Inorganic Chemistry
Cite This: Inorg. Chem. XXXX, XXX, XXX−XXX
Communication
pubs.acs.org/IC

Brønsted Basicity in Metal−Organic Framework-808 and Its Application in Base-Free Catalysis

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Supporting Information

ABSTRACT: The Brønsted basicity in activated metal−organic framework-808 (hereinafter denoted as MOF-808a) was confirmed by the analyses of CO_2-TPD-MS, in situ DRIFTS, and acid−base titration. MOF-808a exhibited efficient recyclable catalytic activities for Heck coupling and oxidation of alcohol as a one-pot tandem reaction in base-free catalysis. It is the first evidence of the Brønsted basicity in zirconium metal−organic frameworks (Zr-MOFs) and gave rise to a new opportunity to extend the catalytic application of Zr-MOFs.

Metal−organic frameworks (MOFs) are an exciting class of porous crystalline materials that are orderly constructed from multidentate organic linkers and discrete metal ions or clusters. Compared to other porous materials such as zeolites or activated carbon, the high porosity, tunable pore size, and adjustable internal surface of MOFs make them eligible candidates for gas storage/separation, catalysis, chemical sensing, drug delivery, etc.[1−4] Zirconium-based MOFs (Zr-MOFs), in particular, are regarded as some of the most important MOF materials for practical applications. Besides having high porosities, Zr-MOFs possess exceptional thermal and chemical stabilities because of the high charge density of Zr^{IV} and strong affinity between the Zr atom and carboxylate-based ligand, which endows them with a promising capacity for heterogeneous catalysis.[5] This includes the various hitherto known types of catalytic reaction over Zr-MOFs, and their functionalized derivatives, including Lewis acid catalysis,[6] Brønsted acid catalysis,[7] oxidation catalysis,[8] biomimetic catalysis,[9,10] electrocatalysis,[11] and photocatalysis,[12] have been discussed in the current literature. Further exploration of new types of catalysis over Zr-MOFs will be highly desirable for quite a long time in the future.

During our research on the catalytic behavior of zirconia-based material, we noticed that monoclinic zirconium oxide (ZrO_2) not only featured an acid catalytic property but also presented a basic catalytic behavior. The in situ IR study proved that its basicity came from the OH species that existed on the ZrO_2 cluster.[13,14] Considering that Zr-MOFs are constructed by polyatomic inorganic zirconium oxo clusters with OH groups, which are similar to that of zirconia, we proposed that some of the Zr-MOFs might exhibit interesting Brønsted basic sites, which would expand their heterogeneously catalytic application, especially on most of the organic reaction that needs a base when the Zr-MOFs host noble nanoparticles (NPs). Herein, we demonstrated the Brønsted basic property of formate-free metal−organic framework-808 (MOF-808),[7] a famous Zr-MOF reported by Yaghi et al., and its catalytic behavior for base-free olefin Heck coupling reaction and tandem reaction oxidation of benzyl alcohol when MOF-808a encapsulated palladium (Pd) NPs.

In the structure of MOF-808 (Figure S1), each $Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(HCOO)_6(CO_2)_6$ second building unit (SBU) is interconnected to six 1,3,5-benzenetricarboxylate (BTC^{3-}) ligands, and each BTC^{3-} ligand coordinates with three SBUs, leading to the formation of a spn topological 3D framework containing two different types of pores with 4.8 and 18.4 Å diameter, respectively.[7,15] Surprisingly, the six formate ions $HCOO^-$ of the $Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(HCOO)_6(CO_2)_6$ SBU can be removed by heating the material in a fresh solvent, forming a new $Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(OH)_6(H_2O)_6(CO_2)_6$ core.[9,16,17] This new Zr-SBU of the activated formate-free MOF-808 (denoted as MOF-808a; Figure 1) has more OH^- species, which inspired us to investigate its possibility for generating Brønsted basic sites.

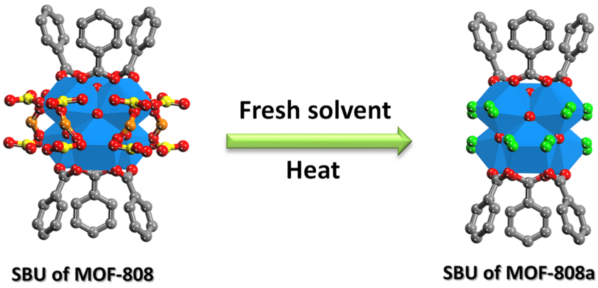

Figure 1. Formate ions of MOF-808 replaced by ligated water and hydroxy groups via heating of the material. Color code: Zr atoms, blue polyhedra; formate C atoms, yellow spheres (site occupancy of 0.25) and earthy yellow spheres (site occupancy of 0.5); other C atoms, gray spheres; O atoms of ligated water or hydroxyl groups, green spheres; other O atoms, red spheres. H atoms were omitted for clarity.

