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Synthesis of a Metal–Organic Framework Material, Iron Terephthalate, by Ultrasound, Microwave, and Conventional Electric Heating: A Kinetic Study

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Abstract: A metal–organic framework material named MIL-53(Fe), iron terephthalate, has been synthesized sovothermally at a relatively low temperature by not only conventional electric (CE) heating, but also by irradiation under ultrasound (US) and microwave (MW) conditions to gain an understanding of the accelerated syntheses induced by US and MW. The kinetics for nucleation and crystal growth were analyzed by measuring the crystallinity of MIL-53(Fe) under various conditions. The nucleation and crystal growth rates were estimated from crystallization curves of the change in crystallinity with reaction time. The activation energies and pre-exponential factors were calculated from Arrhenius plots. It was confirmed that the rate of crystallization (both nucleation and crystal growth) decreases in the order US > MW ≫ CE, and that the accelerated syntheses under US and MW conditions are due to increased pre-exponential factors rather than decreased activation energies. It is suggested that physical effects such as hot spots are more important than chemical effects in the accelerated syntheses induced by US and MW irradiation. The syntheses were also conducted in two steps to understand quantitatively the acceleration induced by MW and it was found that the acceleration in crystal growth is more important than the acceleration in nucleation, even though both processes are accelerated by MW irradiation.

Keywords: kinetics · metal–organic frameworks · microporous materials · microwave chemistry · ultrasound

Introduction

Recently, remarkable developments in metal–organic frameworks (MOFs), crystalline porous materials, have been reported.[1] The interest in MOF materials arises from their huge porosity and the easy tunability of their pore size and shape from the microporous to the mesoporous scale by changing the connectivity of the inorganic moiety and the nature of the organic linkers.[1] Moreover, MOFs have many potential applications, for example, in gas adsorption/storage,[2] separation,[3] catalysis,[4] the adsorption of organic molecules,[5] drug delivery,[6] luminescence,[7] electrode materials,[8] carriers for nanomaterials,[9] and magnetism.[10]

The majority of research on MOFs so far has been devoted mainly to their synthesis, structure analysis, and potential applications in various fields. The facile synthesis of MOFs is very important, not only for a fundamental understanding of the synthesis, but also for viable applications in industry. MOFs, especially the phases having stable structures, have mainly been synthesized by hydro- or solvothermal crystallization at relatively high temperatures using conventional electrical (CE) heating.[1] To find effective alternative methods for the synthesis of MOFs a few new techniques have been explored with a view to decreasing the reaction time or reaction temperature. For example, ultrasound (US) has been applied in the synthesis of $Cu_3(BTC)_2$ (Cu–BTC or HKUST-1),[11] $Zn_3(BTC)_2{\cdot}12H_2O$,[12] $[Zn(BDC)(H_2O)]_n$,[13] and MOF-5[14] (BTC and BDC represent 1,3,5-benzenetricarboxylate and 1,4-benezenedicarboxylate or terephthalate, respectively). Microwaves (MW) have been used for the synthesis of MOFs because MW synthesis of porous materials has several advantages, for example, fast crystallization,[15] phase selectivity,[16] diverse morphology/size,[17] and the facile evaluation of reaction parameters.[18] MOFs have also been synthesized with MW to show fast crystallization,[19] phase-selectivity,[20] and decreased size.[21] $Cu_3(BTC)_2$, composed of copper and BTC, has been made by an electrochemical route.[22] Parnham and Morris have also synthesized MOFs successfully by ionothermal synthesis and several new phases have successfully been discovered by

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this approach.[23] Stock and co-workers used the so-called high-throughput synthesis in the crystallization of MOFs to evaluate rapidly the effect of reaction conditions on the synthesis[24] and to search for optimum conditions for a phase that is hard to synthesize.[25] A MOF named MIL-101-NDC was recently discovered by using the high-throughput synthesis approach.[25] Cheetham and co-workers used immiscible solvents for biphasic syntheses that usually lead to single crystals of the desired phase.[26]

Among the new methods described, the ultrasound and microwave syntheses are particularly interesting as the reaction temperature and/or reaction time can be reduced, which would be very helpful for commercial applications of MOFs. However, little information has been reported on the beneficial effects of the US and MW syntheses of MOFs.

