Heterogeneous Catalysis

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Inserting CO_2 into Aryl C–H Bonds of Metal–Organic Frameworks: CO_2 Utilization for Direct Heterogeneous C–H Activation

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Abstract: *Described for the first time is that carbon dioxide (CO_2) can be successfully inserted into aryl C–H bonds of the backbone of a metal–organic framework (MOF) to generate free carboxylate groups, which serve as Brønsted acid sites for efficiently catalyzing the methanolysis of epoxides. The work delineates the very first example of utilizing CO_2 for heterogeneous C–H activation and carboxylation reactions on MOFs, and opens a new avenue for CO_2 chemical transformations under mild reaction conditions.*

Carbon dioxide (CO_2), the major component of greenhouse gases, accumulates in the atmosphere at an alarming rate and is deemed as the main culprit for global warming and climate change. Thus, there are increasing demands for carbon capture and sequestration as CO_2 emissions are currently a matter of genuine public concern.[1] In contrast with CO_2 capture and storage by sorbent materials,[2] the chemical transformation of CO_2 into value-added products represents an alternative which is attractive and sustainable, and has been of an escalating interest.[3] CO_2 could serve as an ideal C1 source for organic synthesis because of its abundance, nontoxicity, and potential as a renewable resource. Nonetheless, the inertness of CO_2 makes it a formidable challenge to directly activate a CO_2 molecule and form a C–C bond, particularly under mild reaction conditions.[4] This challenge has triggered continuous yet intensive interest in the research of CO_2 activation, for example, chemical fixation and reduction of CO_2.[3–5]

Over the past two decades, metal–organic frameworks (MOFs)[6] have emerged as a new family of functional porous materials with great potential for applications in gas storage/separation,[7] catalysis,[8] sensing,[9] conductivity,[10] etc.[11] In particular, MOFs have been extensively investigated as sorbents for CO_2 capture and storage,[12] and recently there has also been increasing interest in exploring MOFs as catalysts for CO_2 chemical fixation and/or reduction.[13] Distinct from existing studies, we herein describe a new approach for the utilization of CO_2 as a C_1 building block by chemically inserting CO_2 into aryl C–H bonds of MOF backbones to generate free carboxylate groups, which not only remains as the most obviously incompatible functional group within MOFs because carboxylate groups are used as linking motifs, but also features as a prominent functionality in various applications.[14] Our work delineates the very first example of utilizing CO_2 for direct solid-state C–H activation and carboxylation reactions on a MOF, and the generated carboxylate group provides an opportunity for further exploration in terms of application and modification of the MOF. This proof-of-concept study thereby presents a new scenario for the utilization of CO_2 with a MOF platform and also contributes a different perspective to the current landscape of CO_2 capture and transformation.

Our inspiration to insert CO_2 into the aryl C–H bond of the backbone of a MOF for direct heterogeneous C–H activation is based upon the tremendous progress recently made in the field of C–H functionalization/activation in homogeneous systems.[15] To demonstrate the proof-of-concept, we selected the MOF UiO-67 as the platform for studies because of its remarkable chemical stability and large pore size.[16] The linear linker of 2-phenylpyridine-5,4′-dicarboxylic acid (dcppy) is employed to construct the UiO MOF, which can facilitate the introduction of cyclometalated complexes into the host framework for further postsynthetic modification.[17] As shown in Figure 1, the resultant UiO-67(dcppy) is constructed from the inorganic SBUs (secondary building units) of $Zr_6O_4(OH)_4$ bound to twelve organic linkers of dcppy, thus affording a three-dimensional periodic fcu-type network. Two types of cages sustain the structure: a centric octahedral cage connected to eight tetrahedral cages through triangular windows.

Experiments were then conducted to insert gaseous CO_2 into the aryl C–H bond of the backbone in UiO-67(dcppy), and they were promoted by a catalytic species, methylrhodium(I), in *N*,*N*′-dimethylacetamide as the solvent

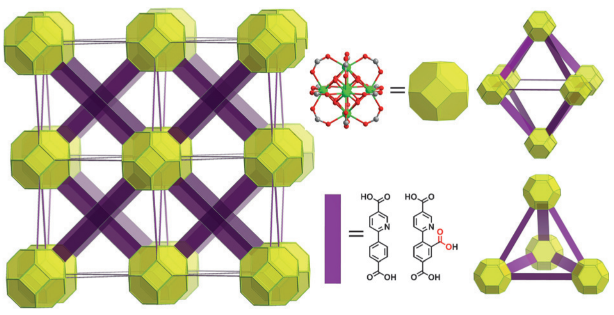

Figure 1. Structures of either UiO-67(dcppy) or UiO-67(dcppy)-COOH, composed of the cuboctahedral SBU, $[Zr_6(OH)_4O_4(CO_2)_{12})\}$, and linear linkers, sustained by octahedral and tetrahedral cages.

