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ARTICLE

Metal-organic framework MIL-101 supported bimetallic Pd-Cu Nanocrystals as an efficient catalyst for Chromium Reduction and Conversion of Carbon Dioxide at Room Temperature

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This paper reports a series of bimetallic Pd-Cu nanocrystals (NCs) supported on the zeolite-type metal-organic framework MIL-101 to yield Pd-Cu/MIL-101 nanocomposites by a double solvents method. The obtained composites, Pd-Cu/MIL-101 are 5.5-11 nm and supported on the surface of the MIL-101. TEM images reveal that the loading of nanocrystals is uniform across the MIL-101. These represent the highly active MOF-supported metal catalysts for the reduction of Cr(VI) to Cr(III) using formic acid and the conversion of terminal alkynes into propiolic acids with CO₂ at room temperature. The observed catalytic activities toward the reduction of Cr(VI) to Cr(III) and the conversion of terminal alkynes into propiolic acids, Pd-Cu/MIL-101 nanocomposites showed better performance, a factor of 3-5 times faster than Pd-Cu nanocrystals. Being heterogeneous, the Pd-Cu/MIL-101 nanocomposites catalysts are also easy to handle and separate from the reaction mixture, and can be recycled five times with no loss of activity.

Introduction

Metal nanoparticles (M-NPs) with controllable size and distribution have received enormous interest because of their unique properties and potential applications.¹⁻³ Heterogeneous catalysis is one of the most important applications of metal NPs.⁴⁻⁷ Their catalytic performance is highly dependent on the dispersion of active metal sites. Therefore, many techniques have been designed to avoid the aggregation during their synthesis.⁸⁻¹⁰ Among them, the stabilizing M-NPs in the matrices of solid materials is one of most common and efficient ways to prevent aggregation. A number of porous materials such as zeolite,¹¹ metal oxide,¹² polymers,¹³ carbon nanotube,¹⁴ and graphene¹⁵ have been designed for restraining the aggregation of metal NPs till date. Metal-organic frameworks (MOFs) have shown promise as a new class of porous materials owing to their high porosity, large surface area, chemical tunability and thus specific applications, such as gas sorption and storage,^{16,17} molecular recognition, and separation,^{18,19} drug delivery,^{20,21} luminescence,^{22,23} magnetic properties,^{24,25} and catalytic properties.^{26,27} Given the similarity to zeolites, loading M-NPs into MOFs is expected to control the limited growth of metal NPs in the confined cavities and produce monodispersed

NPs, which could further increase their catalytic activities.²⁸ Moreover, the three-dimensional pore structures, presence of organic linkers, and chemical tunabilities make MOFs possess unique advantages over other porous materials.²⁹⁻³¹ However, up to now, reports about MOF-supported metal NPs were mainly focused on monometallic systems,³² while the bimetallic NPs supported on MOFs with more obvious synergistic effect, to the best of our knowledge, have not been widely studied.^{33,34} El-Shall et al. have reported metallic and bimetallic nanocatalysts incorporated into highly porous coordination polymer MIL-101 by microwave irradiation.^{34d} Hexavalent chromium (Cr(vi)) is believed to be the third most common pollutant at hazardous waste sites as well as the second most common inorganic contaminant after lead (Pb).³⁵ The water solubility of Cr and hence mobility in the environment and its toxicity to humans are governed by its oxidation state. Although Cr oxidation states range from +6 to -2, its most stable states found in the environment are +6 and +3. In contrast to highly water-soluble and toxic Cr(vi), Cr(III) is much less soluble in water where it typically forms (hydr)oxides in the absence of complexing ligands and is much less toxic to humans. Reductive transformation of Cr(vi) to Cr(III), therefore, is a promising approach to remediate Cr(vi) contamination. This could be attained *via* numerous reductants including Fe(0),³⁶ Fe(II)-bearing minerals,³⁷ organic compounds,³⁸ H₂S,³⁹ strong acids,⁴⁰ and so on. Formic acid (HCOOH), which has been extensively investigated for organic transformation,⁴¹ electrochemical oxidation⁴² and hydrogen storage,⁴³ has strong reducing properties and is a promising agent used for reducing Cr(vi) to Cr(III). Only Pd and Pt catalysts have been reported thus far to be active for the reduction of Cr(vi) using formic

