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Exploiting Microwave Chemistry for Activation of Metal–Organic **Frameworks**

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Supporting Information

ABSTRACT: Microwave is thought of as a useful electromagnetic radiation tool because it is often used in real life as well as in a variety of chemical processes. Meanwhile, activation of metal-organic frameworks (MOFs), which must be essentially done to remove coordinating and pore-filling solvents before the use of MOFs for various applications, has been performed commonly with the methods of heat supply or solvent exchange. Here, we show a new methodological microwave activation (MA), realizing it with various MOFs such as HKUST-1, UiO-66, and MOF-74s. For instance, microwave irradiation to the MOF samples for 4-35 min leads to the complete activation of the MOFs without structural damage. As described



below, we further demonstrate that the solvent-assisted MA, which is the MA process performed after the solvent exchange, can substantially reduce the time for the activation by 4 min.

KEYWORDS: microwave, metal-organic framework (MOF), microwave activation, solvent-assisted microwave activation, activation of MOF, HKUST-1, UiO-66, MOF-74, dissipation factor

INTRODUCTION

Over the past few decades, porous solids have been intensively studied as promising functional materials in the multidisciplinary field of chemistry, chemical engineering, and environmental science, leading to a variety of academic research areas such as host-guest chemistry, inclusion chemistry, supramolecular chemistry, and separation technology. Metal-organic frameworks (MOFs) are a highly crystalline subset of the porous materials that are assembled by the multidimensional link of coordination bonds between the inorganic metal node and the multitopic organic linker.^{1,2} Because of their permanent porosity, modular topology, and extraordinarily broad chemical tunability, the study of MOFs has been thought of as an exciting subject, particularly for potential applications including gas uptake,^{1–9} molecular separation,^{4,8,10–15} drug delivery,^{16–19} sensor,^{20–24} electronic conductivity,^{25–30} ionic conductivity,^{31–33} and catalysis.^{34–36}

Activation of MOF, which promotes the energy state of MOF to a higher level by removing the pore-filling solvent residing in the pores and the coordinating solvent binding at the open-metal site (OMS) of the metal node, is an essential step that must be performed prior to use of MOFs in the aforementioned applications. The evacuation of the solvent molecules from the pore and framework needs the guest molecules to move through the pore freely and thereby to include in or react with the MOF appropriately. So far, thermal activation (hereafter TA), which is typically performed at relatively high temperature under vacuum conditions, has been most popularly used for the activation of MOF because the supplied heat energy can be used for the evaporation of the pore-filling solvent and the dissociation of the coordinating

solvent.³⁷⁻⁴³ However, TA has often shown negative influence on the structural integrity of the MOF because of (i) the high temperature exceeding the thermal energies required for the evaporation of pore-filling solvents and the dissociation of coordinating solvents and (ii) the inhomogeneous distribution of heat energy that is commonly transferred by thermal diffusion in solids (see Section S1). Thus, the TA process has been evolved more effectively by combining it with the solventexchange process before TA. For instance, the replacement of pore-filling and coordinating solvents by a solvent with weak coordination bonding and low boiling point [i.e., dichloromethane (DCM), trichloromethane (TCM), or methanol (MeOH)] can aid in lowering the activation temperature, thereby minimizing the possible negative influence on the structural integrity of MOFs.⁴³⁻⁴⁶ Although the solvent exchange with DCM or TCM can completely activate MOFs even without TA, the solvent exchange can also be a cumbersome process that consumes a large quantity of the solvents.^{43–46} Here, we report on the third method, "microwave activation (MA)," that enables to efficiently remove both coordinating and pore-filling solvents by microwave irradiation (we call this process MA for the sake of brevity although it does activate MOFs rather than the microwave; see Figure 1a). While many of the MOFs should be capable of capitalizing on this new approach, we initiate our studies with HKUST-1 [also known as $Cu_3(BTC)_2$, where BTC^{3-} is 1,3,5-benzenetricarboxylate; see Section S2]. One might think that MOF crystals