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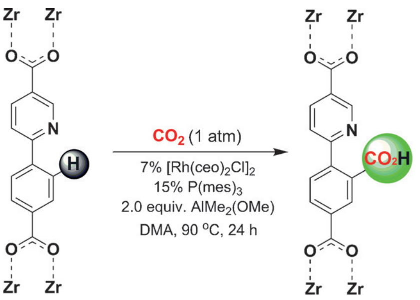


Scheme 1. Schematic representation of insertion of CO_2 into the aryl C–H bond within UiO-67(dcppy).

to generate the postmodified framework UiO-67(dcppy)-COOH. As illustrated in Scheme 1, the heterogeneous C–H bond activation experiment on UiO-67(dcppy) utilizes the combination of a rhodium catalyst and methylaluminum reagent as a stoichiometric reductant. The reaction details can be found in the Supporting Information. The framework integrity before and after CO_2 insertion were verified by powder X-ray diffraction (PXRD) studies. As shown in Figure 2a, the resultant UiO-67(dcppy)-COOH retains all the diffraction peaks from the parent UiO-67(dcppy), and all peaks are consistent with the calculated ones. These results are in line with the claimed structural resistance and stability of UiO-67 toward various solvents and other conditions. In addition, UiO-67(dcppy) maintained its permanent porosity after insertion of CO_2. As shown in Figure 2b, the N_2 adsorption isotherm of UiO-67(dcppy), collected at 77 K, indicates that it possesses a Brunauer–Emmett–Teller (BET) surface area of about 2750 $m^2 g^{-1}$ ($P/P_0 = 0.0001$–0.1). After the insertion of CO_2 into the aryl C–H bond of UiO-67(dcppy), UiO-67(dcppy)-COOH displays a decreased BET surface area of about 2160 $m^2 g^{-1}$ ($P/P_0 = 0.0001$–0.1), as expected for MOFs after introduction of new constituents by postsynthetic modification reactions.[18]

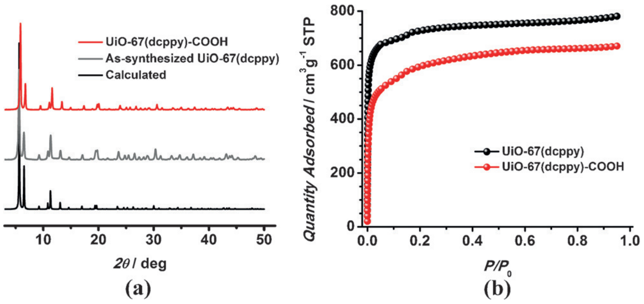
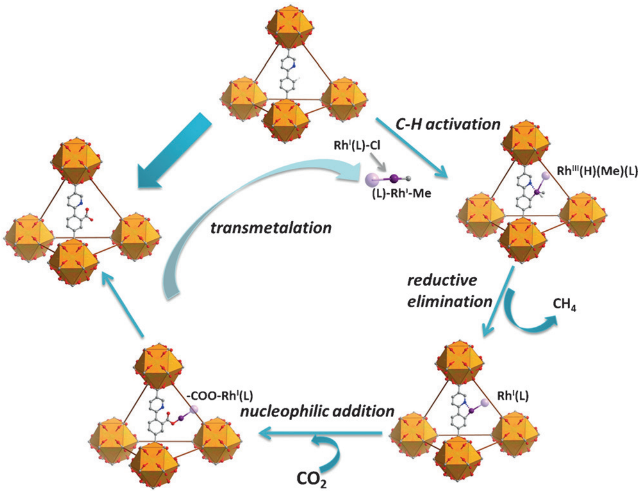


Figure 2. a) Powder X-ray diffraction patterns of UiO-67 (calculated), as-synthesized UiO-67(dcppy), and UiO-67(dcppy)-COOH. b) N_2 adsorption isotherms at 77 K of UiO-67(dcppy) and UiO-67(dcppy)-COOH.