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acid.⁴⁴ On the other hand, currently the emission of CO₂ has focused a vital issue as it causes global warming and a consequent series of environmental problems.⁴⁵ A lots of efforts have been carried out towards the efficient utilization of CO₂ by chemical methods, which may provide high-value products from a non-toxic, renewable, and low-cost resource.⁴⁶ Among them the best strategies for CO₂ conversion is the synthesis of propiolic acids through the C-H bond activation of terminal alkynes with CO₂ as a C₁ building block⁴⁷ because the alkynyl carboxylic acid products can serve as important synthetic intermediates⁴⁸ for further applications in medical chemistry as well as organic synthesis⁴⁹ to give coumarins, flavones, aminoalkynes, alkynylarenes, and arylidene oxindoles.⁵⁰ Several catalysts have developed but either reusability problems or synthetic complications limit the further application of these catalytic systems.⁵¹ The search for an efficient, inexpensive, and easily prepared catalysts for this type of reactions are immediately require further developments. To the best of our knowledge, only one report has been published till date for the carboxylation of terminal alkynes with CO₂ by using MOFs as a matrix and template.⁵² In this paper, we report the synthesis of highly dispersed bimetallic nanocrystals supported with metal-organic framework, MIL-101⁵³, a chromium-based MOF with the molecular formula Cr₃F(H₂O)₂O[(O₂C)C₆H₄(CO₂)₃]_nH₂O (where n is ~25) and catalytic application in the reduction of Cr(VI) to Cr(III) using formic acid and the conversion of terminal alkynes into propiolic acids with CO₂ at room temperature.

Experimental

Chemicals and materials

Reagents used in this work, including Cu(NO₃)₂·3H₂O, ethanol, and dry cyclohexane, were of analytical grade from the S.D. Fine Chem. Limited. Palladium pentanedionate (Pd(acac)₂, 34.7% Pd basis), octadecylamine (ODA), Terephthalic acid, Chromium(III) nitrate nonahydrate, Formic acid, and Alkynes were purchased from Sigma Aldrich Chemicals Pvt. Ltd. All the chemicals were used without further purification.

Synthesis of MIL-101

MIL-101 was synthesized using the reported procedure.⁵⁴ Terephthalic acid (0.83 g, 5.0 mmol), Cr(NO₃)₃·9H₂O (2.0 g, 5.0 mmol), and deionized water (20 mL) were blended and briefly sonicated resulting in a dark blue-colored suspension with a pH of 2.58. The suspension was placed in a Teflon-lined autoclave bomb and kept in an autoclave oven at 218°C for 18 h without stirring. After the synthesis and equilibration at room temperature, pH 0.5 was recorded in the suspension. After synthesis, the MOF solids were separated from water using a centrifuge (5,000xg, 10 min) and washed with water, methanol and acetone. The suspension in acetone was centrifuged and separated, the solids were placed in N,N-dimethylformamide (20 mL) and the suspension was sonicated for 10 min and then kept at 70°C overnight.⁵⁵ The resulting solids were separated by centrifugation, repeatedly washed with methanol and acetone, dried at 75°C overnight, and then under vacuum (1 X 10⁻⁵ Torr)

at ambient temperature for 2 days. Total yield of dry MIL-101 particles based on chromium was 63 wt%.

Synthesis of Pd_{0.5}Cu_{0.5} NCs

Pd_{0.5}Cu_{0.5} NCs was synthesized using the reported procedure.⁵⁶ 20 mg Pd(acac)₂ and 15.9 mg Cu(NO₃)₂·3H₂O were mixed with 7.5 g ODA and heated at 110°C to form a clear solution. Then the temperature was elevated to 240°C and maintained at this temperature for 10 min. The reaction mixture was cooled down to 70°C, followed by addition of 20 mL ethanol. The products were collected at the bottom of the flask by decanting the supernatant and further washed with hexane and ethanol for several times.