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Figure 1. Schematic illustrations for (a) the MA of MOFs, (b) the energy transfer of microwave and usual heat energies, and (c) three primary mechanisms in the microwave-matter interaction.

could be burnt when the crystals are irradiated by microwave. As shown below, however, microwave irradiation for approximately 5-35 min (depending on the coordinating solvent) led to the complete activation of the MOF crystals without structural damage. Thus, MA can be thought of as a time-efficient and energy-saving method when compared to the conventional TA and solvent-exchange methods. As also described below, we found that this MA is a more efficient strategy to reduce the activation time to 4 min when it is assisted by the solvent exchange with MeOH, which has a high dissipation factor and a low boiling point (we call this process "solvent-assisted MA," SAMA). Further, we demonstrate that this SAMA can be adapted to other MOFs such as UiO-66 and MOF-74 series. Also, we demonstrate that SAMA is a safer way than conventional TA, especially when it is applied to thermally unstable MOFs such as Ni-based MOF-74.

RESULTS AND DISCUSSION

Microwave has often been used not only in real life but also in various chemical analyses and processes⁴⁷ such as electron spin resonance, organic synthesis,^{48–50} inorganic synthesis,⁵¹ solid synthesis,⁵² and even MOF synthesis^{53–56} and purification.⁵⁷ While the usual heat energy is transferred by thermal diffusion or convection through lattice vibration or molecular collision,

microwave irradiation directly transfers its energy into the core of a chemical substance in the fashion of wave penetration. The transfer of microwave energy arises by the coupling of the electromagnetic field of microwave with the electrons in the chemical substance on the atomic or molecular level (Figure 1b). Microwave chemistry is commonly interpreted by three main mechanisms depending on the phase of chemical substances: (1) ionic conduction, (2) dipolar rotation of permanent or field-induced polar molecules, and (3) dielectric polarization (Figure 1c). Charged particles (usually ions) are excited by the electromagnetic field of microwave, behaving in a translational oscillation motion. By contrast, the dipoles in polar molecules and dielectric solids are excited by the field, behaving in rotational oscillation and oscillating polarization in the substance, respectively. Subsequently, the excited motions are relaxed to the ground-state energy level, emitting heat energy. Based on this theory, we hypothesized that microwave irradiation can promote the energy state of MOF solvent molecules to excited states, and subsequently, the excitation could spontaneously lead to relaxation, with simultaneous emission of heat energy on the atomic scale. We further hypothesized that the emitted heat energy can be utilized for the dissociation and evaporation of coordinating and porefilling solvent molecules, respectively. Also, we postulated that, if this process is feasible, the microwave irradiation can be a

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Figure 2. (a,b) ¹H NMR spectra and (c,d) PXRD patterns of pristine-, EtOH-, MeOH-, MeCN-, and DMF-coordinated HKUST-1 (a,c) before and (b,d) after microwave irradiation. The NMR spectra were taken after completely digesting the samples in D_2SO_4 . Insets show the optical microscope images of a pristine-HK single crystal before and after MA. (e) N_2 adsorption isotherms of thermally activated and microwave-activated DMF-HK samples. N_2 adsorption isotherms of thermally activated and microwave-activated pristine-HK samples were also examined for comparison. TA of DMF-HK and pristine-HK was performed at 150 °C for 12 h under vacuum conditions, while the microwave-activated DMF-HK and pristine-HK were pretreated only under vacuum. (f) Expanded (left panel) and wide (right panel) views of Raman spectra obtained from pristine-HK (black), TA-pristine-HK (red), and MA-pristine-HK (blue) samples.

safe process to activate MOFs because microwave energy can be more uniformly transferred in a whole MOF crystal, and thereby, the temperature distribution in the crystal can be more homogeneous, in contrast to the conventional TA process (Figure 1b).

