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Microwave Synthesis of Hybrid Inorganic–Organic Porous Materials: Phase-Selective and Rapid Crystallization

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Abstract: Microwave synthesis of two porous nickel glutarates was compared with conventional hydrothermal synthesis. The cubic nickel glutarate, $[Ni_{20}(C_5H_6O_4)_{20}(H_2O)_8]\cdot 40\,H_2O$ (**1**), was synthesized by conventional electrical heating in several hours or days, depending on synthesis temperature. Crystallization was greatly accelerated by microwave irradiation, in which more stable, tetragonal nickel glutarate, $[Ni_{22}(C_5H_6O_4)_{20}(OH)_4(H_2O)_{10}]\cdot 38\,H_2O$ (**2**), was formed within a few minutes, suggesting the efficiency of the microwave technique in the synthesis of porous hybrid materials. The cubic phase **1** is formed preferentially at low pH, low temperature, and especially under conventional electrical heating. In contrast, the tetragonal phase **2** is obtained favorably at high pH, high temperature, and especially with microwave irradiation. This work demonstrates that the microwave method provides not only the very fast synthesis of a hybrid material, but also the possibility to discover a new porous hybrid material not yet identified by conventional hydrothermal synthesis. The hydrothermal formation of metal–organic hybrid materials in a matter of minutes is an important step towards developing commercially viable routes for producing this valuable class of materials.

Keywords: hydrothermal synthesis · microporous materials · microwave synthesis · organic–inorganic hybrid composites · phase selectivity

Introduction

The number of materials exhibiting permanent nanoporosity has rapidly expanded in recent years, due in large part to the discovery of hybrid inorganic–organic materials, such as metal–organic frameworks (MOFs) and coordination polymers.[1–3] The major applications currently considered for these compounds involve gas storage,[4] catalysis,[5] separations,[6] and as carriers for nanomaterials.[7] For these applications, their large surface areas and unique pore structures are likely to offer many potential advantages over existing compounds. However, the reactions used to synthesize many hybrid materials, particularly those with good thermal stability, require hydro/solvothermal synthesis conditions. Because hydro/solvothermal reactions typically take up to several days, it is important to develop facile, rapid, inexpensive, and commercially viable routes for the production of these compounds if they are to have applications.

Recently, the microwave synthesis method has attracted growing attention in the synthesis of nanoporous inorganic materials[8] that normally require several days for their hydrothermal crystallization. This method has been shown to provide an efficient way to synthesize purely inorganic porous materials with short crystallization times,[9] narrow particle-size distributions,[10] facile morphology control,[11] phase selectivity,[12] and the efficient evaluation of process parameters.[13] However, to our knowledge, the microwave method has been applied very rarely to the synthesis of porous hybrid materials.[14] Additionally, there has been no report on the microwave synthesis of hybrid materials containing metal–oxygen–metal connectivity. Here, we examine

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the utility of the microwave method for the synthesis of porous nickel glutarates. We chose nickel-containing hybrid materials because of our previous successes at synthesizing nickel phosphates[15,16] and succinate[17,18] with three-dimensional nickel–oxygen frameworks and good thermal stability.

Guillou et al. succeeded recently in the hydrothermal synthesis of a ferromagnetic, porous, and chiral nickel glutarate with a cubic structure and chemical formula of $[Ni_{20}(C_5H_6O_4)_{20}(H_2O)_8]\cdot 40H_2O$, named MIL-77[19] (**1**, Figure 1).