A few reports detailing quantitative acceleration in the MW synthesis of porous materials such as silicalite-1,[27] nickel phosphate (VSB-5),[27] AlPO-11,[28] and SAPO-11 have recently been published.[28] Conner and co-workers showed that the acceleration of AlPO-11 and SAPO-11 by MW synthesis is mainly due to an increased number of reaction sites and/or increased reaction probability.[28] However, the activation energies of both the nucleation and crystal growth steps are increased under MW conditions.[28] A few porous materials have been synthesized by ultrasound,[11–14,29] however, little information on the kinetics under these conditions has been reported.

In this work we have quantitatively analyzed for the first time the accelerations induced in the synthesis of a MOF under US and MW conditions even though there are a few reports on the acceleration for inorganic porous materials by US and MW.[27–29] Moreover, the synthesis was also carried out in two steps (MW/MW, MW/CE, CE/MW, CE/CE) to gain an understanding of the quantitative accelerations in the nucleation and crystal growth. The reaction mode was changed just after the nucleation was completed, similarly to our previous work[27] and the study of Gharibeh et al.[30]

For the kinetic study, a MOF called MIL-53(Fe),[31] composed of iron and BDC (1,4-benezenedicarboxylate or terephthalate), was selected. MIL-53(Fe) is one of the well-known group of MIL-53 MOFs, metal (Al, Cr, Fe)–BDCs, and has potential applications in drug delivery,[32] H_2S adsorption,[33] and lithium ion batteries.[34] MIL-53[35] has the chemical formula $M(OH)(O_2C\text{-}C_6H_4\text{-}CO_2)$ ($M = Al^{3+}$, Cr^{3+} or Fe^{3+}) and is composed of infinite $MO_4(OH)_2$ octrahedra connected by 1,4-benzenedicarboxylate ligands.[35] MIL-53(Fe) can be synthesized under mild conditions at a relatively low temperature and pressure.[31,32] Therefore the synthesis can be carried out easily under a range of conditions. Moreover, because the synthesis could be carried out at a low pressure, the reaction kinetics could be analyzed accurately by adding one component after the desired reaction temperature is reached.

Results and Discussion

Accelerated syntheses of MIL-53(Fe) under US and MW conditions: In this study MIL-53(Fe) was synthesized under a wide range of reaction conditions, especially at low temperature ($\leq 80\,^{\circ}C$), by US, MW, and CE. As shown in Figures S1–S3 of the Supporting Information, the XRD intensity increases with increasing reaction time, reaching a maximum at a certain time. The XRD patterns of the fully crystallized samples (Figure 1) are very similar to the patterns reported

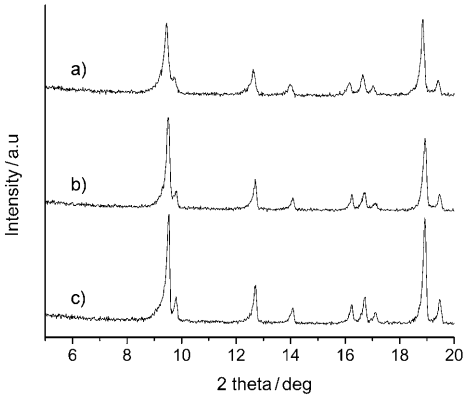

Figure 1. Typical XRD patterns of fully crystallized samples of MIL-53(Fe) synthesized at 70 °C by a) US for 35 min, b) MW for 2 h, and (c) CE for 3 d.

earlier.[31,32] As shown in Figure 2, the crystallinity changes with reaction temperature, time, and method. The dependence of crystallinity on synthesis method and duration are compared in Figure 2d at a temperature of 70 °C. All the crystallization curves show typical sigmoidal forms. Figure 3 shows typical SEM images of the fully crystallized MIL-53(Fe)s obtained by the three methods at the same temperature (70 °C). The SEM images of the fully crystallized MIL-53(Fe)s do not change noticeably with reaction temperature or time for the three methods, as shown in Figures S4–S6 of the Supporting Information. The morphologies, especially those obtained under US and MW conditions, are very homogeneous, which shows the purity of the crystallized phase and the efficiency of the syntheses by the two methods. Even though the SEM image of MIL-53(Fe) obtained by conventional electric heating is not so homogeneous (probably due to concomittant nucleation and crystal growth under CE heating[27]), the phase should be MIL-53(Fe) based on the similarity of its XRD pattern with those of the other MIL-53(Fe)s shown in Figure 1 and one previously reported.[31,32] The SEM images show that US and MW irradiation can produce homogeneous and small crystals of MIL-53(Fe). Small crystals of porous materials are effective in the fields of adsorption, diffusion, and catalysis.

