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Carbon Dioxide Fixation Very Important Paper

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An Efficient Nanoscale Heterogeneous Catalyst for the Capture and Conversion of Carbon Dioxide at Ambient Pressure**

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Abstract: *Silver nanoparticles were successfully supported on the zeolite-type metal–organic framework MIL-101 to yield Ag@MIL-101 by a simple liquid impregnation method. For the first time, the conversion of terminal alkynes into propiolic acids with CO_2 was achieved by the use of the Ag@MIL-101 catalysts. Owing to the excellent catalytic activity, the reaction proceeded at atmospheric pressure and low temperature (50°C). The Ag@MIL-101 porous material is of outstanding bifunctional character as it is capable of simultaneously capturing and converting CO_2 with low energy consumption and can be recovered easily by centrifugation.*

The emission of CO_2 has become an urgent issue of our decade as it causes global warming and a consequent series of environmental problems.[1] Many efforts have been directed towards the efficient utilization of CO_2 by chemical methods, which may also provide access to high-value products from a non-toxic, renewable, and low-cost resource.[2] One of the best strategies for CO_2 conversion is the synthesis of propiolic acids through the C−H bond activation of terminal alkynes with CO_2 as a C_1 building block[3] because the alkynyl carboxylic acid products can serve as important synthetic intermediates[4] for further applications in medical chemistry as well as organic synthesis[5] to give coumarins, flavones, aminoalkynes, alkynylarenes, and arylidene oxindoles.[6] Several procedures and catalysts, including both homo-[3c–e,7] and heterogeneous catalytic[3a] systems, have been developed in this area, but either reusability problems or synthetic complications limit the further application of these catalytic systems. The design and synthesis of efficient, inexpensive, and easily prepared catalysts for this type of reactions are only at the beginning and urgently require further developments.

Recently, the application of metal–organic frameworks (MOFs) for utilizing CO_2 as a C_1 building block[8] or for encapsulating metal nanoparticles (MNPs)[9] has received tremendous attention. MOFs are an attractive class of porous crystalline materials[10–14] and have well-defined pores and mechanically robust walls, which can thus act as a template or scaffold to direct the formation of NPs with tunable size and uniform shape as well as to efficiently stabilize MNPs without blocking their surface by strongly binding ligands.[15] Herein, we describe the design and synthesis of an efficient, easily regenerated MNP-MOF nanoscale heterogeneous material, namely Ag@MIL-101, which can act as a bifunctional material and achieve both the capture and the high-efficient conversion of CO_2 at low temperature (50°C) and 1 atm in a single process. To the best of our knowledge, this is the first example of an active and reusable catalyst for the carboxylation of terminal alkynes with CO_2 by using MOFs as a matrix and template.

Ag@MIL-101 catalysts with different Ag loadings were prepared via a simple impregnation–reduction method (Figure 1) by immobilizing Ag NPs in MIL-101(Cr),[16] which was selected as the support not only because of the very large pore size (2.9–3.4 nm) and high specific surface area, but also because of its long-term chemical stability in various organic solvents, water, and air.[16,17] The obtained Ag@MIL-101 catalysts were characterized by X-ray photoelectron spectroscopy (XPS; Supporting Information, Figure S1) and powder X-ray diffraction (PXRD; Figure S2). Catalysts **1a**, **1b**, **1c**, and **1d** have Ag loadings of 1.66, 2.58, 4.16, and 6.97 wt%, respectively, as confirmed by inductively coupled plasma (ICP) analysis.

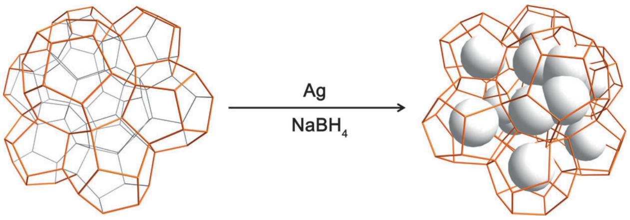

Figure 1. Synthesis of Ag@MIL-101.