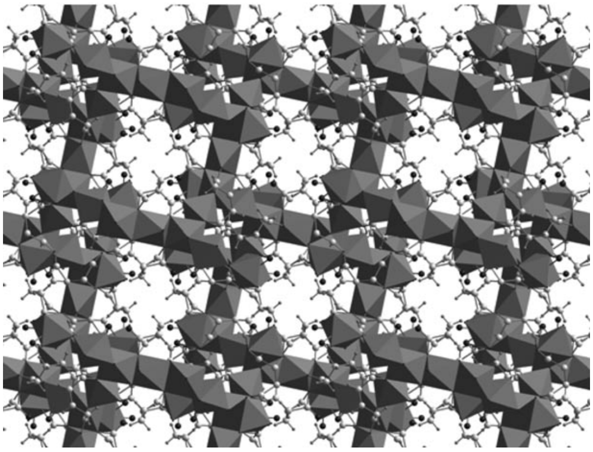

Figure 1. The structure of **1** viewed in the *c* direction. NiO_6 octahedra are shown as gray polyhedra, with light and dark gray spheres representing carbon and oxygen atoms, respectively. The structure **2** is a tetragonally distorted version of **1**.

This material has a framework of helical octahedral chains and very large intersecting 20-membered ring channels based on a three-dimensional Ni–O–Ni network. Very recently, we found a second nickel-glutarate phase with tetragonal structure,[20] $[Ni_{22}(C_5H_6O_4)_{20}(OH)_4(H_2O)_{10}]\cdot 38H_2O$. This structure, **2**, contains the same helical chains found in **1**, but in an alternating arrangement, resulting in a centrosymmetric space group. Unlike **1**, **2** contains μ_3-hydroxide groups that bridge to partially occupied nickel(II) sites lining the pores.

Here, we present the results of phase-selective and very fast crystallization of porous nickel glutarates by using microwave irradiation. Microwave reactions were compared with similar reactions carried out by using conventional hydrothermal synthesis. Additionally, we investigated the effects of reaction parameters, such as temperature, KOH/$NiCl_2$ ratio, and reaction time on the syntheses of nickel glutarates.

Results

The cubic nickel glutarate (**1**) was synthesized by conducting a classical hydrothermal reaction at 180 °C for 48 h using the precursor composition of $NiCl_2\cdot 6H_2O$:1.5 glutaric acid (GTA):2 KOH:30 H_2O:9 isopropyl alcohol (IPA) (pH 4.8), as reported previously.[19] The powder XRD pattern in Figure 2a is consistent with the simulated diffraction pattern. To our surprise, crystalline powders are formed very quickly, within a minute, from an identical starting mixture under microwave irradiation at temperatures of between 150 and 220 °C. To the best of our knowledge, such a very fast crystallization of a porous hybrid material has not yet been demonstrated. Additionally, as shown in Figure 2b, the second nickel-glutarate phase (**2**), rather than **1**, is observed under microwave irradiation, indicating the crystallization of a new phase, depending on the synthesis method.

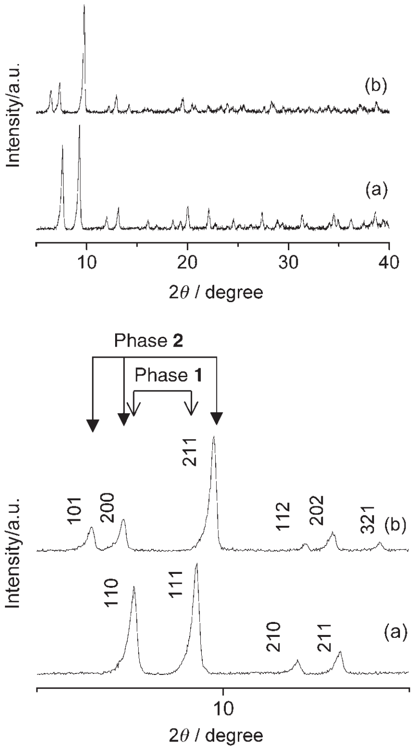

Figure 2. XRD patterns of porous nickel glutarates synthesized by using conventional electric heating and microwave irradiation. Top: a) phase **1**, synthesized by a conventional hydrothermal method at 180 °C for 48 h and b) phase **2**, synthesized by the microwave method at 220 °C for 1 min. The molar composition of the reaction mixtures was Ni:1.5 GTA:2 KOH:30 H_2O:9 IPA in both cases. Bottom: Selected regions of the patterns showing the nickel-glutarate phases.