The successful insertion of CO_2 into the C–H bond to form the carboxylate group has been initially evidenced by infrared spectroscopy studies (see Figure S1 in the Supporting Information), which reveal the appearance of a broad band centered at about 3300 cm^{-1}, and corresponds to O–H bond stretching for the fully activated UiO-67(dcppy)-COOH sample as compared to the fully activated parent material of UiO-67(dcppy). The formation of the new C–C bond from the insertion of CO_2 into the C–H bond of dcppy has also been proven by ^{13}C NMR spectroscopy (see Figure S2). The ^{13}C NMR spectrum of digested UiO-67(dcppy) exhibited one set of expected signals attributed to dcppy. In contrast, the ^{13}C NMR spectrum of digested UiO-67(dcppy)-COOH showed a unique peak at $\delta \approx 169.5$ ppm, which is characteristic of the carbon atom in a carboxylic group deshielded by a nearby nitrogen atom. Moreover, an isotopic-labelling experiment was employed and $^{13}CO_2$ was used as the reagent to track the fate of CO_2. As illustrated in Figure S3, the as-synthesized sample of UiO-67(dcppy)-COOH was directly digested in deuterated solvent and unambiguously provides an enhanced ^{13}C NMR signal from the resultant carboxylate group, and thus determines that CO_2 was successfully inserted into the C–H bond of UiO-67(dcppy) to form the carboxylate group. The formation of the new carboxylate moiety on the dcppy linker is further supported by the ESI-MS (electrospray ionization-mass spectroscopy) spectrum of the digested UiO-67(dcppy)-COOH, and it reveals a dominant peak at m/z 288.1 which corresponds to the resultant linker 2-phenylpyridine-5,2′,4′-tricarboxylic acid (tcppy) as shown in Figure S3. High-performance liquid chromatography (HPLC) analysis of the digested UiO-67(dcppy)-COOH also verified the formation of the tcppy linker from CO_2 insertion into the C–H bond of dcppy linker (see Figure S4), and suggests a yield of about 80 % for the CO_2 insertion reaction on UiO-67(dcppy). The single-crystal structure of the separated tcppy was also obtained as supporting evidence (see Figure S7 and Table S1).

NH_3 temperature-programmed desorption (TPD) analysis was conducted to characterize the acidity for UiO-67(dcppy) and UiO-67(dcppy)-COOH. As illustrated in Figure S5, both MOF samples share a NH_3 desorption peak in the range of 350–425 K, which can be attributed to relative weak Lewis-acidic sites from the Zr-based SBUs. Additionally, UiO-67(dcppy)-COOH displays an extra desorption peak at the higher temperature of about 450 K, and it corresponds to NH_3 bound to the stronger Brønsted acid sites. This peak should be ascribed to the existence of the free carboxylate groups in UiO-67(dcppy)-COOH.

A tentative mechanism is proposed for the chemical insertion of CO_2 into the aryl C–H bond of the UiO-67(dcppy) backbone (Scheme 2). The reaction starts with generation of a methylrhodium(I) complex from rhodium(I) chloride and methylaluminum reagent, followed by C–H bond activation directed by chelation effect of 2-phenylpyridine unit (oxidative addition). Subsequently, reductive elimination of methane affords a highly reactive arylrhodium(I) species, which then undergoes CO_2 nucleophilic addition reaction to give a rhodium(I) benzoate complex. The transmetalation with a methylaluminum reagent closes the catalytic cycle, thus forming the carboxylate groups on the backbone of UiO-67(dcppy). Compared to the homogeneous C–H activation by CO_2 as a liquid–gas biphasic reaction, the heterogeneous C–H activation on the MOF represents a liquid–solid–gas triphasic reaction, which shares a similar



Scheme 2. A representation of the tentatively proposed catalytic mechanism for chemical insertion of CO_2 into aryl C–H bonds of the UiO-67(dcppy) backbone.

reaction mechanism with that of a homogeneous reaction system. Nonetheless, because of the large pore size and pore volume of the host framework, the catalytic species and reagent molecules can readily migrate from one reactive site to another, thus facilitating the reaction under the triphasic conditions.