To address the above hypothesis, we employed ¹H nuclear magnetic resonance (NMR) spectroscopic analysis. We prepared the "as synthesized" version of HKUST-1 (hereafter denoted as pristine-HK; HK = fully desolvated HKUST-1) via the solvothermal reaction of copper(II) nitrate and H₃BTC in a mixed solvent of water and ethanol (see details in Section S2).^{43–46} The pristine-HK contains both H_2O and EtOH as axial ligands at Cu²⁺ centers. For systematic studies of MA, we also prepared pure EtOH-, MeOH-, MeCN-, and dimethyl formamide (DMF)-coordinated HKUST-1 samples (denoted as EtOH-HK, MeOH-HK, MeCN-HK, and DMF-HK, respectively) after preferentially removing both H2O and EtOH in the pristine-HK via solvent-exchange process with DCM at room temperature and then coordinating pure EtOH, MeOH, MeCN, or DMF by soaking the HKUST-1 sample in the corresponding neat solvent (see Section S2).⁴³⁻⁴⁶ Figure 2a shows the ¹H NMR spectra of pristine-HK, EtOH-HK,

MeOH-HK, MeCN-HK, and DMF-HK, which were taken after each sample was completely digested in deuterated sulfuric acid, D_2SO_4 .⁴³⁻⁴⁶ While the peak for three identical protons in BTC appears at ~8.8 ppm, the peaks for the two identical CH₂ protons and three identical CH₃ protons in EtOH appear at 4.1 and 1.1 ppm, respectively. Also, the peaks for the three identical CH₃ protons in MeOH and MeCN appear at 3.7 and 2.1, respectively. The peaks for a formyl proton and the two sets of the three identical CH₃ protons appear at 7.8, 2.9, and 2.8 ppm, respectively. To observe the ability of microwave, we irradiated microwave to the samples in a microwave oven (hereafter MA-pristine-HK, MA-EtOH-HK, MA-MeOH-HK, MA-MeCN-HK, and MA-DMF-HK) and monitored the continuous progress of activation with the ¹H NMR spectra every minute (see Section S3). As a result, all peaks for the solvents disappeared after microwave irradiation for 4-35 min, although the times required for the complete activation were different depending on the solvents (Figure 2b). What is more notable is that only 4 min were taken for the complete removal of MeOH and EtOH from MeOH-HK and EtOH-HK samples, whereas MeCN-HK and DMF-HK samples took 8 and 35 min, respectively. This result is highly reliable because in the regime of dissipation factor (also known as loss tangent) 47

$$\tan \delta = \varepsilon'' / \varepsilon' \tag{1}$$

where ε' and ε'' are the dielectric constant and the dielectric loss, respectively; the conversion efficiency of microwave energy into heat energy is commonly proportional to the dissipation factor, and the dissipation factors of MeOH and EtOH are higher than the factors of MeCN and DMF (see Table S1 in Section S4). More concretely, the activation time can be interpreted as a multidimensional function combined with the dissipation factor, coordination strength, and boiling point that are associated with the microwave-to-heat energy conversion, the dissociation energy of the coordinating solvent, and the evaporation energy of the pore-filling solvent, respectively. Meanwhile, we have observed that the coordination strengths of the examined solvents are in the order MeOH \approx EtOH \approx MeCN \ll DMF.^{44,45} Considering the above coordination strengths, the boiling points [in the order MeOH $(64 \ ^{\circ}C) < EtOH \ (78 \ ^{\circ}C) < MeCN \ (81 \ ^{\circ}C) \ll DMF \ (153)$ $^{\circ}$ C)], and the dissipation factors [in the order EtOH (0.941) > MeOH (0.659) > DMF (0.161) > MeCN (0.062)], it is reasonable that the activation time increases in the order MeOH-HK (4 min) \approx EtOH-HK (4 min) < MeCN-HK (8 min) < DMF-HK (35 min). Therefore, these results underscore the ability of microwave to perform the activation of HKUST-1. Given that the conventional TA process requires at least several hours for complete desolvation, the microwave process can be considered as a more efficient way to activate MOF.