Because of the unexpected formation of **2** by microwaves under conditions that should have produced **1**, we carried out similar reactions under a wider range of reaction conditions. Figure 3 shows the XRD patterns of nickel glutarates as a function of the heating methods and crystallization times at 180 °C from the same reactant mixture with a KOH/$NiCl_2$ ratio of 2 (pH 4.8). The content of **2** in the product increases as the crystallization times increases, for both conventional hydrothermal and microwave syntheses. However, as mentioned earlier, **1** is found to be dominant in hydrothermally prepared samples, whereas **2** is the major product in the microwave reactions. Therefore, pure **1** might

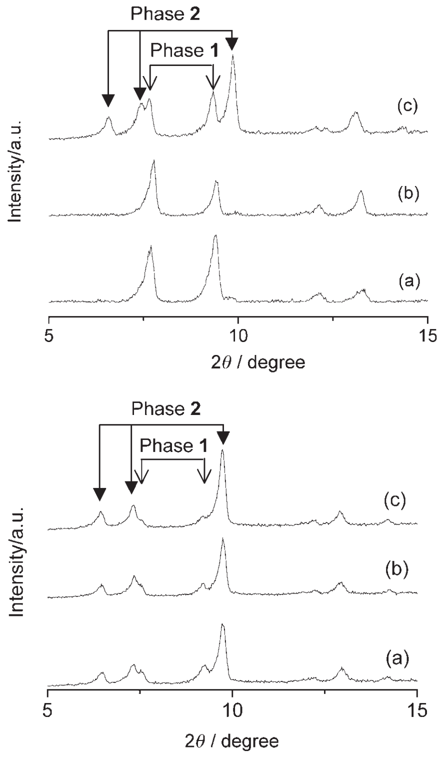

Figure 3. XRD patterns of as-synthesized nickel glutarates as a function of crystallization time and synthesis method. Top: Conventional hydrothermal synthesis at 180 °C for a) 6 h, b) 96 h, and c) 336 h. Bottom: Microwave synthesis at 180 °C for a) 1 min, b) 1 h, and c) 2 h.

be obtained preferentially from the conventional heating in the early stage of the synthesis, whereas pure **2** might be synthesized selectively from the microwave technique in the later stages of reaction. As shown in Figure 4, the contribution of **2** increases as the KOH/$NiCl_2$ ratio or pH increases. If the KOH/$NiCl_2$ ratio is too low or too high, however, the two porous nickel glutarates do not form. No solid product is formed in very acidic conditions (KOH/$NiCl_2$ ratio <1.0), whereas unknown, nonporous phases are obtained in highly basic conditions (KOH/$NiCl_2$ ratio ≥ 3.5). Additionally, the content of **2** increases slightly as the reaction temperature is raised from 160 to 200 °C (Supporting Information Figure S1).

Figure 5 compares the crystallization yields of nickel glutarates obtained by using microwave and conventional hydrothermal syntheses as a function of reaction time at 190 °C. It is evident that the microwave method leads to significantly faster crystallization of **2** with improved yields relative to the conventional heating required to derive **1**. Indeed, the microwave method leads to extremely fast crystallization of **2** (the reaction is essentially complete within 1 min), in contrast to the complete formation of **1** after 48 h by conventional heating. Moreover, pure **2** cannot be obtained even after 336 h at 190 °C by using classical hydrothermal synthesis with the same reaction mixture. The acceleration effect by microwaves in this study to crystallize phase **2** (within a few minutes), which forms very slowly (**2** cannot be obtained by the synthesis for 336 h) by conventional electric heating, is even more drastic. The acceleration effect in the crystallization of nickel glutarate by microwave irradiation is remarkable compared with the crystallization of aluminosilicate zeolites (such as ZSM-5[21] and Beta[22]),

