known phases can be produced from nearly the same reactant composition.[7,8]

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In this work, the effects of process parameters such as water concentration and acidity on the syntheses of Cr-BDCs are reported. In this study, syntheses were carried out not only by conventional electric (CE) heating but also by microwave (MW)[18] irradiation, because the MW-syntheses of porous materials have many advantages, such as fast crystallization[18] and phase selectivity.[19] Recently, the MW technique has also been applied in the synthesis of organic–inorganic hybrid materials including MOFs, and several advantages such as high reaction rate,[20] homogeneous and decreased crystal size,[21] and phase selectivity[22] were reported. The MW syntheses are especially helpful for rapid evaluation of process parameters of a synthesis, because of the increased reaction rate.[23]

Results and Discussion

In this study, the effect of water concentration was studied at first, because the MIL-53 and MIL-101 were obtained from reaction mixtures having the same composition except for slightly different water concentrations.[7,8] The synthesis was carried out by starting from chromium chloride hexahydrate, H_2-BDC (TPA), and water.[7,8]

Figure 1 shows the XRD patterns of Cr-BDCs obtained by both conventional electric (CE) heating and microwave (MW) irradiation, depending on the concentration of water in the reaction mixture. By comparing them with previous XRD patterns,[7,8] it can be found that the MIL-53 and MIL-101 are formed mainly when the water content is low and high, respectively, for both CE and MW syntheses. However, the existence of other Cr-BDCs, such as MIL-88B,[24] cannot be completely ruled out because of the low signal/noise ratios of the XRD patterns. Figure 2 clearly demonstrates that the MIL-101 yield increases with increasing water concentration. However, the yield of MIL-53 decreases with increasing water content. From the same reaction mixtures, excluding the effect of water concentration, MIL-101 and MIL-53 are selectively obtained when the H_2O/Cr molar ratio is greater than or equal to 500 and less than or equal to 200, respectively.

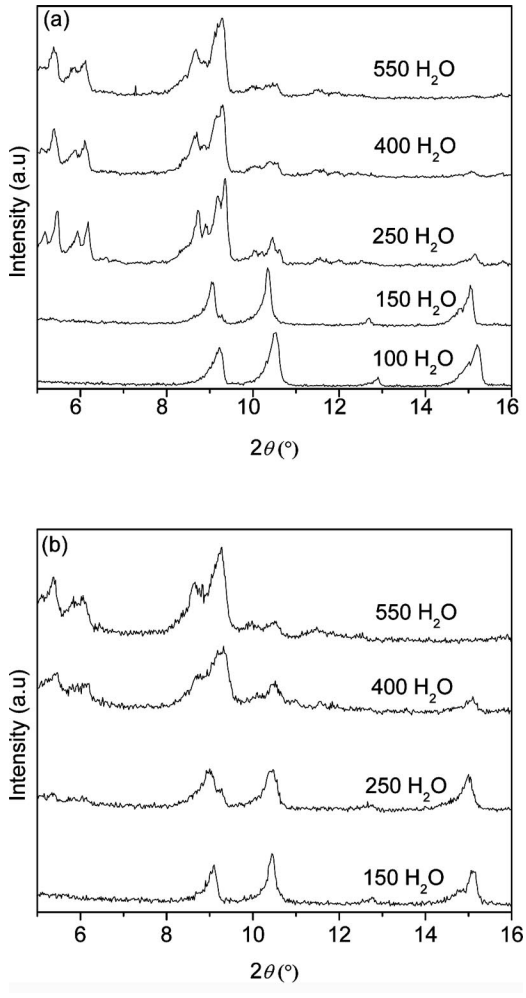

Figure 1. XRD patterns of the as-synthesized Cr-BDCs depending on the water concentration. The reactant composition was $CrCl_3 \cdot 6H_2O$/TPA/xH_2O, and the reaction was carried out at 210 °C with: (a) CE heating for 12 h; (b) MW heating for 3 h.