The crystalline phase purities of HKUST-1 samples before and after MA were determined via powder X-ray diffraction (PXRD) measurements (see Figure 2c,d). The PXRD patterns of microwave-irradiated HKUST-1 samples indicate that the structural integrities of the MOF samples were well preserved, although all solvent coordinations were eliminated. To confirm this structural integrity, we also examined N₂ adsorption isotherms [Brunauer-Emmett-Teller (BET)] with both thermally activated and microwave-irradiated pristine-HK and DMF-HK samples (see Figure 2e). Whereas the TA of both pristine-HK and DMF-HK samples was performed at 150 °C for 12 h under vacuum condition before the BET measurements (TA-pristine-HK and TA-DMF-HK, respectively), the MA of the samples was performed only by applying vacuum at room temperature (MA-pristine-HK and MA-DMF-HK, respectively). The results show that while the TA-pristine-HK sample exhibited an internal surface area (SA) of approximately 1950 $m^2 g^{-1}$, TA-DMF-HK exhibited an internal SA of 1400 $m^2 g^{-1}$. The low SA of TA-DMF-HK is ascribed to a low activation temperature (150 °C) in comparison to the high coordination strength and boiling point of DMF. In contrast to the TA-DMF-HK sample, MA-DMF-HK and MA-pristine-HK samples exhibited high internal SAs (~1840 and 2000 m² g⁻¹, respectively) comparable to that of TA-pristine-HK (~1950 m²·g⁻¹), although the microwave was irradiated for only 35 min or less (also see Section S5). Thus, the PXRD and BET results provide compelling evidence for the safety of MA in terms of the structural integrity of the MOF. Scanning electron microscope image of DMF-HK taken after microwave irradiation for 35 min also supports the above results (see Section S6).

Raman spectroscopy is a suitable analysis to monitor the change in coordination bonds around the Cu^{2+} center in

HKUST-1. More concretely, the presence or absence of the coordinating solvent at the Cu2+ center is reflected on the vibrational strength of the Cu–Cu bond in HKUST-1.^{43–46} To corroborate the activation function of the microwave, we examined the Raman spectra of a pristine-HK sample before and after microwave irradiation. We also examined a TApristine-HK sample for comparison. To avoid water coordination in a moist atmosphere, we prepared the samples by sealing them in cylindrical quartz containers under moisture-free conditions of an argon-charged glovebox. Figure 2f shows that pristine-HK exhibited the stretching vibration of Cu-Cu bond at the Raman shift of approximately 174 cm⁻¹. By contrast, the stretching vibration in MA-pristine-HK appeared at the shift of 229 cm⁻¹, indicating that all coordinating EtOH and H₂O molecules were eliminated from the pristine-HK sample, and all OMSs at Cu²⁺ centers became open-state after microwave irradiation. This result is highly consistent with the trend observed in the above NMR results and, therefore, underlines the ability of microwave for the activation of HKUST-1. Also, we confirmed the microwave function by taking the ultraviolet-visible (UV-vis) absorption spectra and thermogravimetric analyses of HKUST-1 samples before and after microwave irradiation (see Sections S7 and S8).

As described above, MeOH is a more efficient solvent for MA than other solvents because of its low coordination strength and boiling point and a high dissipation factor. Based on this fact, we wondered if SAMA, which is a MA process performed after solvent exchange with, for example, MeOH, can be a more efficient way to reduce the activation time. To address this question, we monitored the successive progress of MA with DMF-HK and MeOH-exchanged DMF-HK (MeOH-DMF-HK) using ¹H NMR measurements. As expected, Figure 3 shows that, while a DMF-HK sample required 35 min until



Figure 3. Time-dependent plots for the degree of activation of MeOH-DMF-HK and DMF-HK after microwave irradiation.

complete activation, a MeOH-DMF-HK sample needed only 4 min (also see Section S9). Thus, we concluded that SAMA is an effective way to reduce the activation time substantially.