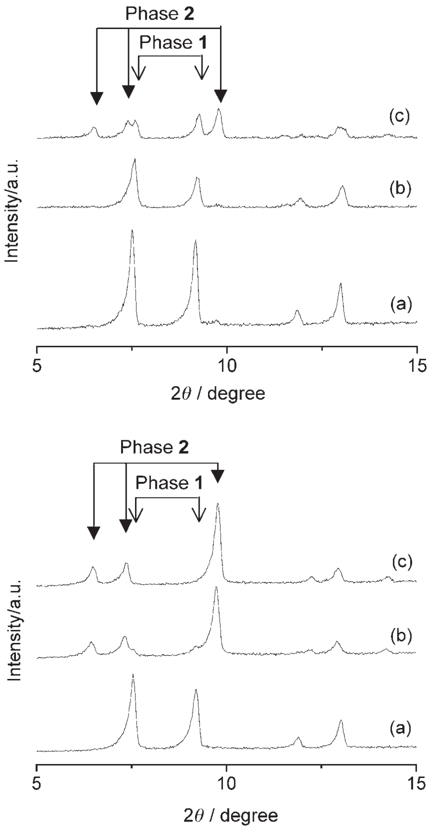

Figure 4. XRD patterns of as-synthesized nickel glutarates as a function of KOH/$NiCl_2$ ratio and heating methods. Top: Conventional hydrothermal synthesis at 180 °C for 2 d using reactant mixtures with KOH/$NiCl_2$ ratios of a) 1.0, b) 2.0, and c) 3.0. Bottom: Microwave synthesis at 180 °C for 2 h using reactant mixtures with KOH/$NiCl_2$ ratios of a) 1.0, b) 2.0, and c) 3.0.

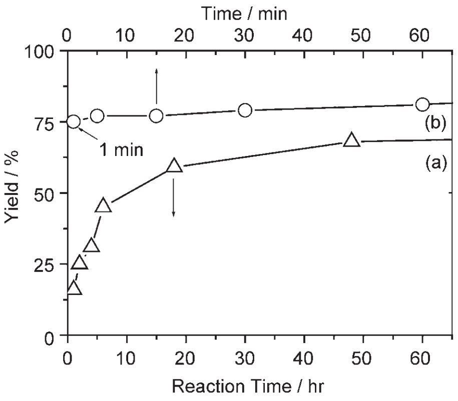

Figure 5. Dependence of product yield on crystallization time in the synthesis of nickel glutarates from reactant mixture (KOH/$NiCl_2$ ratio 2.0) at 190 °C: a) phase **1**, synthesized by a conventional hydrothermal method and b) phase **2**, synthesized by the microwave method.

in which microwave synthesis was less than ten times faster than hydrothermal crystallization.

The physicochemical properties of the two pure nickel glutarates were compared. Pure **1** and **2** were obtained by conventional electrical heating at 180 °C for 48 h and microwave irradiation at 220 °C for 1 min, respectively. The XRD patterns of pure **1** and **2** are shown in Figure 2a and b, respectively. The homogeneity of the nickel glutarates is very high, which is confirmed by the SEM images (Figure 6). As illustrated in Figure 7, the nitrogen adsorption–desorption isotherms are similar and are both type-I. The Brunauer–Emmett–Teller (BET) surface areas of **1** and **2** are 356 and 418 $m^2 g^{-1}$, respectively, and the micropore volumes of **1** and **2** are 0.11 and 0.14 $mL g^{-1}$, respectively. These results indicate the permanent porosity and reversible adsorption and desorption of nitrogen on these nickel glutarates. The surface areas of both nickel glutarates decreased to less than 50 $m^2 g^{-1}$ following evacuation of the sample above 350 °C, in agreement with the thermogravimetric analysis (TGA) results shown in Figure 8.