Generally, the rate of Cr-BDCs synthesis may be decreased by increasing solvent (water) concentration. In this study, it has also been established that MIL-101 can be con-

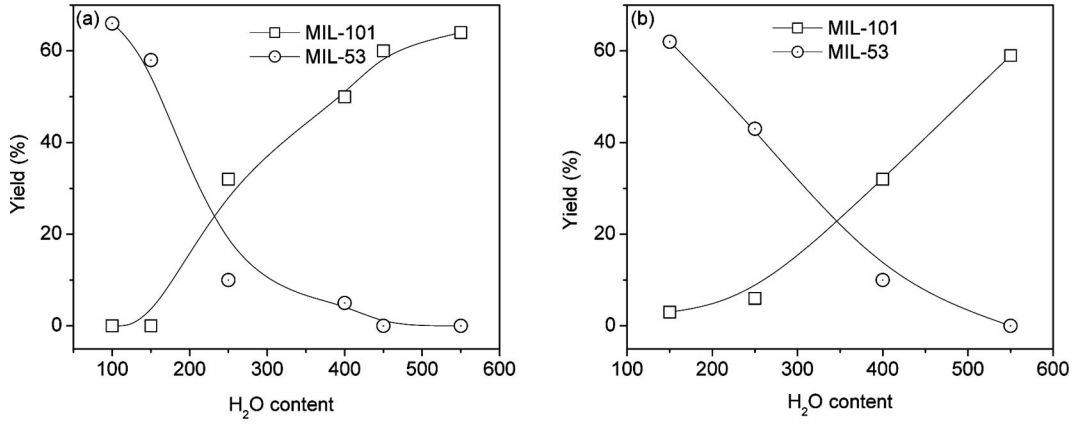

Figure 2. Changes in the yields of Cr-BDCs depending on the concentration of water. The reactant composition was $CrCl_3 \cdot 6H_2O$/TPA/xH_2O, and the reaction was carried out at 210 °C with: (a) CE heating for 12 h; (b) MW heating for 3 h.

verted into MIL-53 with the progress of the reaction, or as the reaction time increases (Figure 3), and this phase transformation can be explained by the relative stabilities of MIL-53 and MIL-101 (MIL-53 is more stable than MIL-101 under the reaction conditions). Such phase transformation between MIL-101 and MIL-53 will be reported in detail elsewhere.[25] Therefore, it may be assumed that the synthesis rate is decreased by increasing the water concentration, and the selective formation of MIL-101 at high water concentration is due to the slow reaction rate. On the contrary, MIL-53 is obtained at low water content, because MIL-101 (a transient phase), even if it is formed initially, may be converted into MIL-53. Interestingly, Forster et al. have shown that concentration is relatively unimportant[15] in the synthesis of cobalt succinates, probably because Co^{II} does not appear to have more complex solution species than Cr^{III}.

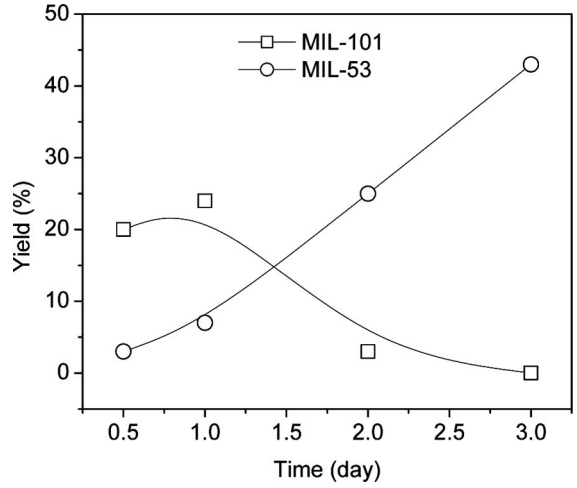

Figure 3. Changes of yields of Cr-BDCs depending on the reaction time. The reactant composition was $CrCl_3{\cdot}6H_2O$/TPA/$300H_2O$, and the reaction was carried out at 210 °C with conventional electric heating.

