Chemistry in confined spaces: Reactivity of the Zn-MOF-74 channels

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Using infrared spectroscopy combined with ab initio methods we study reactions of H2O and CO inside the confined spaces of Zn-MOF-74 channels. Our results show that, once the water dissociation reaction H2O → OH+H takes place at the metal centers, the addition of 40 Torr of CO at 200 °C starts the production of formic acid via OH+H+CO → HCO2H. Our detailed analysis shows that the overall reaction H2O+CO → HCO2H takes place in the confinement of MOF-74 without an external catalyst, unlike the same reaction on flat surfaces. This discovery has several important consequences: It opens the door to a new set of catalytic reactions inside the channels of the MOF-74 system, it suggests that a recovery of the MOF’s adsorption capacity is possible after it has been exposed to water (which in turn stabilizes its crystal structure), and it produces the important industrial feedstock formic acid.

I. INTRODUCTION

Metal organic framework (MOF) materials are porous crystals widely studied for important applications and industrial processes such as gas storage and sequestration,1–10 molecular sensing,11–15 polymerization,16,17 luminescence,18,19 non-linear optics,20 magnetic networks,21 targeted drug delivery,22 multiferoics,23,24 and catalysis.25 In particular, MOF-74 [M2(dobdc), M = Mg2+, Zn2+, Ni2+, Co2+, and dobdc=2,5-dihydroxybenzenedicarboxylic acid] has shown great potential for the adsorption of small molecules such as H2, CO2, N2, CH4 among others.

The favorable reactivity of MOF-74 has been widely studied.25–29 For example, Co-MOF-74 exhibits a catalytic activity towards CO oxidation30 originating from the high density of Lewis acidic coordinatively unsaturated sites and the MOF’s porosity. The inclusion of Co atoms into Ni-MOF-74 results in a mixed system (Co/Ni-MOF-74) that shows activity towards the oxidation of cyclohexene, where the catalytic performance of the mixed system is higher than the one of pure Co-MOF-74.31 On the other hand, our previous results have shown that several members of the MOF-74 family are able to catalyze the dissociation of water into H and OH groups (H2O → OH+H, see Fig. 1) at low temperatures and pressures, i.e. above 150 °C and at 8 Torr of H2O.32–35 This particular catalytic reaction is responsible for the loss of crystal structure and adsorption capacity after exposure of MOF-74 to water33 and constitutes one of the main hurdles for wide-spread applications of MOFs in general and MOF-74 in particular. This challenge has motivated our efforts to look for new catalytic reactions inside the confined channels of MOF-74, further reacting the undesirable products of the H2O → OH+H reaction in order to overcome these hurdles.

In this work, we show that introducing CO molecules into the pores of MOF-74—after the H2O → OH+H reaction has taken place—enables the reaction OH+H+CO → HCO2H. Our results show that the overall reaction H2O+CO → HCO2H takes place in the confinement of the MOF without an external catalyst, with a number of important consequences: First, it showcases the reactivity inside the well-controlled and isolated environment of the MOF-74 channels. This aspect is very important, as the confinement of the MOF-74 environment catalyzes reactions that would otherwise require very high pressure, bringing significant simplifications for experiments and possible MOF applications. Next, it shows initial indications of a partial adsorption capacity recovery after exposure of MOF to water, as the OH groups that otherwise poison the metal centers are now visible. The open-metal sites at the corners form the primary adsorption sites. The arrow indicates how the H of the water is transferred to the O of the linker during the H2O → OH+H reaction. Black, red, white, and blue spheres represent C, O, H, and Zn atoms. The box shows the portion of MOF-74 visible in other figures, albeit from a slightly different angle.