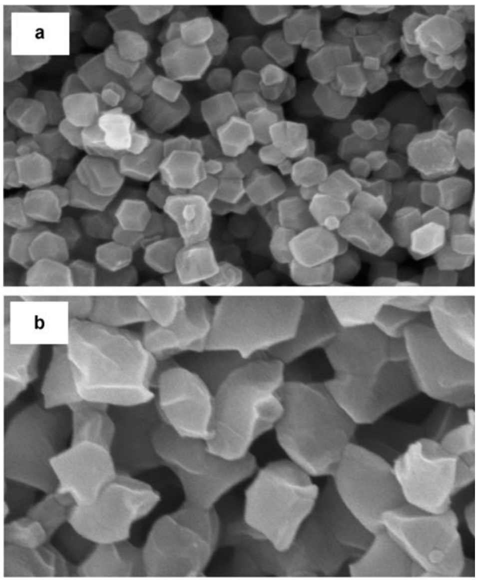

Figure 6. SEM images of pure nickel glutarates: a) phase **1** synthesized by conventional hydrothermal heating at 180 °C for 48 h, b) phase **2** synthesized by the microwave method at 220 °C for 1 min.

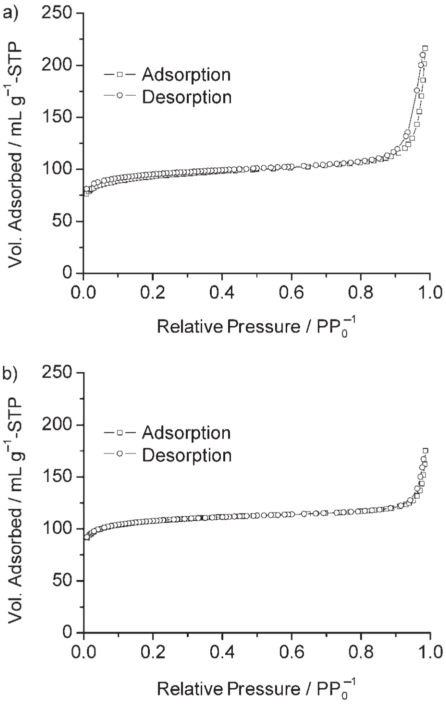

Figure 7. Adsorption–desorption isotherms of nitrogen over pure nickel glutarates: a) nickel glutarate, phase **1**, synthesized by a conventional hydrothermal method at 180 °C for 48 h and b) nickel glutarate, phase **2**, synthesized by the microwave method at 220 °C for 1 min. STP = standard temperature and pressure.

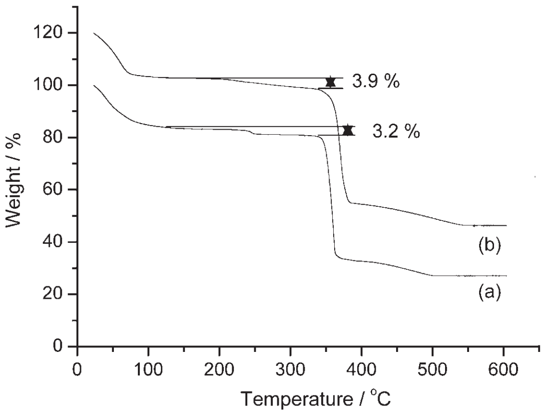

Figure 8. TGA patterns of pure nickel glutarates: a) phase **1** synthesized by conventional hydrothermal heating at 180 °C for 48 h and b) phase **2** synthesized by the microwave method at 220 °C for 1 min. For clarity, the TGA pattern of b) has been shifted upward by 20 wt %.