Synthesis of Pd_{0.2}Cu_{0.8} NCs

Pd_{0.2}Cu_{0.8} NCs was synthesized using the reported procedure.⁵⁶ 20 mg Pd(acac)₂ and 79.7 mg Cu(NO₃)₂·3H₂O were mixed with 7.5 g ODA and heated at 110°C to form a clear solution. Then the temperature was elevated to 240°C and maintained at this temperature for 10 min. The reaction mixture was cooled down to 70°C, followed by addition of 20 mL ethanol. The products were collected at the bottom of the flask by decanting the supernatant and further washed with hexane and ethanol for several times.

Synthesis of Pd_{0.3}Cu_{0.7} NCs

Pd_{0.3}Cu_{0.7} NCs was synthesized using the reported procedure.⁵⁶ 20 mg Pd(acac)₂ and 47.8 mg Cu(NO₃)₂·3H₂O were mixed with 7.5 g ODA and heated at 110°C to form a clear solution. Then the temperature was elevated to 240°C and maintained at this temperature for 10 min. The reaction mixture was cooled down to 70°C, followed by addition of 20 mL ethanol. The products were collected at the bottom of the flask by decanting the supernatant and further washed with hexane and ethanol for several times.

Synthesis of Pd_{0.7}Cu_{0.3} NCs

Pd_{0.7}Cu_{0.3} NCs was synthesized using the reported procedure.⁵⁶ 20 mg Pd(acac)₂ and 5.31 mg Cu(NO₃)₂·3H₂O were mixed with 7.5 g ODA and heated at 110°C to form a clear solution. Then the temperature was elevated to 240°C and maintained at this temperature for 10 min. The reaction mixture was cooled down to 70°C, followed by addition of 20 mL ethanol. The products were collected at the bottom of the flask by decanting the supernatant and further washed with hexane and ethanol for several times.

Synthesis of Pd_{0.8}Cu_{0.2} NCs

Pd_{0.8}Cu_{0.2} NCs was synthesized using the reported procedure.⁵⁶ 20 mg Pd(acac)₂ and 3.18 mg Cu(NO₃)₂·3H₂O were mixed with 7.5 g ODA and heated at 110°C to form a clear solution. Then the temperature was elevated to 240°C and maintained at this temperature for 10 min. The reaction mixture was cooled down to 70°C, followed by addition of 20 mL ethanol. The products were collected at the bottom of the flask by decanting the supernatant and further washed with hexane and ethanol for several times.

Synthesis of Pd-Cu/MIL-101 (Pd-Cu NCs = Pd_{0.2}Cu_{0.8}, Pd_{0.3}Cu_{0.7}, Pd_{0.5}Cu_{0.5}, Pd_{0.7}Cu_{0.3}, and Pd_{0.8}Cu_{0.2})

Supported Pd-Cu nanoparticles were prepared *via* double-solvents method. Typically, 150 mg of green MIL-101 powder activated by heating at 150°C for 12 h under vacuum which has

a pore volume of $1.45 \text{ cm}^3 \text{ g}^{-1}$ as determined by N_2 sorption isotherm, was suspended in 30 mL of dry cyclohexane as hydrophobic solvent and the mixture was sonicated for 15 min until it became homogeneous. After stirring of 2 h, 2 wt% Pd-Cu NCs aqueous solution as the hydrophilic solvent was added dropwise over a period of 15 min with constant vigorous stirring. The resulting solution was continuously stirred for 24 h. After careful filtration, the green powder was dried in air at room temperature. These synthesized samples were further dried at 150°C for 10 h to yield 2 wt% Pd-Cu/MIL-101 (Pd-Cu = $\text{Pd}_{0.2}\text{Cu}_{0.8}$, $\text{Pd}_{0.3}\text{Cu}_{0.7}$, $\text{Pd}_{0.5}\text{Cu}_{0.5}$, $\text{Pd}_{0.7}\text{Cu}_{0.3}$, and $\text{Pd}_{0.8}\text{Cu}_{0.2}$).