FIG. 1. Zn-MOF-74 with its hexagonal channels clearly visible. The open-metal sites at the corners form the primary adsorption sites. The arrow indicates how the H of the water is transferred to the O of the linker during the H2O → OH+H reaction. Black, red, white, and blue spheres represent C, O, H, and Zn atoms. The box shows the portion of MOF-74 visible in other figures, albeit from a slightly different angle.
bound to and removed as formic acid. In turn, it increases the crystal structure stability of MOF-74 by removing the OH and H groups that cause the instability (note that, due to their strong binding, those groups cannot be removed by thermal activation). And finally, it binds the toxic CO and produces formic acid, a non-toxic liquid with 4.4 wt% hydrogen and thus a promising hydrogen carrier, and an important feedstock medicinal/industrial chemical. The use of Pd as catalytic material in direct formic acid fuel cells has brought interesting developments in this area highlighting formic acid as a valuable asset for a hydrogen economy.

II. EXPERIMENTAL AND THEORETICAL METHODS

A. Zn-MOF-74

Out of the isostructural M-MOF-74 family, Zn-MOF-74 exhibits the highest catalytic activity towards the H$_2$O $\rightarrow$ OH+H reaction. We thus use this system to study the H$_2$O+CO $\rightarrow$ HCO$_2$H reaction through a combination of ab initio simulations and experiments.

B. Hydrogen vs. Deuterium

Only recently, our work showed direct evidence of the water dissociation reaction H$_2$O $\rightarrow$ OH+H at the metal centers of MOF-74 above 150 °C. In this reaction, the water first binds to an open-metal site and then donates one H to the nearby O at the linker; the remaining OH group stays at the open-metal site, see Fig. 1. Interestingly, this reaction can only be observed when heavy water D$_2$O is used. Its fingerprint is a sharp peak at 970 cm$^{-1}$ in the IR spectrum, corresponding to the O–D vibration at the linker. When H$_2$O is used instead, the peak appears at a higher frequency, where it couples with and is masked by the vibrational modes of the MOF and becomes impossible to detect. Therefore, the main focus of our experiments is on the water reaction with D$_2$O. We refer to the resulting deuterated formic acid as FA(D). Nonetheless, we do show that the reaction also occurs with H$_2$O, referring to the resulting formic acid as FA(H). For simplicity, throughout the text we may generally say water, even when experiments are done with heavy water.

C. Experimental Details and Procedure

Our experiments are divided into 3 steps:

(i) Preparation and activation of the sample: Zn-MOF-74 powder (~2 mg) was pressed onto a KBr pellet (~1 cm diameter, 1–2 mm thick). The sample was placed into a high-pressure high-temperature cell (product number P/N 5850c, Specac Ltd, UK) at the focal point of an infrared spectrometer (Nicolet 6700, Thermo Scientific, US). The sample was activated under vacuum at 180 °C for 4 hours and then cooled down to room temperature to measure CO$_2$ absorption by introducing 6 Torr of CO$_2$ into the cell until saturation (30 minutes). Then, the area under the peak at 2386 cm$^{-1}$ was determined, which is a characteristic peak of CO$_2$ adsorbed on the Zn site and thus a quantitative measure of the CO$_2$ uptake. Thereafter, the cell was evacuated under vacuum (< 20 mTorr) at a temperature of 150 °C for a period of 4 hours.

(ii) Dissociation reaction: The sample was heated to 200 °C. 8 Torr of D$_2$O were then introduced into the cell until saturation occurred (8 hours) to start the dissociation reaction. Spectra were recorded as a function of time during the adsorption process to evaluate the 970 cm$^{-1}$ peak, i.e. the fingerprint of the D$_2$O $\rightarrow$ OD+D reaction. Thereafter, evacuation under vacuum (< 20 mTorr) for a period of 4 hours at 150 °C was required to evacuate the water gas phase completely and avoid further reaction. Note that this temperature is not high enough to also remove the OD and D products of the dissociation reaction. Then, at room temperature, CO$_2$ adsorption was measured again and the cell was evacuated as in step (i).