Figure 4 shows the typical nitrogen adsorption isotherms of MIL-53 and MIL-101, which were synthesized by CE heating for 12 h from reaction mixtures having H_2O/Cr = 100 and H_2O/Cr = 400, respectively. The nitrogen adsorption isotherms of MIL-53 and MIL-101 are similar to those reported earlier.[7,8] The adsorption isotherm of MIL-53 is typically of type-I, confirming the microporous structure of MIL-53. The BET surface area and pore volume of MIL-53, calculated from the adsorption isotherm, are 1436 m^2/g and 0.55 cm^3/g, respectively, and are similar to the previous results.[7] The adsorption isotherm of MIL-101 is similar to that of a type-IV material, because of the mesoporous structure of MIL-101.[8] The BET surface area and total pore volume are 3310 m^2/g and 1.56 cm^3/g, respectively, which are also similar to reported values.[8,13b] The SEM images (Figure 5) of MIL-101 and MIL-53 are homogeneous, illustrating the phase purity of the synthesized materials. However, it should be mentioned that MIL-101 may be slightly contaminated with MIL-53 considering the presence of a phase (in Figure 5a) having a morphology similar to that of MIL-53 in Figure 5b. From nitrogen adsorption isotherms and SEM images, it can be inferred that MIL-101 and MIL-53 can be selectively synthesized under the same reaction conditions, including the Cr/TPA ratio, by adequately changing only the water concentration.

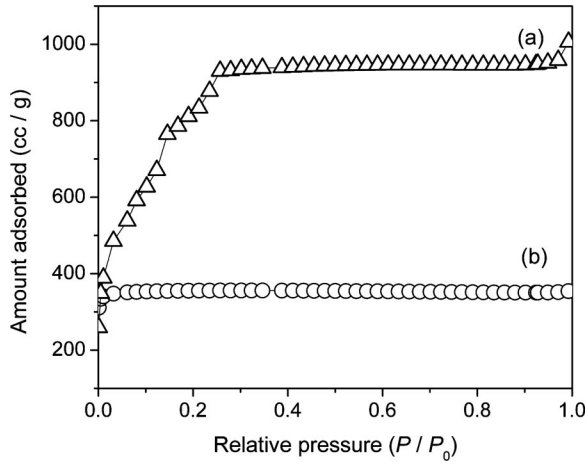

Figure 4. Nitrogen adsorption isotherms of typical Cr-BDCs that were obtained in 12 h at 210 °C by CE heating: (a) MIL-101 synthesized with a reactant composition of $CrCl_3{\cdot}6H_2O$/TPA/$400H_2O$; (b) MIL-53 obtained from a reactant composition of $CrCl_3{\cdot}6H_2O$/TPA/$100H_2O$.

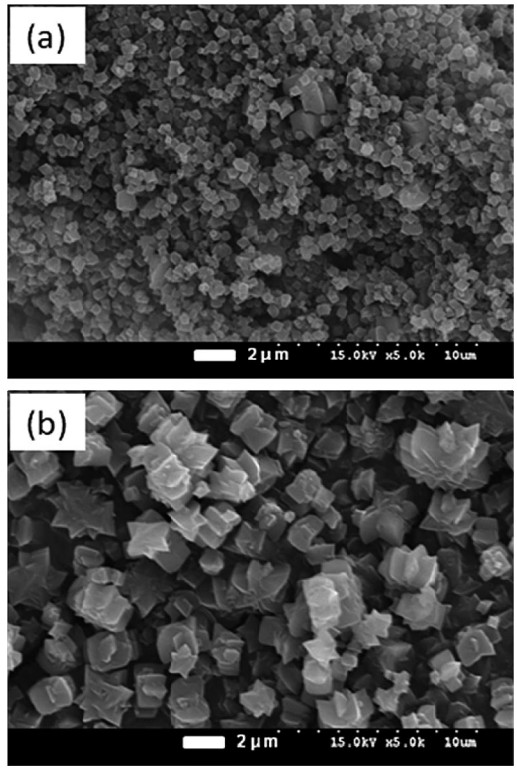

Figure 5. SEM images of typical Cr-BDCs that were obtained in 12 h at 210 °C by CE heating: (a) MIL-101 synthesized with a reactant composition of $CrCl_3{\cdot}6H_2O$/TPA/$400H_2O$; (b) MIL-53 obtained from a reactant composition of $CrCl_3{\cdot}6H_2O$/TPA/$100H_2O$.