Given the presence of free carboxylate groups on the accessible inner surface of the framework, we investigated the resultant UiO-67(dcppy)-COOH as a solid-state Brønsted acid catalyst in the context of an epoxide ring-opening using methanol.[19] Cyclohexene oxide was chosen as the primary substrate in the study (Table 1, entries 1–7). Control experiments were performed with the parent UiO-67(dcppy), dcppy ligand, tcppy ligand, benzoic acid, and blank. The MOF solids were predried overnight and were then added to a CD_3OD solution containing the epoxide. After 2 days under ambient conditions, ^1H NMR analysis indicated that the yield of methanolysis of the epoxide was as high as 85.0% when the reaction was catalyzed by UiO-67(dcppy)-COOH (entry 1). This outcome is in contrast with the almost no conversion for the blank control experiment (entry 6) and very low yield (36.8%, entry 2) for the reaction catalyzed by the parent UiO-67(dcppy). Since dcppy and tcppy have very poor solubility in methanol, meaning the Brønsted acid sites are not quite accessible for the substrates, both of them display very low yields (< 5%, entries 3 and 4) in the epoxide ring-opening. Benzoic acid, which completely dissolves in methanol, serves as a homogeneous catalyst to afford a yield of about 84% for the methanolysis of the epoxide and is comparable to that of UiO-67(dcppy)-COOH. The recycle experiment of UiO-67(dcppy)-COOH was conducted and a yield of about 80% was attained (entry 7), and indicates that UiO-67(dcppy)-COOH can be recovered and reused as a heterogeneous catalyst (more detailed information in the Supporting Information). Moreover, for ring-opening of *trans*-stilbene oxide, which is a larger molecule, no activity was observed when using UiO-67(dcppy)-COOH (entry 8), and in striking contrast to 84.2% yield of the product is observed when just benzoic acid was used (entry 9). This difference can be ascribed to the size-selective pore size and pore volume of UiO-67(dcppy)-COOH, as it precludes the access of larger substrate molecules to the active Brønsted acid sites within the framework. These results highlight the essential role of the free carboxylate groups as Brønsted acid centers in UiO-67(dcppy)-COOH to efficiently and size-selectively catalyze the methanolysis of epoxides.

Table 1: The ring-opening reactions of epoxides by methanol.

Entry[a]	Substrate	Catalyst	Yield [%]
1	cyclohexene oxide	UiO-67(dcppy)-COOH	85.0
2	cyclohexene oxide	UiO-67(dcppy)	36.8
3	cyclohexene oxide	dcppy	< 5.00
4	cyclohexene oxide	tcppy	< 5.00
5	cyclohexene oxide	benzoic acid	84.0
6	cyclohexene oxide	blank	≈0
7	cyclohexene oxide	UiO-67(dcppy)-COOH recycled	80.0
8	*trans*-stilbene oxide	UiO-67(dcppy)-COOH	≈0
9	*trans*-stilbene oxide	benzoic acid	84.2
10	*trans*-stilbene oxide	blank	≈0

[a] Reaction conditions: substrate (0.2 mmol), CD_3OD (1 mL), catalyst (MOF: 15 mg; dcppy/tcppy/benzoic acid loaded as the same molar number as that of the free carboxylates found in UiO-67(dcppy)-COOH; see the details in the Supporting Information) at room temperature for 2 days. The reaction yield is determined by ^1H NMR spectroscopy.

In summary, we have demonstrated, for the first time, the successful insertion of CO_2 into the aryl C–H bonds of the backbone of MOFs to generate carboxylate groups. The Brønsted acidity of the generated carboxylate group was examined by NH_3-TPD analysis, thus showing that the resultant UiO-67(dcppy)-COOH performs well as a solid-state Brønsted acid catalyst to catalyze the methanolysis of an epoxide. Our work thus advances a new application of CO_2 as C1 building block, and also delineates the very first example of utilizing CO_2 for direct solid-state C–H activation and carboxylation reactions on MOF. This proof-of-concept study provides a different perspective for CO_2 utilization on the MOF platform and enriches the current landscape of CO_2 capture and transformation. Ongoing research in our laboratory, including the detailed mechanistic studies to probe the intermediates during the CO_2 insertion reaction on the MOF and the employment of UiO-67(dcppy)-COOH for further modification and functionalization to target specific applications. The development of new routes for CO_2 chemical fixation and/or CO_2 reduction based upon MOFs is underway in our laboratory as well.

Experimental Section

Experimental details: A mixture of activated UiO-67-dcppy (85 mg), chlorobis(cyclooctene)rhodium(I) dimer (12.1 mg, 0.015 mmol), tris(2,4,6-trimethylphenyl)phosphine (13.0 mg, 0.036 mmol) and *N,N*-dimethylacetamide (4 mL) was loaded in a Schlenk tube in a nitrogen glove box. The N_2 gas was then carefully displaced with CO_2 gas by the Schlenk line. The aluminum reagent (0.3 mL, 0.6 mmol) prepared as described in the Supporting Information was added into the Schlenk tube at room temperature. The tube was then heated up to 85 °C for 24 hours. 1 M aq. HCl was added and the solid was separated with the solution by centrifugation. The collected powder was fully washed with DMA and then exchanged with methanol.

Crystal data for tcppy: $C_{14}H_{10}NO_7K$, $fw = 343.33$, orthorhombic, $Pbca$, $a = 13.5736(11)$, $b = 7.1113(6)$, $c = 27.567(2)$ Å, $V = 2660.94(4)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.714$ g cm^{-3}, R_1 $(I > 2\sigma(I)) = 0.0606$, ωR_2 (all data) $= 0.1830$. CCDC 1441139 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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