(iii) Formic acid production and removal: The temperature in the cell was raised back to 200 °C and 40 Torr of CO were introduced for 1 hour to start the formic acid production. Spectra were recorded. Thereafter, the cell was evacuated for 3 hours under vacuum (< 20 mTorr) at 200 °C, removing the formic acid and unreacted CO, while spectra were recorded. Then, CO$_2$ adsorption at room temperature was measured and the cell was evacuated as in step (i). This production and removal step was repeated two times and we refer to each occurrence as removal 1 and removal 2.

D. Computational Details

Ab initio modeling was performed at the density functional theory level, using Quantum ESPRESSO with the vdW-DF functional. Ultrasoft pseudo potentials were used with cutoffs of 544 eV and 5440 eV for the wave functions and charge density. Due to the large dimensions of the unit cell, only the Γ-point was used. During relaxations all atom positions were optimized until forces were less than 2.6×10$^{-4}$ eV/Å. Reaction barriers were found with a transition-state search algorithm, i.e. the climbing-image nudged-elastic band method. The primitive cell of our pristine Zn-MOF-74 system contained 54 atoms and has space group R3. Additional atoms/molecules were added as appropriate for the reactants. The rhombohedral axes are $a = b = c = 15.105$ Å and $\alpha = \beta = \gamma = 117.78^\circ$. 

III. RESULTS AND DISCUSSION

A. Confirming Formic Acid Production and Removal

We begin by showing experimental evidence that the reactive environment inside the MOF-74 channels catalyses the formic acid production (through water dissociation) \( \text{OH}^+ + \text{H}^+ + \text{CO} \rightarrow \text{HCO}_2\text{H} \). After the water dissociation reaction has taken place, the \( \text{FA}^\text{D} \) peaks \((\text{CD}_{\text{bend}}\) and \(\text{OD}_{\text{bend}}\)) are red shifted with respect to \(\text{FA}^\text{H}\) peaks \((\text{CH}_{\text{bend}}\) and \(\text{OH}_{\text{bend}}\)) by a factor of \(\sim 1.4\). C-O and C=O modes are less disturbed (shifted), as they are not directly affected by the presence of deuterium or hydrogen. The \(\text{OH}_{\text{bend}}\) vibrational mode signal at \(\sim 1550\) cm\(^{-1}\) for \(\text{FA}^\text{H}\) appears very close to a strong MOF mode at \(\sim 1530\) cm\(^{-1}\), and this vibrational mode may be contributing to the \(\text{OH}_{\text{bend}}\) signal. On the other hand, the signal at \(\sim 1530\) cm\(^{-1}\) in the \(\text{FA}^\text{D}\) spectrum may be due to a hydrogen contamination of the deuterated water, increased by the vibrations of the MOF modes.

In Fig. 3 we show how the characteristic peaks of \(\text{FA}^\text{D}\) disappear as a function of time during the removal in step (iii), showing that the produced formic acid can readily be removed. Note that these experiments rely on the detection of the linker O–D mode at \(970\) cm\(^{-1}\) and are thus only performed for the deuterated case (see Sec. II B). We will henceforth only discuss the deuterated case. It is interesting to note that—while the starting point for removal 1 and 2 are comparable to within 6%—the desorption becomes faster. For example, in the former case 35% of \(\text{FA}^\text{D}\) was removed after 20 min, while in the latter 62% was removed during the same time. This fact, together with the fact that several removals are necessary to react all OD and D groups suggests a bottleneck in diffusion of the reactants and products, discussed further below.