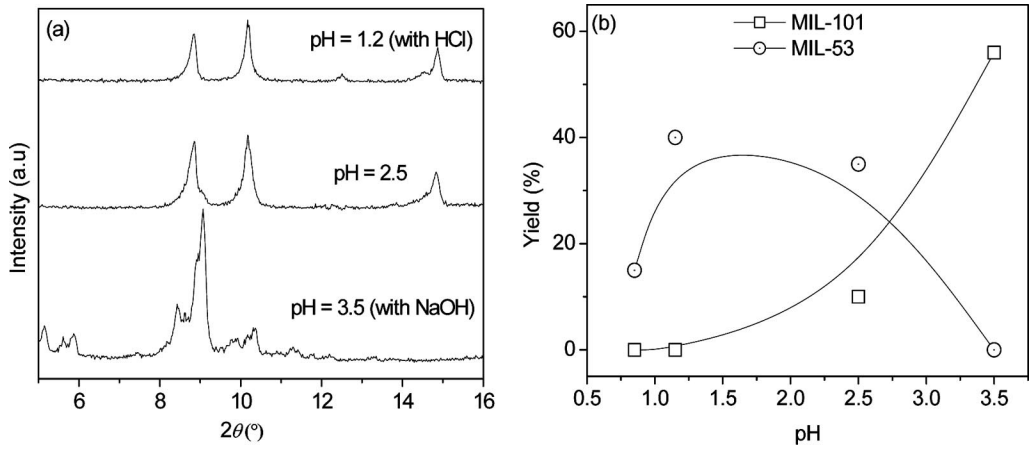

Figure 6. (a) XRD patterns of as-synthesized Cr-BDCs depending on the pH of the reaction mixture. (b) Yields of Cr-BDCs depending on the pH of the reaction mixture. For both cases, the reaction was carried out for 10 min at 210 °C by MW heating. The composition of the reaction mixture was $CrCl_3 \cdot 6H_2O$/TPA/100H_2O, and aqueous NaOH or HCl solution was used to control the pH.

The acidity, or pH, is very important[26] in the synthesis of many materials, because the chemical status of a reactant may be changed very much depending on the pH. As shown in Figure 6, the yield of MIL-101 increases with increasing pH, which is controlled by the addition of NaOH or HCl. *N,N*-dimethylformamide has a similar effect: it leads selectively to MIL-101 rather than MIL-53 (data not shown). However, too high a pH is not recommended for the synthesis of Cr-BDCs, because little product is obtained. On the contrary, the yield of MIL-53 is high at a low pH. At a very low pH of less than about 1.0, however, the synthesis is very ineffective (Figure 6b). At first, we thought that high pH would be beneficial for MIL-53, because the benzenedicarboxylate concentration would be increased and the reaction rate would also be high (to lead to MIL-53 rather than MIL-101) as the pH increases. However, MIL-101 is selectively obtained at a higher pH of around 3.5.

Even though it is not easy to explain the effect of pH on the synthesis of Cr-BDCs, it can be noted that a chromium trimer or super tetrahedron (ST) is necessary to build up the MIL-101 structure;[8] however, the trimer or ST is not necessary for the MIL-53 structure.[7] It has been known that the concentration of a chromium trimer increases (with decreasing monomer) upon increasing the pH from 2 or 4 depending on the concentration of the Cr^{III} monomer.[27] So, the yield of MIL-101 may be increased by increasing the pH as observed in this study. Therefore, it may be concluded that the concentration of the chromium trimer is more important than the concentration of benzenedicarboxylate for the synthesis of MIL-101.