MOF-808a was synthesized according to previous reports with slight modifications and then activated by heating it in fresh *N,N*-dimethylformamide (DMF) and ethylene glycol for 24 h.[9,15] The structure and purity were confirmed by the powder X-ray diffraction (PXRD) and scanning electron microscopy (SEM) analyses (Figures S2 and S3a). In addition, ^1H NMR

Received: April 16, 2018

DOI: 10.1021/acs.inorgchem.8b01044
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spectroscopy upon digestion of the material in a hydrogen fluoride/deuterated dimethyl sulfoxide solution confirmed that the formate ions of MOF-808 were totally removed to form the activated MOF-808a (Figure S4).

The basicity of MOF-808a was determined by temperature-programmed desorption of CO_2, and the released gas was analyzed by multichannel mass spectrometry (CO_2-TPD-MS). As shown in Figure 2, in comparison with the blank sample without CO_2, MOF-808a that has adsorbed CO_2 exhibited one strong CO_2 desorption peak within the range of 160−240 °C. It can therefore be inferred that basic sites existed on the framework of MOF-808a. According to the literature,[18,19] the adsorbed CO_2 could be assigned to the type of CO_2 that has been strongly adsorbed on and/or the type that has interacted with the OH species on the surface of the Zr-based material. Because two types of OH groups existed in MOF-808a [bridged (b-)OH and terminal (t-)OH groups], the samples were performed on CO_2 with in situ diffuse-reflectance infrared Fourier transform spectroscopy (DRIFTS) characterization for an understanding of how CO_2 adsorbed on the basic sites of MOF-808a. As shown in Figure 3, the IR bands of adsorbed species were observed upon heating from room temperature to 300 °C after gaseous CO_2 had been introduced to MOF-808a in the cell at room temperature and the system purged by argon (100 mL/min) for 2 h. Although the IR spectra of the carboxylate group of the BTC ligand in MOF-808a would interfere with the IR observation for CO_2 adsorption on MOF-808a, several new bands were still observed at 3675, 3635, 2336, 1620, 1250, 830, and 735 cm^{-1} in the sample being introduced to CO_2 in comparison to that of blank MOF-808a. With an increase of the temperature, these bands disappeared gradually, indicating that MOF-808a might have absorbed CO_2 and produced new species. According to the literature, the bands at 3635 cm^{-1} (ν_{OH}), 1620 cm^{-1} (ν_{aCO}), and 1250 cm^{-1} (ν_{OH}) should be attributed to the formation of bicarbonate species from the reaction of acidic CO_2 with a t-OH group having O lone pairs.[20,21] The weak band at 830 cm^{-1} might be caused by the production of bidentate carbonate species. It is worth noting that the bands at 2336 and 735 cm^{-1} belonging to the physical adsorption of CO_2 were strong even if the sample was purged by helium gas for 2 h, indicating that MOF-808a has good CO_2 adsorption capacity. According to IR analysis, only one type of titratable base, t-OH, is expected. Indeed, as shown in Figure S5 of the acid titration curve, only one equivalence point at pH = 3.5 ± 0.1 was observed, indicating that a t-OH group is the exclusive base site in MOF-808a. The pK_b value for t-OH is about 10.2, which is determined as the pH at half the volume of the titrant added to reach the equivalence point.[22−24]

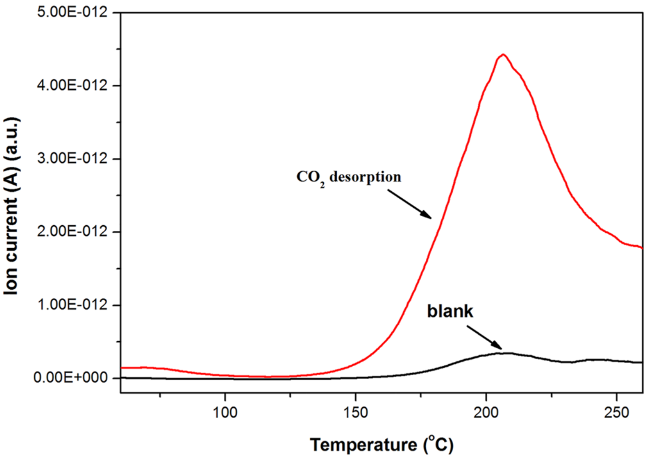


Figure 2. CO_2-TPD-MS profiles over the blank sample MOF-808a without adsorbing CO_2 and a sample initially adsorbing CO_2.