Catalytic reduction of aqueous solution of Cr(IV)

To an aqueous solution (5 mL) of $\text{K}_2\text{Cr}_2\text{O}_7$ (29.4 mg, 1 mmol, $2 \times 10^{-2} \text{ M}$) and HCOOH (0.3 mL), 2 wt% $\text{Pd}_{0.5}\text{Cu}_{0.5}$ /MIL-101 (0.1 g), 2 wt% $\text{Pd}_{0.2}\text{Cu}_{0.8}$ /MIL-101 (0.1 g), 2 wt% $\text{Pd}_{0.3}\text{Cu}_{0.7}$ /MIL-101 (0.1 g), 2 wt% $\text{Pd}_{0.7}\text{Cu}_{0.3}$ /MIL-101 (0.1 g) or 2 wt% $\text{Pd}_{0.8}\text{Cu}_{0.2}$ /MIL-101 (0.1 g) catalyst was added. After introducing the catalyst, the yellow solution gradually faded as the reaction proceeded and finally a colorless solution was obtained. UV-Vis spectra were recorded on a Shimadzu UV-1601 spectrophotometer on the solutions in transmittance at short intervals to monitor the progress of the reaction. The absorption spectra of the solution were measured in the range of 220-600 nm. Addition of an excess of sodium hydroxide solution to the above resulting colorless solution resulted in a green solution, confirming the presence of Cr(III) as the reduction product of Cr(VI).

General Experimental Procedure for Carboxylation of Terminal Alkynes

Pd-Cu/MIL-101 (100 mg) and Cs_2CO_3 (1.5 mmol) were added to DMF (5 mL) in the reaction tube (10 mL). A CO_2 (balloon) and 1 mmol of terminal alkynes were introduced into the reaction mixture under stirring. The reaction mixture was stirred at room temperature for 24 h, then the reaction mixture was cooled to room temperature. The reaction mixture was diluted with water (15 mL) and the solid residue was separated *via* centrifugation. The mixture was washed with CH_2Cl_2 and the aqueous layer was acidified with concentrated HCl to pH=1 at low temperature, then extracted with ethyl acetate. The combined organic layers were washed with saturated NaCl solution, dried over Na_2SO_4 and filtered. The solvent was removed in vacuum to afford the acid products.

Procedure for the recycle of the catalyst

The Pd-Cu/MIL-101 catalyst was recovered in the solid residue after centrifugation and separation from the organic layer (DMF solution) containing the product. The solid residue was washed with DMF and then respectively soaked in water and ethanol for 10 h and the solid residue containing recovered catalyst then directly used as recycled catalyst in the subsequent runs without the addition of more catalyst.

Characterization methods

The powder XRD patterns were recorded with a Bruker D8 Discover X-ray diffractometer, with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$). The size and morphology of as-synthesized samples were determined by using a FEI TECNAI G2200 kV transmission electron microscope equipped with energy-dispersed X-ray detector (EDX). The surface area

measurements were performed with N_2 adsorption/desorption isotherms at liquid-nitrogen temperature (77K) using micropore physisorption analyzer (Micromeritics ASAP 2020, USA) after pretreatment under vacuum at 150°C for 12 h. The pore volume was calculated by a single point method at $P/P_0 = 0.99$. The Pd and Cu content in different Pd-Cu/MIL-101 catalyst was measured by using an IRIS Intrepid II XSP inductively coupled plasma-atomic emission spectrometer (ICP-AES). The ^1H and ^{13}C NMR spectra were recorded on a JEOL DELTA2 spectrometer at 400 MHz using TMS as an internal standard. The chemical shift values are recorded on the δ scale and the coupling constants (J) are in Hz. GCMS studies were done with the Shimadzu-2010 instrument containing a DB-5/RtX-5MS-30Mt column of 0.25mm internal diameter with an oven temperature range of $90\text{-}180^\circ\text{C}$ (5 min) at $4^\circ\text{C}/\text{min}$ raised to 300°C at $4^\circ\text{C}/\text{min}$.