As shown in Figure 2, fully crystallized MIL-53(Fe) is obtained in around 0.5–1 h, 1.5–2.5 h, and 1.5–3 d by US (50–70 °C), MW (60–70 °C), and CE (70–80 °C) synthesis, respectively, which shows that the rate of synthesis decreases in

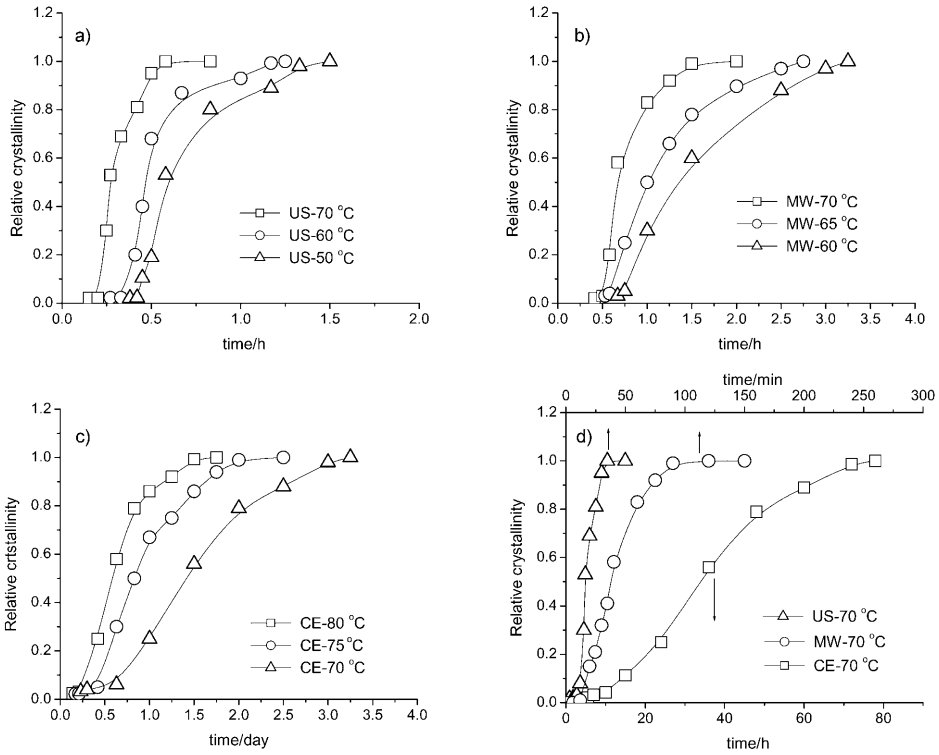

Figure 2. Crystallization curves for the synthesis of MIL-53(Fe) by a) US, b) MW, c) CE heating, and d) at 70 °C by the three methods.

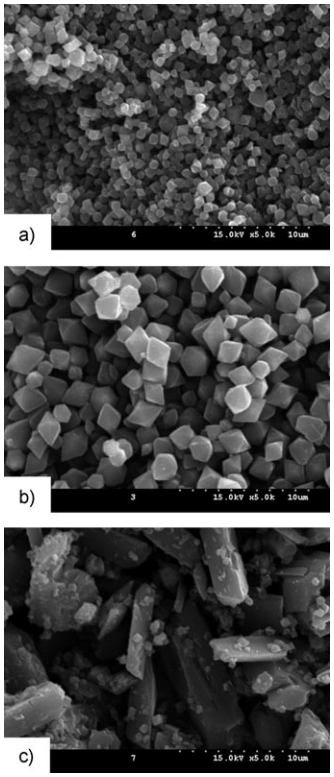

Figure 3. Typical SEM images of fully crystallized MIL-53(Fe) synthesized at 70 °C by a) US for 35 min, b) MW for 2 h, and c) CE for 3 d.

the order US > MW ≫ CE. The rates of nucleation and crystal growth were evaluated from the times of the first appearance of XRD peaks and the slopes of the crystallization curves (between 20 and 80% of the fully crystallized MIL-53(Fe)) of Figure 2, respectively. The times required for complete nucleation (or the induction period) and the rates of nucleation and crystal growth are summarized in Table 1.