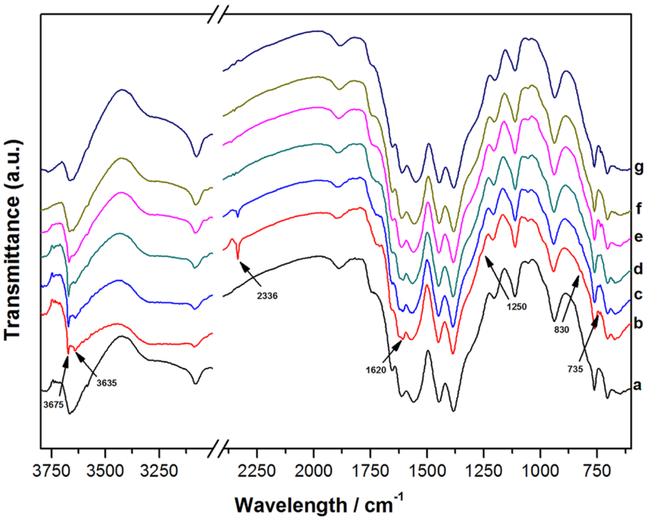


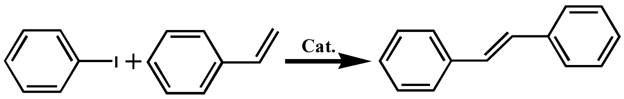
Figure 3. DRIFTS spectra of MOF-808a (a) and the samples after CO_2 introduced to MOF-808a and then heated at various temperatures: 30 °C (b); 70 °C (c); 110 °C (d); 170 °C (e); 220 °C (f); 300 °C (g). Each spectrum was taken 10 min after the desired temperature was reached.

To further understand the basicity of MOF-808a and expand its application, we immobilized Pd NPs onto MOF-808a (denoted as Pd/MOF-808a) and evaluated its catalytic performance for Heck coupling between halogenated aromatic compounds and olefins.[25−27] The Heck coupling reaction is an effective way to increase the C−C chain that is widely used in organic and drug intermediate syntheses.[28,29] With Heck coupling reaction proceeding, a halogen acid byproduct would be generated and would adhere to the Pd NP active center, which would decrease the catalytic activity of the catalyst. Hence, an additional base such as sodium carbonate and tertiary amine should be introduced to the catalytic system for neutralizing the halogen acid and reexposing the active center. However, as a result, the complexity of the reaction system and separation difficulty would be increased. The inherent basicity of Pd/MOF-808a might make it an excellent candidate for catalyzing the Heck reaction in the absence of additional base, exhibiting bifuctional catalytic activity.

As shown in the transmission electron microscopy (TEM) images of as-synthesized Pd/MOF-808a (Figure S3b,c), Pd NPs were highly dispersed with a diameter of 4.0 ± 2.0 nm, which indicated that the Pd NPs were mainly dispersed on the external surface because they were much bigger than the pores of MOF-808a. The actual Pd loading amount was 3.0 ± 0.1 wt %, as shown by inductively coupled plasma analysis. PXRD patterns (Figure S2c) showed that no Pd diffraction peaks of Pd/MOF-808a were observed, also indicating that Pd NPs were highly dispersed and the size was small. The catalytic activity of Pd/MOF-808a for Heck coupling reactions was investigated using a model coupling reaction of iodobenzene with styrene. As listed in Table 1, Pd/MOF-808a without any additional base exhibited high catalytic activity, with the diphenylethene yield being 93.6%. In contrast, there was no appreciable catalytic activity of MOF-808a because there was no Pd active center on it.

DOI: 10.1021/acs.inorgchem.8b01044

Table 1. Heck Coupling Reaction[a]



entry	catalyst	base	yield (%)[b]
1	Pd/MOF-808a	none	93.6
2	MOF-808a	none	0
3	Pd/MIL-101	none	14.0
4	Pd/UiO-66	none	12.0
5	$Pd(OAc)_2$[c]	none	10.0
6	Pd/MIL-101	KOAc	93.4
7	Pd/UiO-66	KOAc	97.8
8	Pd/ZrO_2	none	16.0
9	none	none	0

[a] The reaction was carried out in 0.5 mmol of iodobenzene, 0.6 mmol of styrene, 100 mg of catalyst (ca. 3 mmol % equiv of Pd), and 0.6 mmol of ethylene glycol in 4 mL of DMF at 130 °C for 24 h unless otherwise noted. [b] The yields were determined by gas chromatography on a HP-5 column with dodecane as the internal standard. [c] A total of 0.03 mmol of palladium acetate was used as the homogeneous catalyst.