Conclusions

The effect of synthesis conditions on the phase and yield of Cr-BDCs such as MIL-53 and MIL-101 has been studied to elucidate the synthesis of the MOF materials. A low water concentration is helpful to synthesize MIL-53, probably because of rapid reaction rate. It is also observed that MIL-101 is converted into MIL-53 with increasing reaction time. Therefore, MIL-101, even if it is obtained at low water concentration at the initial stage of the reaction, may be transformed into MIL-53, the product obtained from reaction mixtures having low water concentration.

Low acidity (relatively high pH up to 3.5) selectively leads to MIL-101 formation, even though it may be expected that the deprotonation of terephthalic acid to benzenedicarboxylate will be accelerated (and therefore MIL-53 may be selectively obtained) at a high pH. The selective formation of MIL-101 at relatively low acidity (pH of about 3) is probably due to the increase in concentration of the chromium trimer with pH (up to about 5–6). The chromium trimer is one of the essential components for the MIL-101 structure; however, the trimer is not necessary for the structure of MIL-53. Therefore, the concentration of the Cr trimer is more important than the concentration of benzenedicarboxylate for the synthesis of MIL-101.

Experimental Section

Cr-BDCs were synthesized from chromium chloride hexahydrate ($CrCl_3 \cdot 6H_2O$, Aldrich), terephthalic acid (99%, Junsei), and deionized water by a procedure similar to the methods[7,8] reported earlier. The reactant molar composition was $CrCl_3 \cdot 6H_2O$/TPA/(100–550)H_2O. To study the effect of acidity, aqueous solutions of NaOH (10 N, Duksan Reagent & Chemicals) and HCl (35%, Duksan Reagent & Chemicals) were added to control the pH. Syntheses were conducted at 210 °C under autogenous pressure unless otherwise specified. The gel (ca. 20 g) was loaded in a 100 mL Teflon autoclave, which was sealed and placed in a microwave oven (Mars-5, CEM, maximum power of 1200 W). The autoclave in the microwave oven was heated in about 2 min to the reaction temperature of 210 °C and kept at that temperature for a predetermined time. The microwave power was 400 W throughout all synthesis steps, including the heating-up stage. The detailed operation procedure of the microwave oven is described elsewhere.[28]

For conventional electric crystallization, the gel (ca. 20 g) was loaded in a Teflon-lined autoclave and stored in a preheated electric oven for a fixed time. During the microwave and conventional reactions, the reactant mixtures were not agitated. After the reaction,

the autoclave was cooled to room temperature, and the solid products were recovered by centrifugation, washed with water, and dried. For the purification, the as-synthesized MOF samples were treated for 1 h at 70 °C with *N*,*N*-dimethylformamide under ultrasound to follow the reported method.[29] The purified Cr-BDCs were dried at 150 °C for 5 h and stored over saturated aqueous ammonium chloride solution after being cooled to room temperature. The crystal phase of the samples was verified by using X-ray diffractometry (MO3X-HF, Model No. 1031, Cu-K_α radiation). The yield of the solid product was calculated by comparing the amount of recovered solid with the expected weight based on chromium. Relative XRD intensity was also used to calculate the content of a mixture.

The morphology was examined with a field emission scanning electron microscope (Hitachi, S-4300). The nitrogen adsorption isotherms of purified samples were obtained at –196 °C with a surface area and porosity analyzer (Micromeritics, Tristar II 3020) after evacuation at 150 °C for 12 h. The surface area and micropore volume were obtained by using the BET equation (P/P_0 = 0.05–0.2) and *t*-plot, respectively. The total pore volume of MIL-101 was measured at P/P_0 = 0.99.

Acknowledgments

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MEST) 2008-0055718, 2009-0083696).

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Received: November 3, 2009
Published Online: January 27, 2010