After the water dissociation reaction happens, its products (OD or OH) are strongly bound to primary and secondary adsorption sites. This undesirable decrease of the MOF’s adsorption capacity is well known and unfortunately limits the applicability of MOF materials to non-humid environments. Note that the water dissociation products bind so strongly to the MOF that a simple removal through activation is not possible before the MOF disintegrates. Other means to recover the uptake capacity of MOFs after exposure to water are thus highly desirable. Our production and removal of formic acid reacts those unwanted groups that are otherwise bound to the MOF after the water dissociation reaction. We now show that this process also partially restores the MOF’s small-molecule uptake capacity. In Fig. 3 we track the \(970\) cm\(^{-1}\) peak (a measure for the amount of dissociated heavy water present in the MOF cavity) as well as the \(2338\) cm\(^{-1}\) peak (a measurement of the \(\text{CO}_2\) adsorption capacity) at different stages of our experiment. We see that the former decreases as we introduce CO into the system, i.e by 1.6% after removal 1 and 7.9% after removal 2. This confirms that we have successfully removed the D groups from the linkers of the MOF. On the other hand, the latter—after an expected big reduction in the \(\text{CO}_2\) uptake capacity after the \(\text{D}_2\text{O}\) dissociation (22%)—increases by 1.5% and 5.1% after removal 1 and 2. While the MOF’s uptake capacity recovery is relatively small per removal cycle, our results constitute
### Figure 4

Integrated areas of the 970 cm$^{-1}$ peak (a measure of the amount of dissociated water) and 2338 cm$^{-1}$ peak (a measure of the CO$_2$ uptake capacity).

| MOF activated | after desorption | after removal 1 | after removal 2 |
|---------------|------------------|-----------------|-----------------|
| Integrated area [a. u.] | 0.7 | 0.65 | 0.6 |

### Figure 5

CO region of the IR spectrum during removal 1. The black line is taken just before CO evacuation and is measured on a scale of 0.005, since the CO gas-phase signal is very strong. Thereafter, IR spectra are taken at 1, 10, 20, and 60 minutes during evacuation, measured on the smaller scale of 0.0002.

The first proof-of-principle that such a recovery is even possible.

As expected, the decrease in the amount of dissociated water (area under the peak at 970 cm$^{-1}$) goes hand-in-hand with the increase of the CO$_2$ uptake capacity (area under the peak at 2338 cm$^{-1}$). However, it is interesting to see that more than one removal cycle is necessary to restore a significant amount of uptake capacity. In principle, the partial pressure of 40 Torr CO introduced into the system should be more than enough (we estimate that it results in at least 6 CO molecules per unit cell) to react all OD and D groups. However, this is not the case, see Fig. 4. We conclude that the produced formic acid inhibits diffusion of CO deeper into the bulk. After each removal of formic acid and the renewed introduction of CO, the process picks up where it had left off earlier, working from the MOF surface into the bulk until, eventually, all OD and D groups have been reacted. Work to reduce the number of cycles thus needs to focus on diffusion in MOF-74 as well as using similar reactions with different products.

The CO region in the IR spectrum also provides information on the mechanism of formic acid formation. Figure 5 shows the CO region during removal 1 at several stages. When CO gas is still inside the MOF, the predominant signal is at 2173 cm$^{-1}$. However, after 1 min of desorption, a shift to lower frequencies (2150 cm$^{-1}$) is observed. This indicates that the majority of the CO gas phase has been evacuated and now the IR spectrum is dominated by a signal that suggests a stronger interaction between the CO and the MOF, such as in the CO$_2$H+H state (see Fig. 6). After longer periods of desorption, the intensity of the signal is reduced as the chamber is evacuated.

Before we continue to study the nature of the reaction, we give an estimate of how much formic acid is produced. From our calculations we know that the crystal density of Zn-MOF-74 is 1.231 g/mL, with a volume of 3944.65 Å$^3$ for the hexagonal cell (note that the hexagonal cell contains 18 metal centers and is three times bigger than the rhombohedral representation). Based on that, we calculate that in our sample (2 mg of Zn-MOF-74) we have 4.12×10$^{17}$ hexagonal unit cells. According to Fig. 4, we observe a reduction of 22% in the CO$_2$ adsorption capacity, suggesting that we produced ∼4 OD+D groups every 18 metal centers. Therefore, when CO is introduced into the cell and 5.1% of the CO$_2$ adsorption capacity is recovered, we estimate a production of 3.95×10$^{17}$ formic acid molecules. This corresponds to 2.311×10$^{-5}$ mL of formic acid in the 2 mg of Zn-MOF-74, or 11.55 µL/g$_{\text{MOF}}$. Clearly, this is a small quantity, but as mention before, our goal is to investigate the chemistry in the confined spaces of Zn-MOF-74 and not the mass production of formic acid.