The thermal behavior of nickel glutarates was evaluated by TGA. The two phases show similar TGA patterns, as shown in Figure 8. The TGA pattern of **1** is very similar to the previous result,[18] showing the desorption of occluded water molecules and eight coordinated water molecules (found: 3.2 wt %; calculated: 3.1 wt %) per unit formula from 25 to 100 °C and from 100 to 300 °C, respectively. The thermal behavior of **2** is consistent with the unit-cell formula. The first gentle slope of weight loss observed at temperatures less than 100 °C corresponds to the loss of occluded water molecules without significant structural change. The loss of the ten coordinated water molecules (found: 3.9 wt %, calculated: 3.7 wt %) occurs between 100 and 300 °C on the TGA curve. Weight losses above around 350 °C correspond to structural collapse associated with the decomposition of the organic moieties.

The FTIR spectra (Supporting Information Figure S2) of the two nickel glutarates do not show any noticeable differences, confirming the similarity of the chemical bonds in the two materials, in agreement with the similar chemical formulae or compositions. The UV-visible diffuse reflectance spectra (DRS) (Supporting Information Figure S3) of **1** and **2** are also very similar to each other, and appear to be similar to that of octahedrally coordinated nickel(II) ions (Supporting Information Figure S3c), illustrating the presence of octahedral nickel(II) in both nickel glutarates. The absorption bands at about 400 and 750 nm have been assigned to the transitions of octahedral nickel(II) ions, $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) and $^3A_{2g} \rightarrow {}^3T_{1g}$ (P), respectively.[23] In summary, the physicochemical properties of the two nickel glutarates, including sorption, spectroscopic, and thermal behaviors, are very similar to each other.

Discussion

Effect of reaction conditions on the synthesis and fast crystallization: It was recently shown that the acid:base ratio and temperature are the most important parameters for the synthesis of cobalt succinates.[24,25] Here, several conditions, such as pH, temperature, reaction time, and heating method have been varied. As shown in Figures 2–4 and Supporting Information Figure S1, the concentration of the phase **2** increases as pH, reaction temperature, and reaction time increase.

Forster et al. have shown that more condensed cobalt succinates can be obtained as the temperature and basicity of the reactant mixtures increase.[24,25] Considering their chemical compositions, **2** $[Ni_{22}(C_5H_6O_4)_{20}(OH)_4(H_2O)_{10}]\cdot 38H_2O$ is a slightly more condensed phase than **1** $[Ni_{20}(C_5H_6O_4)_{20}(H_2O)_8]\cdot 40H_2O$, because **2** contains a higher nickel concentration per glutarate than **1**. Moreover, **2** contains μ^3-hydroxide species that bridge to the nickel(II) sites. Therefore, based on our previous results,[24,25] it is reasonable to anticipate that the formation of **2** would be favored under conditions of higher temperature and higher pH, as observed. Phase **1** can be synthesized preferentially under conditions of low $KOH/NiCl_2$ ratio and low temperatures. Moreover, in reactions producing a mixture of **1** and **2**, the percentage of **2** in the product increases as the reaction time increases (Figure 3), implying that **1** forms initially (possibly during heating) and is replaced by **2**, which is more thermodynamically favorable (see below) under the present reaction conditions.

Phase **2** can be synthesized within one minute from the reaction mixture containing a $KOH/NiCl_2$ ratio of 2 by using microwave synthesis (Figure 5). Phase **1** can be also obtained within one minute under microwave irradiation at 180 °C if the $KOH/NiCl_2$ ratio is 1, due to the fast crystallization possible with this method (data not shown). Our observations of very fast synthesis achieved by using the microwave method are consistent with an increase in the effectiveness relative to conventional hydrothermal synthesis. It has been shown that the microwave excitation of strongly polarizable species results in highly effective heating, due to superheating or creation of a hot spot of the media.[8,26] We attribute the exceptionally rapid crystallization of nickel glutarates to different formation pathways, in contrast to conventional zeolites. Although the formation of aluminosilicate zeolites appears to involve complex crystallization pathways of hydrolysis, hydrophobic hydration, gelation, nucleation, and crystal growth,[8,27] the present nickel glutarates apparently grow directly from the reactants upon raising the reaction temperature of the solution to an appropriate level. Consequently, the long induction periods required for zeolite formation are not necessary for the synthesis of nickel glutarates. This fast crystallization will be very helpful in constructing a continuous production system, as already demonstrated for the production of porous nickel phosphates.[28]

Phase-selective synthesis with microwave heating: This work shows that the synthesis method is also an important parameter for the phase-selective synthesis of nickel glutarates. Structure **2** can be obtained preferentially through the use of microwave synthesis (Figures 2–4) under reaction conditions that would otherwise produce **1** by conventional hydrothermal synthesis. The different products of microwave synthesis are quite puzzling.