To compare the activation energies (E_a) and the pre-exponential factors (A) of the Arrhenius equation for the synthesis by the three methods, the rates of both nucleation and crystal growth were plotted, as shown in Figure 4. The calculated activation energies (E_a) and pre-exponential factors (A) are displayed in Table 1, and it can be seen that E_a decreases in the order $E_a(\mathrm{US}) > E_a(\mathrm{MW}) > E_a(\mathrm{CE})$ for both the nucleation and crystal growth. Likewise, the pre-exponential factors (A) decrease similarly ($A(\mathrm{US}) > A(\mathrm{MW}) > A(\mathrm{CE})$) for both the nucleation and crystal growth. The reaction rates increase in the order $r(\mathrm{US}) < r(\mathrm{MW}) < r(\mathrm{CE})$ if only the activation energy is considered and the pre-exponential factor is the same in all cases. However, the rates increase in the reverse order ($r(\mathrm{US}) > r(\mathrm{MW}) \gg r(\mathrm{CE})$). Therefore, the increased rates of synthesis by US and MW, compared with the synthesis by CE, are due to an increased pre-exponential factor rather than a decreased activation energy. This is unexpected because many accelerated rates observed in MW reactions have been interpreted as being a result of a decreased activation energy.[28]

So far no comprehensive study has been made to explain why the synthesis time is drastically decreased under microwave or ultrasound irradiation. Instead, several hypotheses[15,36] have been proposed to explain the fast synthesis observed under MW conditions: 1) An increase in the heating rate of the reaction mixture, 2) more uniform heating of the reaction mixture, 3) a change in association between species within the mixture, 4) superheating of the mixture, 5) the creation of hot spots, and 6) enhancement of the dissolution of the precursor gel. According to Conner and co-workers, rapid heating and the creation of hot spots are important factors associated with an increase in synthesis rates under MW conditions.[15,36]

The acceleration observed under US conditions in many synthetic reactions has been explained by 'acoustic cavitation',[37] the process composed of the formation, growth, and

Table 1. Nucleation and crystal growth rates by the three synthesis methods at various temperatures and calculated pre-exponential factors (A) and activation energies (E_a) for the synthesis of MIL-53(Fe).[a]

Synthesis method	Temp. [°C]	Nucleation time [min]	Nucleation rate [min^{-1}][b]	A for nucleation [min^{-1}][a]	E_a for nucleation [$kJ\,mol^{-1}$][a]	Crystal growth rate [min^{-1}][c]	A for crystal growth [min^{-1}][a]	E_a for crystal growth [$kJ\,mol^{-1}$][a]
	50	35	2.86×10^{-2}			1.03×10^{-2}		
US	60	16	6.25×10^{-2}	3.57×10^{11}	81.1	3.85×10^{-2}	8.03×10^{14}	104.3
	70	6	1.67×10^{-1}			9.89×10^{-2}		
	60	44	2.27×10^{-2}			8.01×10^{-3}		
MW	65	32	3.13×10^{-2}	1.19×10^{10}	74.8	1.11×10^{-2}	1.23×10^{12}	90.6
	70	20	5.00×10^{-2}			2.08×10^{-2}		
	70	310	3.23×10^{-3}			3.78×10^{-4}		
CE	75	250	4.00×10^{-3}	3.05×10^{3}	39.2	5.16×10^{-4}	4.78×10^{6}	66.4
	80	210	4.76×10^{-3}			7.31×10^{-4}		

[a] Pre-exponential factors (A) and activation energies (E_a) were calculated from the rates at three temperatures. [b] Calculated from 1/(nucleation time). [c] Calculated from the slopes of the crystallization curves (between 20 and 80% crystallinity).