N_2 and CO_2 sorption were measured for samples of **1a**–**1d**. Significant decreases in the amount of both N_2 and CO_2 sorption were observed for all of the Ag-loaded samples in comparison with MIL-101. The decrease in the surface areas should be attributed to the incorporation of the Ag NPs into the pores of MIL-101 and/or a block of Ag NPs located on the framework surface of MIL-101 (Figure S3). The CO_2 sorption properties of samples **1a**–**1d** were investigated at room temperature and 1 atm (Figure 2). The uptake of CO_2 reached 64.25, 61.50, 60.37, and 63.95 mg g^{-1} for **1a**, **1b**, **1c**, and **1d**, respectively (Table S1); these values are comparable to those

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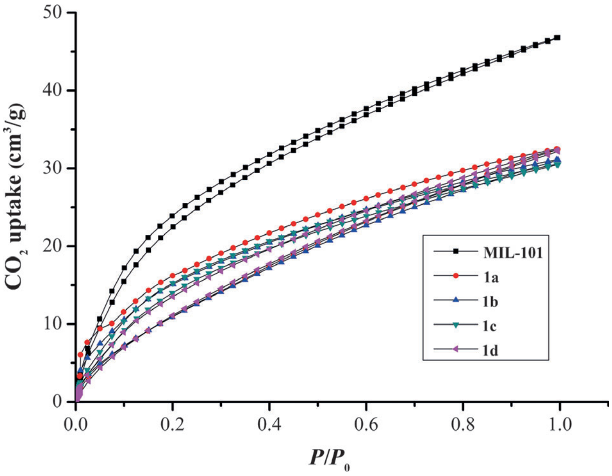
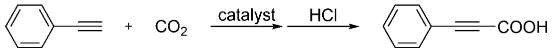


Figure 2. CO_2 adsorption/desorption (298 K) of MIL-101(Cr) and **1a**–**1d**.

reported for MOF materials with good CO_2 uptake properties under identical conditions.[18]

The catalytic activities of the prepared samples (**1a**–**1d**) were determined for the fixation of CO_2 with terminal alkynes into propiolic acids. In the initial investigation, the carboxylation of 1-ethynylbenzene was selected as a model reaction to study the influence of various parameters on the reaction. Table 1 shows the generation of 3-phenylpropiolic acid from CO_2 (1 atm) and 1-ethynylbenzene at 50 °C in the presence of Ag@MIL-101 with different Ag loadings. For 70 mg of **1a**–**d** (entries 1–4), 3-phenylpropiolic acid was obtained in good yields (67.5–96.5 %). Catalyst **1c** with 0.027 mmol of Ag afforded the highest product yield, and the catalytic activity decreased in the following order: **1c** > **1d** > **1b** > **1a**. The product yields depended on the amount of **1c** used in the reaction (entries 5–7). When the amount of **1c** was increased to 100 mg, the yield decreased to 94.1 %, which was slightly lower than the yield obtained with a dosage of 70 mg.

Table 1: Synthesis of 3-phenylpropiolic acid from CO_2 and 1-ethynylbenzene with catalysts **1**.[a]



Entry	Catalyst (mg)	Ag [mmol]	Solvent	Yield[b] [%]
1	**1a** (70)	0.011	DMF	67.5
2	**1b** (70)	0.017	DMF	71.9
3	**1c** (70)	0.027	DMF	96.5
4	**1d** (70)	0.045	DMF	90.9
5	**1c** (25)	0.010	DMF	34.1
6	**1c** (50)	0.019	DMF	80.8
7	**1c** (100)	0.039	DMF	94.1
8[c]	**1c** (70)	0.027	DMF	86.2
9	**1c** (70)	0.027	CH_3CN	71.8
10	**1c** (70)	0.027	NMP	86.5
11	**1c** (70)	0.027	DMSO	92.1
12[d]	**1c** (70)	0.027	DMF	25.2
13[e]	**1c** (70)	0.027	DMF	53.3
14[f]	**1c** (0)	0	DMF	3.8
15	MIL-101(Cr) (70)	0	DMF	21.9
16[g]	**1c** (70)	0.027	DMF	0