Results and discussion

The crystallinity and surface area of the synthesized MIL-101 were in agreement with the literature as confirmed by powder X-ray diffraction (PXRD) measurements. The monodisperse Pd-Cu bimetallic nanocrystals (NCs) with compositions ($\text{Pd}_{0.2}\text{Cu}_{0.8}$, $\text{Pd}_{0.3}\text{Cu}_{0.7}$, $\text{Pd}_{0.5}\text{Cu}_{0.5}$, $\text{Pd}_{0.7}\text{Cu}_{0.3}$, $\text{Pd}_{0.8}\text{Cu}_{0.2}$) were synthesized according to Wang et al. method.⁵⁶ The composition of Pd-Cu NCs was controlled by precursor molar ratios. By keeping the amount of the Pd precursor at 0.066 mmol and changing the amount of the Cu precursor, we could control the Pd-Cu NCs composition for a Cu content of 20 to 80%. The corresponding XRD patterns of the as-obtained Pd-Cu NCs were in good agreement with the literature value of Pd (JCPDS-65-6174) and Cu (JCPDS-04-0836) which indicates the formation of Pd-Cu alloys. These Pd-Cu NCs were supported into the as-synthesized MIL-101 through double solvents method (Fig. 1).⁵⁷ The double solvent approach used to synthesize the metal nanoparticles (MNPs) inside the MOF is not new. It was introduced for the first time by Aijaz et al.^{57a} to avoid the deposition of the metal precursors on the outer surface of the metal-organic framework and from that first report it has been used to prepare different mono-^{44c} and bi-metallic NPs inside metal-organic frameworks, specially inside the MIL-101 metal-organic framework.⁵⁷

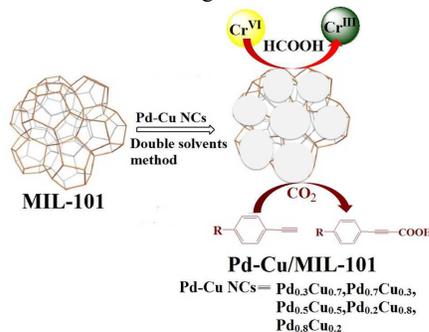


Fig. 1. Schematic illustration of synthetic procedure for Pd-Cu NCs supported with MIL-101 matrix and its catalytic application to reduction of Cr(VI) and the conversion of terminal alkynes into propiolic acids.