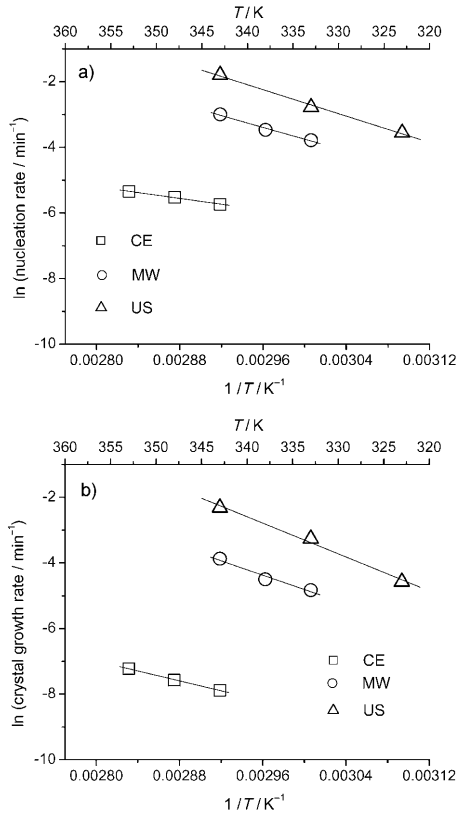

Figure 4. Arrhenius plots for the synthesis of MIL-53(Fe) by US, MW, and CE heating. a) Nucleation rate; b) crystal growth rate.

implosive collapse of micrometer-sized bubbles under ultrasound conditions. Local conditions during bubble implosion lead to hot spots with temperatures of ~5000 °C, pressures of ~1000 atm, and extraordinary high heating/cooling rates of ~10^{10} °C s^{-1}.[37] Therefore various reactions can be accelerated even at room temperature under US conditions because the instantaneous temperature and pressure may be very high. Thus, the acceleration observed in MOF syntheses may be explained by hot spots or transient temperature and pressure. It has also been reported that cavitation is more dependent on physical characteristics (such as vapor pressure, viscosity, and surface tension) than on chemical properties (polarity, acidity, or basicity).[38] Similarly, hot spots are important in accelerated syntheses under MW conditions.[15,36]

At present it is not easy to explain why the acceleration (by US and MW irradiation) is mainly due to a huge increase in the pre-exponential factor rather than a decreased activation energy. In the MW synthesis of inorganic porous materials (such as AlPO-11 and SAPO-11),[28] the accelerated rate has also been interpreted to be a result of large pre-exponential factors (even though the activation energy is increased). The increased pre-exponential factor is explained by an increased number of reaction sites and/or increased reaction probability.[28] MW exposure is also believed to provide a more favorable reaction coordinate (selective heating and changing the reaction profile) in the microwave synthesis.[39] Interestingly, synthesis using US irradition is very attractive because the reaction rate is highly accelerated under US conditions in comparison with the MW synthesis, both in the nucleation and crystal growth.

In this study, little difference, except for the degree of acceleration, is found between the US and MW methods in the accelerated syntheses. In other words, acceleration is due to an increased pre-exponential factor in both cases. Moreover, the increased rates are due to accelerations in both the nucleation and crystal growth even though the acceleration in crystal growth stage is more important than nucleation (see below). Therefore, the accelerations in this study under US and MW conditions, similar to previous work,[39] may be due to physical processes such as hot spots rather than chemical processes.

The reaction rate under US conditions is even faster than in the MW synthesis at the same temperature. Therefore, room-temperature synthesis by US is possible for some MOFs like Cu–BTC,[11] $Zn_3(BTC)_2\cdot12H_2O$,[12] and $[Zn(BDC)(H_2O)]_n$.[13] Therefore many MOFs are expected to be produced at low temperatures by ultrasound.

Accelerated syntheses of MIL-53(Fe) under MW conditions—two-step synthesis: To gain a greater understanding of the acceleration, MIL-53(Fe) was synthesized in two steps at 70 °C, similarly to previous work.[27,30] The US synthesis has not been tried in two-step syntheses because it is not so convenient to use the reactor used under MW or CE conditions directly for US irradiation. As shown in Figure 5, crystallization curves are a typical sigmoidal shape. Howev-

er, the crystallization rates, including the rates of nucleation and crystal growth, are strongly dependent on the synthetic method. The quantitative rates, calculated from Figure 5, are summarized in Table 2.