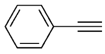
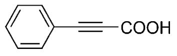
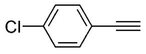
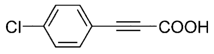
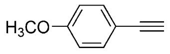
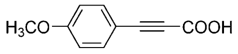
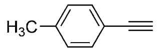
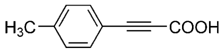
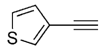
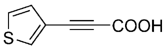
[a] Reaction conditions: 1-ethynylbenzene (1.0 mmol), catalyst, Cs_2CO_3 (1.5 mmol), CO_2 (1.0 atm), 50 °C, solvent (5 mL), 15 h. [b] Yield of isolated product. [c] 12 h. [d] K_2CO_3. [e] 25 °C. [f] In the absence of Ag. [g] In the absence of CO_2. NMP = *N*-methyl-2-pyrrolidone.

Then, we intensively surveyed the influence of other organic solvents on the catalytic system, which confirmed DMF as a superior solvent for this system in comparison with CH_3CN, NMP, and DMSO (entries 9–11) because DMF was a better solvent for both Cs_2CO_3 and CO_2 (DMF is a weak base) than the other organic solvents.[3d] It is noteworthy that the yield dropped to 25.2 % when the base was changed to K_2CO_3 under otherwise identical conditions (entry 12), indicating that Cs_2CO_3 was a superior base for this direct carboxylation reaction of terminal alkynes with CO_2.[3d,e] When MIL-101 or Cs_2CO_3 were used without Ag, the catalytic systems gave phenylpropiolic acid in poor yields of 21.9 % or 3.8 %, respectively (entries 14 and 15).

With the optimized conditions (1.5 equiv Cs_2CO_3, 1 atm CO_2 DMF, 50 °C) in hand, several typical alkyne substrates were subjected to this carboxylation reaction (Table 2). Under the standard conditions, the corresponding products were obtained in excellent yields (96.5–98.7 %) when aromatic alkynes with either electron-donating (CH_3, OCH_3) or electron-withdrawing (Cl) substituents were employed. Even for an alkyne with a heterocyclic group (thiophene), 98.5 % yield was achieved.

Table 2: Synthesis of propiolic acid derivatives from CO_2 and terminal alkynes with catalyst **1c**.[a]

$$R{-}{\equiv} \;+\; CO_2 \xrightarrow{\text{catalyst}} \xrightarrow{\text{HCl}} R{-}{\equiv}{-}COOH$$

Entry	Alkyne	Product	Yield[b] [%]
1			96.5
2			98.4
3			98.2
4			98.7
5			98.5

[a] Reaction conditions: alkyne (1.0 mmol), **1c** (70 mg, 2.7 mol % of Ag), Cs_2CO_3 (1.5 mmol), CO_2 (1.0 atm), 50 °C, DMF (5 mL), 15 h. [b] Yield of isolated product.

As a heterogeneous catalyst, Ag@MIL-101 could not only be simply prepared, but also easily separated from the reaction solution by centrifugation. As shown in Figure 3, catalyst **1c** could be regenerated and reused at least five times without any obvious decreases in catalytic activity in the subsequent reaction under the optimized conditions. The PXRD pattern (Figure S2) showed that the framework of catalyst **1c** was well maintained after the catalytic reaction in DMF, which confirms the stability of the Ag@MIL-101 catalysts during the reaction.