The kinetics and thermodynamics of formation of hybrid materials have been scarcely examined. In the synthesis of cobalt succinates,[24,25] $[Co(H_2O)_2(C_4H_4O_4)]$ was obtained after a short reaction time of 5 h at 150 °C, and after 25 h it was replaced by $[Co_4(H_2O)_2(OH)_2(C_4H_4O_4)_3]\cdot 2H_2O$. This is because the former and latter (more condensed) phases are kinetically and thermodynamically favorable phases, respectively, under these reaction conditions. In this work, the more condensed phase, **2**, is believed to be thermodynamically more stable than **1** under the present conditions. This assumption is further supported by the fact that the percentage of **2** in mixed products tends to increase as the crystallization time and temperature increase, under both microwave and conventional hydrothermal conditions (Figure 3 and Supporting Information Figure S1). Our observations of the increasing content of **2** relative to **1** over time are likely to be the result of the initial formation of **1**, followed by its replacement by **2** (Figure 3). Given the extremely fast crystallizations observed with microwave synthesis, it is likely that a part of material crystallizes during the heating step at low solution temperature, thus, favoring the formation of **1**. The phase **1** would then have to redissolve to recrystallize as **2**. Similar observations over longer time scales were reported in the studies on cobalt succinates mentioned previously.[24,25]

Therefore, we attribute the preferential formation of **2** under microwave irradiation to the extremely fast crystallization (due to superheating or creation of a hot spot of the reactant mixture), in which formation of the less-favorable **1** is merely a transient, intermediate step. Accordingly, **1** cannot be observed easily, especially at high temperatures, because of facile transformation to **2** under microwave irradiation, as observed. However, if the pH is very low, **1** can be obtained even by microwave synthesis, as shown in Figure 4 (bottom part, spectrum a), because it seems that the effect of acidity is more predominant than the heating method employed in the reaction conditions.

We are currently pursuing further studies on nickel glutarates and other hybrid systems, such as cobalt succinates and nickel succinates, to confirm this hypothesis and to provide further information on the synthesis mechanism. At present, there is little detailed understanding of the reaction mechanisms involved in the formation of hybrid inorganic–organic materials. We are optimistic that studies of reaction parameters, such as the present work, will motivate additional investigations into kinetics and mechanism by using in situ XRD, NMR, and other methods.

This work demonstrates that the microwave technique can be used as a phase-selective and very fast synthesis method, and should be applicable in the efficient synthesis within a few minutes of new hybrid materials that have not yet been identified through conventional hydrothermal synthesis.

Conclusion

Two porous nickel glutarates with very similar physicochemical properties were hydrothermally synthesized under various conditions by both microwave irradiation and conventional electric heating. The cubic phase (**1**) is formed preferentially at low pH, low temperature, and in the earlier stage of reaction by conventional electrical heating, whereas the tetragonal phase (**2**) is obtained favorably at high pH, high temperature, and in the later stage of reaction by the microwave irradiation. The microwave method, in contrast to conventional hydrothermal heating for the cubic nickel glutarate (**1**), leads to phase-selective and very fast crystallization of another porous nickel glutarate (**2**) with a tetragonal structure. The phase-selective synthesis of tetragonal nickel glutarate (**2**) by microwave irradiation may be explained in terms of the extremely fast synthesis possible with this technique. Hydrothermal formation of metal–organic hybrid materials in a matter of minutes is an important step towards developing commercially viable routes for producing this valuable class of materials. Therefore, the microwave method might provide us with not only very fast synthesis of a hybrid material, but also the possibility to discover a new porous hybrid material.