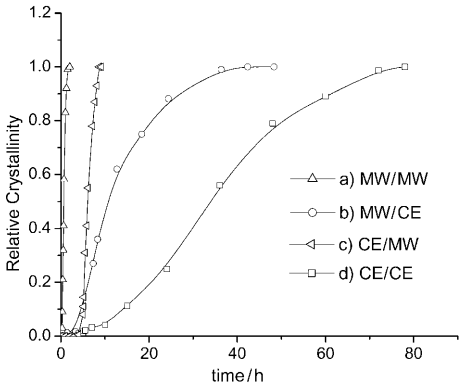

Figure 5. Crystallization curves for the synthesis of MIL-53(Fe) in two steps by a) MW/MW, b) MW/CE, c) CE/MW, and d) CE/CE heating.

With MW irradiation, the nucleation is accelerated by a factor of 15.5, whereas crystal growth experiences a greater acceleration (15.5 or 28.2 times). The cumulative time needed for full crystallization due to increased nucleation and crystal growth rates under MW conditions are calculated[40] to decrease by factors of 1.7–4.1 and 8.8–21.2, respectively, as shown in Table 2. Therefore, it can be concluded that the use of MW irradiation for the synthesis of MIL-53(Fe) has a stronger influence on the acceleration of crystal growth compared with nucleation even though both processes are accelerated.

The quantitative accelerations in the nucleation and crystal growth stages can also be calculated from the pre-exponential factors and activation energies reported in Table 1. The accelerations induced by MW irradition (compared with the reaction performed by the CE method) at 70 °C are calculated to be 14.8 and 53.1 times for nucleation and crystal growth, respectively.[41] This result agrees with the accelerations derived from the two-step syntheses. Similarly, the accelerations induced by US (compared with the reaction performed by the CE method) at the same temperature are calculated to be 48.7 and 284.2 times higher for the nucleation and crystal growth steps, respectively. This result also supports the fact that the acceleration under US conditions is more important for the crystal growth than for the nucleation.

In contrast, in the syntheses (with MW) of inorganic porous materials such as silicalite-1 and VSB-5,[27] the nucleation is accelerated more than crystal growth. Similarly, the acceleration in nucleation (45 times) is higher than crystal growth (8.4 times) in the MW synthesis of another inorganic porous material, SAPO-11.[30] Moreover, very recently, it has been found that the acceleration in the nucleation stage is more important than the acceleration in the crystal growth in the case of Cu–BTC.[42] Therefore, the acceleration in the snthesis of MIL-53(Fe), which is mainly in crystal growth, is different to other cases and needs a more detailed study.

Conclusions

Iron terephthalate, known as MIL-53(Fe), a metal–organic framework (MOF) material, has been synthesized at a relatively low temperature by conventional electric (CE) heating as well as by ultrasound (US) and microwave (MW) irradiation to gain an understanding of the accelerated syntheses observed under US and MW conditions. It has been found that the crystallization rate (both nucleation and crystal growth) decreases in the order US > MW ≫ CE and that the increased rates observed with US and MW are due to increased pre-exponential factors (of the Arrhenius equation) rather than decreased activation energies. It is suggested that physical effects such as hot spots are more important than chemical effects in the accelerated syntheses performed under US and MW conditions. The syntheses have also been conducted in two steps to analyze quantitatively the accelerated synthesis observed under MW conditions, and it can be understood that the acceleration induced by MW irradiation is mainly a result of a significantly greater acceleration in crystal growth compared with nucleation even though both processes are accelerated. The syntheses performed under US and MW conditions may be very promising methods for attaining MOFs, especially small crystals, at lower temperatures and in shorter reaction times, which would reduce the energy consumption of the syntheses. However, it should be noted that the US or MW synthesis of MOFs may be limited because the rapid synthesis of MOFs under US or MW irradiation has not been widely reported.