To further investigate and explain the excellent catalytic activity of the Ag@MIL-101 catalysts, the morphology of the

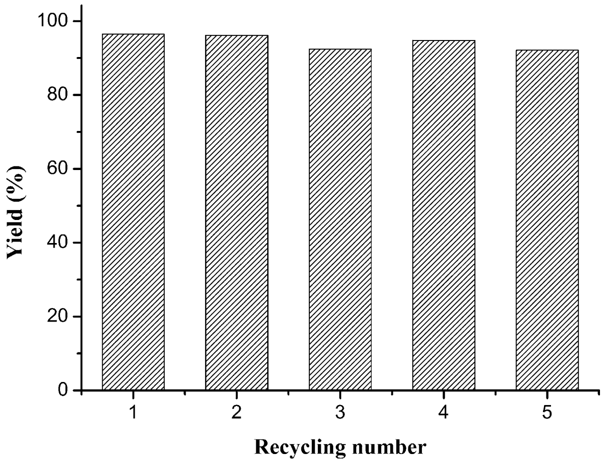


Figure 3. Recycling tests with catalyst **1c** for the carboxylation of terminal alkynes with CO_2.

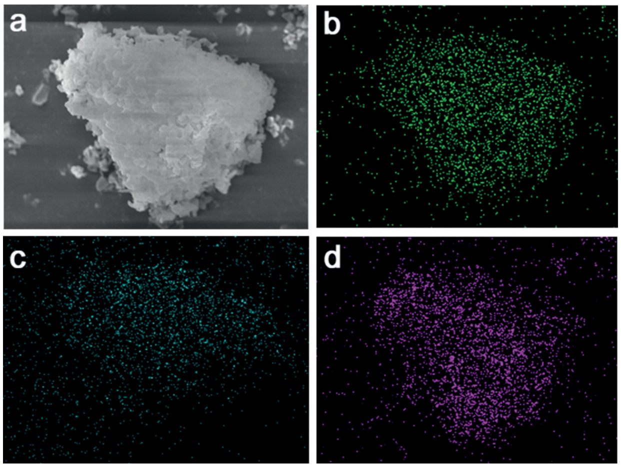


Figure 4. Element maps for a Ag@MIL-101 sample (**1c**): a) SEM image; b) Cr (green); c) O (indigo); d) Ag (purple).

Ag NPs immobilized in MIL-101 in **1a**–**1d** was characterized by energy-dispersive spectroscopy (EDS) and transmission electron microscopy (TEM). EDS images (Figure 4 and Figures S4–S6) confirm the homogeneous three-dimensional distribution of the Ag NPs throughout the interior of the MIL-101 matrix. The TEM images (Figure 5 and Figures S7–S9) show that the Ag NPs in **1c** were sufficiently dispersed and restricted to smaller sizes than those in **1a**, **1b**, and **1d**, so that a larger surface area is available for the reactants, and a higher catalytic performance is achieved with **1c**.[19] The aggregation of NPs in **1d** (Figure S9) leads to its lower catalytic activity, even though **1d** has a higher Ag loading, as was observed for ZIF-8 with MNPs.[9e]