Experimental Section

Nickel glutarates were synthesized hydrothermally by using $NiCl_2 \cdot 6H_2O$, glutaric acid (GTA, $HO_2C(CH_2)_3CO_2H$), KOH, isopropyl alcohol (IPA), and water. The molar composition of typical reaction mixtures was $NiCl_2$:1.5 GTA:2 KOH:30 H_2O:9 IPA, similar to the previous method reported by Guillo et al.[18] To check the effect of pH, the KOH/$NiCl_2$ ratio was changed. The pH values of the reaction mixture ranged from 1.7 to 7.3 as the KOH/$NiCl_2$ ratio was varied from 0 to 3.5.

The precursor mixture of 30 g was loaded in a 100 mL Teflon autoclave (diameter 32 mm, height 124 mm), sealed, and placed in a microwave oven (Mars-5, CEM, maximum power of 1200 W, internal volume of 1.7 ft^3). The reaction mixture was heated to the reaction temperature of 150–220 °C in less than 2 min (microwave power was 600 W) and was maintained at that temperature for a predetermined time of between 1 min and 4 h (maximum microwave power was 300 W). The reaction temperature was controlled by using an EST-300 Plus system (electronic sensor temperature) that monitored and controlled temperature conditions inside sample vessels. In this system, a microwave-transparent fiber-optic temperature probe was inserted into a thermowell of the sample vessel. The temperature sensor was a phosphor located at the tip of the probe. The decay rate of fluorescent light emitted from the phosphor is temperature dependent, allowing a precise determination of temperature. The temperature was calibrated periodically. For safety, the temperature of the reaction vessel in the microwave oven was measured by using an optional TempGuard™ system. An infrared lens and sensor were located in the microwave oven and the temperature of each vessel was measured as the vessels rotated over the sensor. If the temperature in any vessel was higher than the maximum preset temperature, the TempGuard™ stopped the microwave generation. For comparison, the same reactant mixture in a Teflon reactor (volume ~100 mL) was crystallized in an electric convection oven for a time of between 1 and 336 h. The solid product was recovered by centrifugation followed by washing and drying.

The structure and crystallinity of the synthesized samples were determined by X-ray powder diffraction (XRD, Rigaku, D/MAX IIIB, $Cu_{K\alpha}$ radiation). The morphology was examined by using a scanning electron microscope (Philips, XL30S FEG). The reaction yield was determined by comparing the weight of the solid product with the expected weight based on the chemical formulae of the nickel glutarates. The XRD intensity was not considered in calculation of the yield because the homogeneity of the crystals is generally very high, as confirmed by using SEM. Similarly, the phase purity of nickel glutarates was not considered in calculation of the yield because the yield was measured for the nearly phase-pure samples only. The TGA pattern was obtained by using a thermal analyzer (Du Pont 9900) in a nitrogen flow of 100 $mL\,min^{-1}$. The temperature was ramped at a rate of 2 $°C\,min^{-1}$ and the sample weight was approximately 10 mg. The nitrogen-sorption experiments were carried out by using a Micromeritics ASAP 2400 adsorption unit at liquid-nitrogen temperature after evacuation at 200 °C under a vacuum of ~10^{-4} Torr. The surface area and micropore volume were estimated by applying the BET and Dubin–Radushkevich equations,[29] respectively, to the nitrogen-adsorption isotherms. The FTIR spectra of nickel glutarates were obtained by using a Nicolet FTIR spectrometer (Magna 550) with KBr as a diluent. The UV/Vis diffuse reflectance spectra (DRS) were recorded under ambient conditions by using a UV/Vis spectrophotometer (Shimadzu, UV-2501PC) equipped with a quartz flat cell.

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