We also examined UiO-66 and MOF-74 samples to address whether SAMA is useful for the activation of both OMS-free and OMS-containing MOFs. We synthesized UiO-66 crystals with the sources of 1,4-benzenedicarboxylic acid (H₂BDC) and Zr⁴⁺. We also synthesized MOF-74 crystals with the sources of 2,5-dioxido-1,4-benzenedicarboxylic acid (H₄DOBDC) and Ni²⁺, Mg²⁺, Co²⁺, or Cu²⁺, respectively [for MOF-74(Ni), MOF-74(Mg), MOF-74(Co), and MOF-74(Cu); see experimental details in Section S2]. As expected, MeOH-exchanged UiO-66 (10 min) that contains DMF as the pore-filling solvent (Figure 4a,b; and Section S10). Also, all MeOH-exchanged

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Figure 4. ¹H NMR spectra of (a,b) pristine and MeOH-exchanged UiO-66 samples and (c,d) MeOH-exchanged MOF-74(Cu, Mg, Co, and Ni) samples (a,c) before and (b,d) after microwave irradiation. The NMR spectra of the samples were taken after completely digesting the samples in D_2SO_4 .

MOF-74 samples were fully activated within 5 min (see Figure 4c,d; and Section S10). Most notable is that, while thermally unstable MOF-74(Ni) is seriously damaged or collapsed when conventional TA is applied, 44,58 its framework remained intact when SAMA was used.

Finally, we examined the total energy consumptions of both MA and TA using MeOH-HK and DMF-HK samples. Whereas the TA tests of MeOH-HK and DMF-HK were conducted at 150 and 200 °C, respectively, for the full desolvation of the samples, the MA tests of the samples were conducted under the same irradiation condition with the frequency of 2.45 GHz at the power of 600 W (note that the wave frequency of all commercial microwave ovens is fixed at 2.45 GHz by a federal regulation, which is licensed by the Federal Communications Commission). As a result, we observed that while TA consumed 5.4 and 5.8 kW h for the complete activation of MeOH-HK and DMF-HK, respectively, MA consumed only 51 and 385 W h. Thus, MA reduced the energy consumption by approximately 100-fold when compared to TA (see Figure 5). Also, we observed that the MA of MeOH-HK is faster than that of DMF-HK by approximately 9-fold. Therefore, we conclude that MeOHassisted MA is a more efficient method than normal MA, although MA is also more efficient relative to the conventional TA method.

CONCLUSIONS

In summary, we have demonstrated that microwave chemistry can be exploited for the activation of MOF. This new activation can be considered as an excellent method in terms of



Figure 5. Energy consumptions of MA and TA of MeOH-HK and DMF-HK samples. TAs of MeOH-HK and DMF-HK samples were conducted at temperatures of 150 and 200 $^{\circ}$ C, respectively.

performance as well as cost. More concretely, the solvent molecules residing in HKUST-1 could be thoroughly desolvated at least within 35 min. In particular, MeOH could be eliminated within 4 min from MeOH-HK and MeOHexchanged DMF-HK. We ascribe this efficient activation time to the relatively high dissipation factor, low coordination strength, and low boiling point of MeOH. Based on this fact, we suggest that SAMA can be a more excellent way than the normal MA, although the normal MA is also more superior than the conventional thermal method. Further, we demonstrated that this SAMA could be extensively applied to other MOFs such as UiO-66 and MOF-74s. Finally, we expect that, if the dissipation factor and dielectric loss of MOF frameworks can also be further elucidated, the influence of the frameworks themselves on the MA will be comprehensively understood. Also, we expect that these findings will prove transferrable or

adaptable to other MOFs and also be helpful for the MOF industry.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b12201.

Experimental details, list of dissipation factors, and UVvis absorption, PXRD, TGA, and ¹H NMR data (PDF)

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Notes

The authors declare no competing financial interest.

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