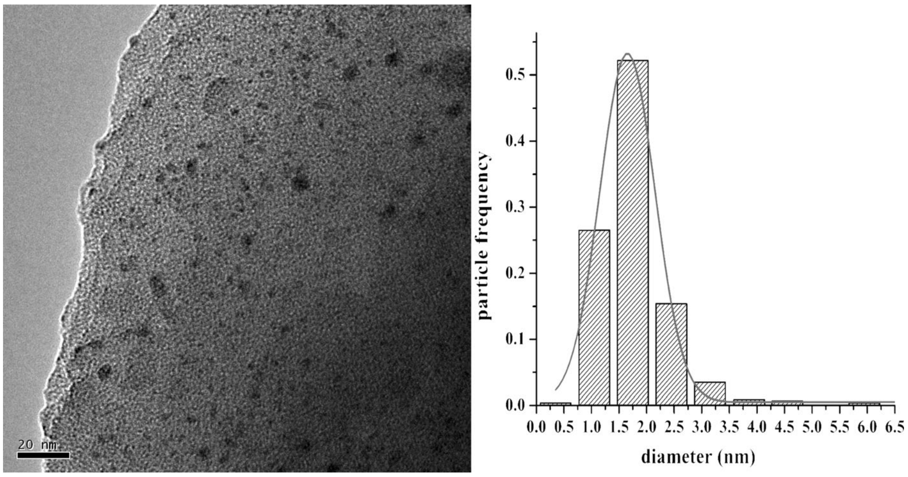


Figure 5. TEM image of a Ag@MIL-101 sample (**1c**; left) and size distribution of the Ag NPs in a sample of **1c** (right).

The average size of the Ag NPs in **1c** is 1.4 ± 0.4 nm (Figure 5) and in good agreement with the size of the mesoporous cavities in MIL-101, indicating that the large pore sizes of MIL-101 are desirable for the metal precursor $AgNO_3$ to diffuse and for the small Ag NPs to deposit. Furthermore, the MOF matrix also plays several other important roles in achieving the excellent catalytic activity of Ag@MIL-101: 1) As a good CO_2 adsorption material, Ag@MIL-101 can efficiently capture CO_2 as a bifunctional catalyst and improve the local concentration of CO_2 around the catalytic centers inside the pores of the framework to promote the activity of the catalyst. 2) The framework and pores act as a "microreactor" to provide a favorable environment for the reaction of CO_2 with terminal alkynes. The outstanding Lewis acidity of the MIL-101 framework, which is due to the unsaturated chromium sites, could lead to a preference for the adsorption of aromatic substrates[20] and therefore enhance the reactivity of catalyst **1c**. 3) The MOF structure stabilizes the whole material and leads to good regeneration properties. After entering the channels of MIL-101, the terminal alkynes can coordinate to the Ag NPs and be deprotonated by Cs_2CO_3 through acidifying the C(sp)−H bond to generate a silver acetylide intermediate. Afterwards, CO_2 inserts into the C−Ag bond to form the carboxylic acid products, as previously proposed.[3c,e]

In summary, we have synthesized the novel nanoscale heterogeneous catalyst system Ag@MIL-101 by a simple liquid impregnation method. The porous material is capable of simultaneously capturing and converting CO_2. This is the first example of stable MOF-supported catalysts for the transformation of CO_2 into carboxylic acids through C−H bond activation of terminal alkynes. These heterogeneous catalysts feature good catalytic activity, high stability, and excellent reusability in the carboxylation of terminal alkynes with CO_2 at mild conditions (50 °C and 1 atm of CO_2). Potential applications of this catalytic system in various areas can be anticipated, for example, in synthetic and industrial chemistry, medicine, and especially for the reduction of greenhouse gases in the environment.

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Keywords: carbon dioxide fixation · heterogeneous catalysis · metal–organic frameworks · propiolic acids · silver nanoparticles

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Communications

Carbon Dioxide Fixation

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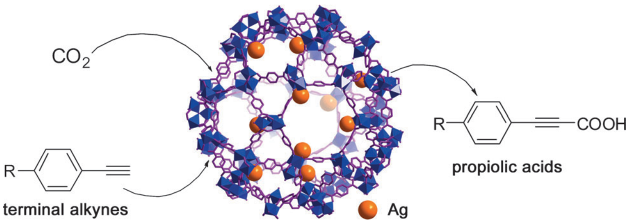
An Efficient Nanoscale Heterogeneous Catalyst for the Capture and Conversion of Carbon Dioxide at Ambient Pressure



Silver nanoparticles were supported on the zeolite-type metal–organic framework MIL-101 by a simple liquid impregnation method to yield Ag@MIL-101. CO_2 and terminal alkynes could be converted into propiolic acids in the presence of the very active Ag@MIL-101 catalyst at atmospheric pressure and low temperature (50 °C).