Table 2. Accelerations in nucleation and crystal growth by the microwave synthesis of MIL-53(Fe).[a]

Synthesis method	Nucleation time [min]	Nucleation rate [min^{-1}][b]	Relative nucleation rate	Crystallization time [min][c]	Crystal growth rate [min^{-1}][d]	Relative crystal growth rate
MW/MW	20	5.00×10^{-2}	15.5	100	2.08×10^{-2}	55.0 (28.2[e])
MW/CE	20	5.00×10^{-2}	15.5	2520	7.36×10^{-4}	1.95 (1.00[e])
CE/MW	310	3.23×10^{-3}	1.00	180	5.87×10^{-3}	15.5
CE/CE	310	3.23×10^{-3}	1.00	4010	3.78×10^{-4}	1.00

[a] Reaction temperature: 70 °C. [b] Calculated from 1/(nucleation time). [c] Time needed to attain fully crystallized MIL-53(Fe) after completed nucleation. [d] Calculated from the slopes of the crystallization curves (between 20 and 80% crystallinity). [e] Relative acceleration in crystal growth by MW of MW-nucleated sample.

Experimental Section

The MIL-53(Fe) samples used in this study were synthesized solvothermally under autogeneous pressure by methods similar to those reported previously.[31,32] MIL-53(Fe) was synthesized by using a mixture of ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$, Duksan Chemicals Co. Ltd., 99.7%), terephthalic acid (TPA, C_6H_4-1,4-$(CO_2H)_2$, Sigma-

Aldrich, 98%), and *N*,*N*-dimethylformamide (DMF, $HCON(CH_3)_2$; DC Chemicals Co. Ltd., 99%) in a Fe/TPA/DMF molar ratio of 1:1.5:130. A low reaction temperature (50–80°C) was used to compare the kinetics accurately, taking advantage of the low reaction rates.

Not only conventional electric heating, but also ultrasound or microwave irradiation was used for the crystallization of MIL-53(Fe). For the ultrasound synthesis, a vial was placed in the probe of an ultrasonic generator (VCX 750, Sonics & Materials, Inc). The temperature was controlled by circulating water at a constant temperature around the vial using a thermostat. The power was also varied at fixed reaction temperatures (25% of maximum power at 50°C, 30% at 60°C, 35% at 70°C, and 40% at 80°C). Microwave syntheses were carried out in a microwave oven (Mars-5, CEM) following synthetic procedures described elsewhere.[43]

To determine precisely the reaction rates of the conventional and ultrasound syntheses, the ferric salt was added to a mixture containing TPA and DMF after the reaction temperature was reached. However, the reaction mixture (room temperature) containing the ferric salt, TPA, and DMF were directly irradiated with MWs because the time required to reach the reaction temperature was less than 1 min.

After completion of the reactions for the predetermined time, the products were collected by cooling, centrifugation, washing with DMF, and drying for 2 h at 70°C. The crystal morphologies of the MIL-53(Fe) samples were examined by field emission scanning electron spectroscopy (Hitachi, S-4300).

The XRD crystallinity was calculated by the relative intensity of the (002) diffraction peak ($2\theta \approx 9.5$) of MIL-53(Fe) compared with fully crystallized samples under selected conditions. The relative rates of nucleation and crystal growth were estimated by the reciprocal of the induction period and the slope of the crystallization curve (crystallinity between 20 and 80%), respectively,[28] and the rates are regarded as kinetic constants. The induction period or nucleation time is the time required to observe any crystallinity (XRD intensity of 0–5%[44] to the fully crystallized samples).

The activation energies and the Arrhenius pre-exponential factors for the nucleation and crystallization were calculated from the nucleation and crystal growth rates determined at various temperatures by plotting $1/T$ against ln(rate); the activation energies and pre-exponential factors were derived from the slopes and intercepts, respectively.[28]

To study the two-step syntheses, four types of reactions were carried out by sequential heating by two methods, as described below (in the order of nucleation–crystal growth). 1) MW/MW: microwave heating; 2) MW/CE: microwave heating and successive conventional electric heating; 3) CE/MW: conventional electric heating and successive microwave heating; 4) CE/CE: conventional electric heating. The two-step synthetic procedures are described in more detail elsewhere.[27,30]

Acknowledgements

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[41] The relative rate of nucleation at 70 °C is calculated as the relative rate $\mathrm{MW/CE}=(1.19\times10^{10}/3.05\times10^{3})\times\exp[-(74.8-39.2)\times1000/8.3144/343]=14.9$. Similarly, the relative rate of crystal growth at 70 °C is calculated as the relative rate $\mathrm{MW/CE}=(1.23\times10^{12}/4.78\times10^{6})\times\exp[-(90.6-66.4)\times1000/8.3144/343]=53.1$.
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