However, the yields of diphenylethene were very low using Pd/MIL-101 and Pd/UiO-66, which had no basicity as catalysts (with the yields being 14.0% and 12.0%, respectively), which is close to the yield of 10% using homogeneous palladium acetate as the catalyst. When alkaline potassium acetate was added to the reaction, the yields remarkably increased to 93.4% for Pd/MIL-101 and 97.8% for Pd/UiO-66. This demonstrated that the inherent basicity of Pd/MOF-808a could replace the additional homogeneous base to neutralize the halogen acid generated in the reaction. The heterogeneous solid of Pd/MOF-808a would greatly reduce the complexity and separation difficulty of the reaction. It is worth noting that Pd/ZrO_2 showed a much lower catalytic activity than Pd/MOF-808a did (16.0% vs 93.6%). This might be caused by the lower surface area and bad Pd dispersion for the ZrO_2 support (Figure S6). The recycling of the catalyst was investigated to further confirm the persistence of the catalytic activity. For each cycle, the used catalyst was separated through filtration, washed with DMF and methanol, dried at 70 °C for 24 h, and then reused directly for the next run. As shown in Figure S7, the yield of the product decreased slightly after the first run and then the selectivity remained constant; at the end of the 10th cycle, the value was 84.0%, which was only ca. 9% lower than the initial value. The PXRD patterns suggest that the Pd/MOF-808a sample retained good crystallinity without experiencing significant degradation of the structural integrity after the 10th cycle of the catalytic reaction (Figure S2d). A filtering experiment was carried out for the Heck coupling reaction. As shown in Figure S8, the catalyst was filtered off after 6 h of reaction and the filtrate mixture was then stirred at 130 °C for 12 and 24 h. The result showed that no significant progress was observed, indicating that Pd/MOF-808a had good stability and capacity for the Heck coupling reaction. The catalyst was also extended to substituted phenyl containing olefins, acrylates, and linear olefins under the optimal conditions without using any basic reagents. As summarized in Table S1, all of the yields were expected, indicating the universality of Pd/MOF-808a for different substrates.

It is well-known that MOF-808 has an acidic nature from the Zr^{IV} node and μ_3-OH group, which was also evidenced by NH_3-TPD-MS and the base titration curve (Figures S9 and S10).[24] This inspired us to combine the acid–base feature as well as Pd NPs of Pd/MOF-808a to catalyze the oxidation of benzyl alcohol as a one-pot tandem reaction. In an alcohol oxidation tandem reaction, as shown in Table S2, Pd NPs were considered to be favorable for the activation of molecular oxygen on their surfaces, and the addition of a base can accelerate the first step reaction by deprotonation of the alcohol.[30,31] In the second step, the benzaldehyde in methanol would transform to methyl benzoate in the presence of an acidic or basic catalytic system. In our base-free tandem reaction, Pd/MOF-808a exhibited a complete conversion of benzyl alcohol and high selectivity of the final product (75% yield of methyl benzoate). In contrast, the Pd/UiO-66 catalyst, which does not possess basicity, gave benzaldehyde as the main product (77% yield) and only 22% of methyl benzoate. This demonstrated that the acid–base of Pd/MOF-808a could indeed synergetically accelerate the tandem reaction. Pd/MIL-101 gave 89% conversion and 50% yield of methyl benzoate, which might be due to the higher acidity of the Cr^{III} ions of Pd/MIL-101. Furthermore, the recyclability test of Pd/MOF-808a showed that the conversion and selectivity for three repeated runs of the recovered catalyst maintained virtually constant values (entries 2 and 3 in Table S2).

In summary, the existence of Brønsted basicity in activated MOF-808 has been confirmed. The Heck coupling and alcohol oxidation tandem reactions have demonstrated that MOF-808a could replace the additional base to neutralize the acid byproduct or activate the reactant, which would greatly reduce the complexity and separation difficulty of the catalytic reaction system. Because of the diversity of zirconium oxo clusters with OH groups in the Zr-MOFs family, we believe that some other Zr-MOFs might possess such basicity, which would extend the potential application of Zr-MOFs. Efforts are underway to fully exploit such a feature of Zr-MOFs for the organic reaction that needed a base.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b01044.

> Experimental details, characterization data, structural description of MOF-808, PXRD patterns, SEM and TEM images, NH_3-TPD-MS, acid–base titration curves, N_2 adsorption/desorption, and additional tables and figures (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was financed by the National Natural Science Foundations of China (Grants 21561020, 21661020, and 21663016) and Jiangxi Province (Grant 20153BCB23021).

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DOI: 10.1021/acs.inorgchem.8b01044
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