## B. Pathway of the Formic Acid Reaction

We now investigate the nature of the formic acid reaction H$_2$O+CO → HCO$_2$H and give an explanation of how it takes place. We know that the first step is the dissociation of water at the metal centers H$_2$O → OH+H, which we have studied in detail before. We find that the water dissociation takes place above 150 °C with an energy barrier up to 1.09 eV, depending on the number of water molecules involved in the reaction. The second step of the reaction starts by the introduction of CO at 200 °C, which catalyses the OH+H+CO → HCO$_2$H reaction. Based on this information, and taking into account that the metal centers are poisoned by the OH groups after the H$_2$O → OH+H reaction, we propose the following mechanism for the overall reaction: Once the H$_2$O → OH+H reaction takes place, the added CO molecules interact with the OH groups at the metal centers to form CO$_2$H adsorbed at the metal center. Ther-
after, the CO$_2$H molecule interacts with the H at the linker to form formic acid HCO$_2$H. Overall, the reaction pathway follows H$_2$O+CO → OH+H+CO → CO$_2$H+H → HCO$_2$H, as depicted in Fig. 6.

We now use our ab initio transition-state search to find the energetically most favorable pathway (i.e. lowest energy barriers) for our proposed reaction pathway. Results for the structures of reactants, stable states, and products are depicted in Fig. 6 and the energy profile along the entire reaction is plotted in Fig. 7. The first step of the reaction is the endothermic water dissociation H$_2$O+CO → OH+H+CO. We have previously calculated its reaction barrier (1.09 eV) and confirmed the separate OH (bound to the open-metal site) and H (bound to the O of the linker) experimentally inside MOF-74 above 150 °C. Thereafter, the reaction proceeds exothermic via OH+H+CO → CO$_2$H+H → HCO$_2$H, resulting in the formation of formic acid adsorbed on the metal centers of Zn-MOF-74. Our calculations show that the energy barrier between the states OH+H+CO and CO$_2$H+H is 0.8 eV, while the barrier between CO$_2$H+H and HCO$_2$H is 1.04 eV. The final state, i.e. HCO$_2$H, has an energy 0.23 eV lower than the energy of the initial state H$_2$O+CO, and the formic acid binds to the metal centers with an energy of 0.68 eV (65.61 kJ/mol), comparable to the binding of other molecules to Zn-MOF-74.

Thus, removal of the formic acid product from the open-metal sites can proceed through simple activation of the sample, as confirmed in Fig 6.

The overall barrier for the reaction in Fig. 7 is significant and explains why only a small amount of formic acid is produced. But, that barrier corresponds to the presence of only one water molecule. In related work, we show that the barrier to the first step of the reaction is lowered by 37% when the water molecules create clusters above the linkers. It is conceivable that the presence of several CO and/or H$_2$O molecules can also lower the energy barrier of the OH+H+CO → HCO$_2$H reaction. However, due to the large number of stable geometries and possible paths for the H$_2$O+CO → HCO$_2$H reaction when more than one molecule is involved, a comprehensive ab initio transition-state search becomes computational prohibitively expensive.

IV. CONCLUSIONS

Our experimental and theoretical work confirms that we can use the OH and H groups—produced by the H$_2$O → OH+H reaction—to start a new reaction mechanism catalyzed inside the confined environment of the Zn-MOF-74 channels through water dissociation and produce formic acid via H$_2$O+CO → HCO$_2$H. This discovery has several important consequences: It opens the door to a new set of catalytic reactions inside a well controlled system (MOF-74), it provides a proof-of-principle that a recovery of the adsorption capacity and structural stability of Zn-MOF-74 is possible after exposure to water, and finally it produces the important medical/industrial feedstock formic acid.
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