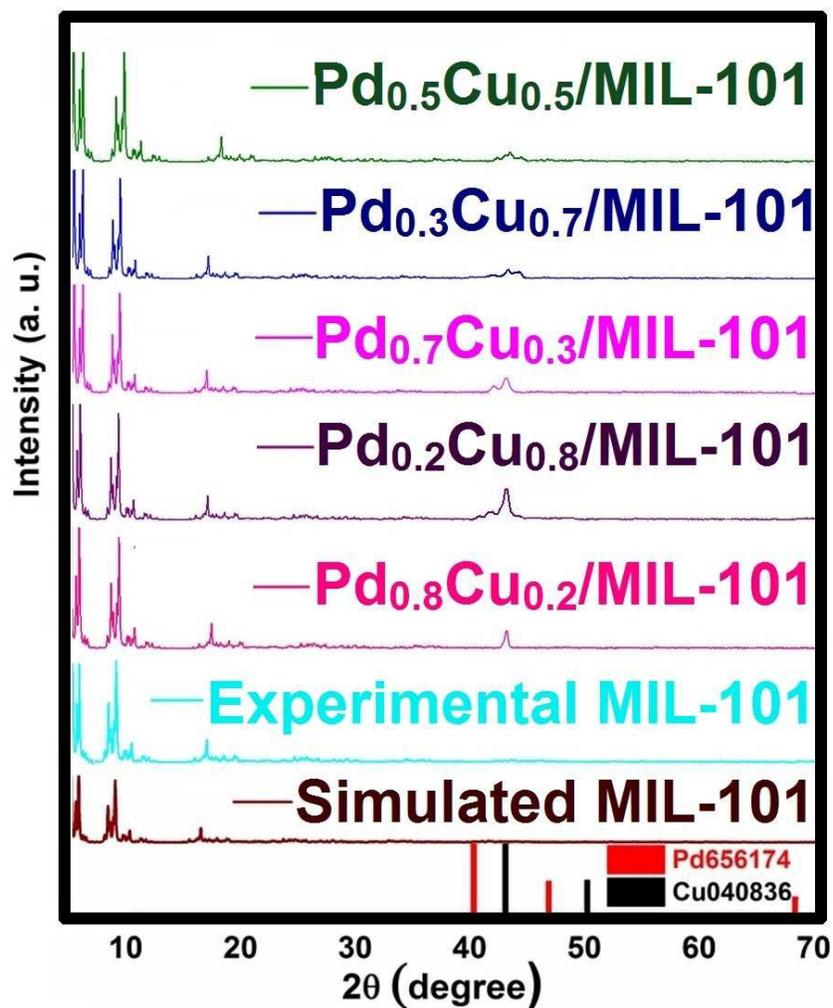


Fig. 2. PXRD patterns of MIL-101 and 2 wt% Pd-Cu/MIL-101 (Pd_{0.8}Cu_{0.2}, Pd_{0.2}Cu_{0.8}, Pd_{0.7}Cu_{0.3}, Pd_{0.3}Cu_{0.7}, Pd_{0.5}Cu_{0.5}).

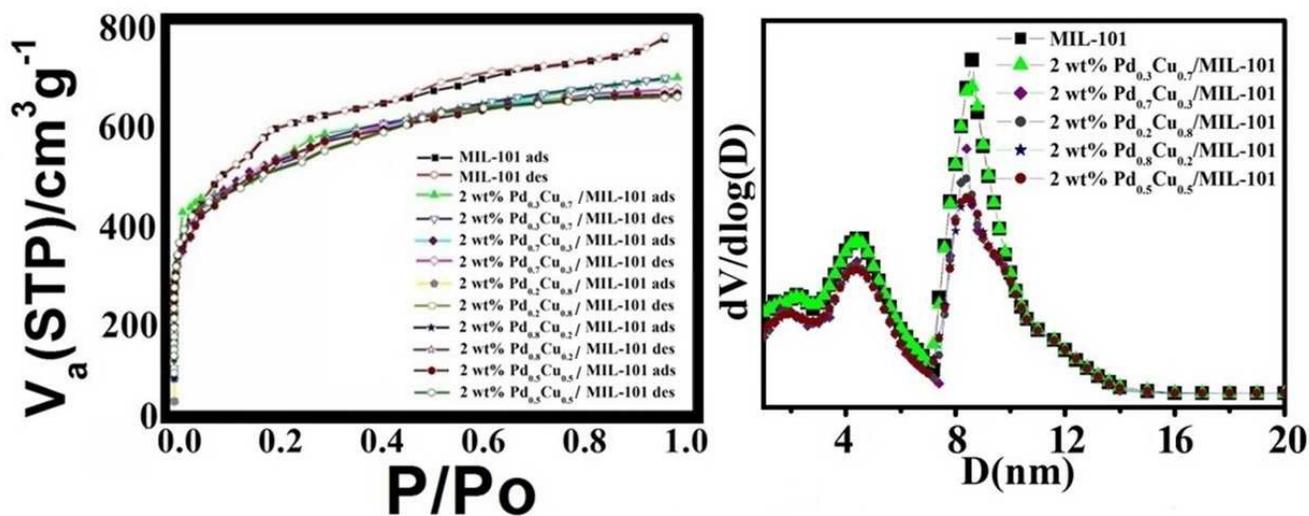


Fig. 3. N₂ adsorption-desorption isotherms (left) and pore size distribution curves (right) of the 2 wt% Pd-Cu/MIL-101 (Pd-Cu = Pd-Cu/MIL-101(Pd_{0.8}Cu_{0.2}, Pd_{0.2}Cu_{0.8}, Pd_{0.7}Cu_{0.3}, Pd_{0.3}Cu_{0.7}, Pd_{0.5}Cu_{0.5}) at 77 K.

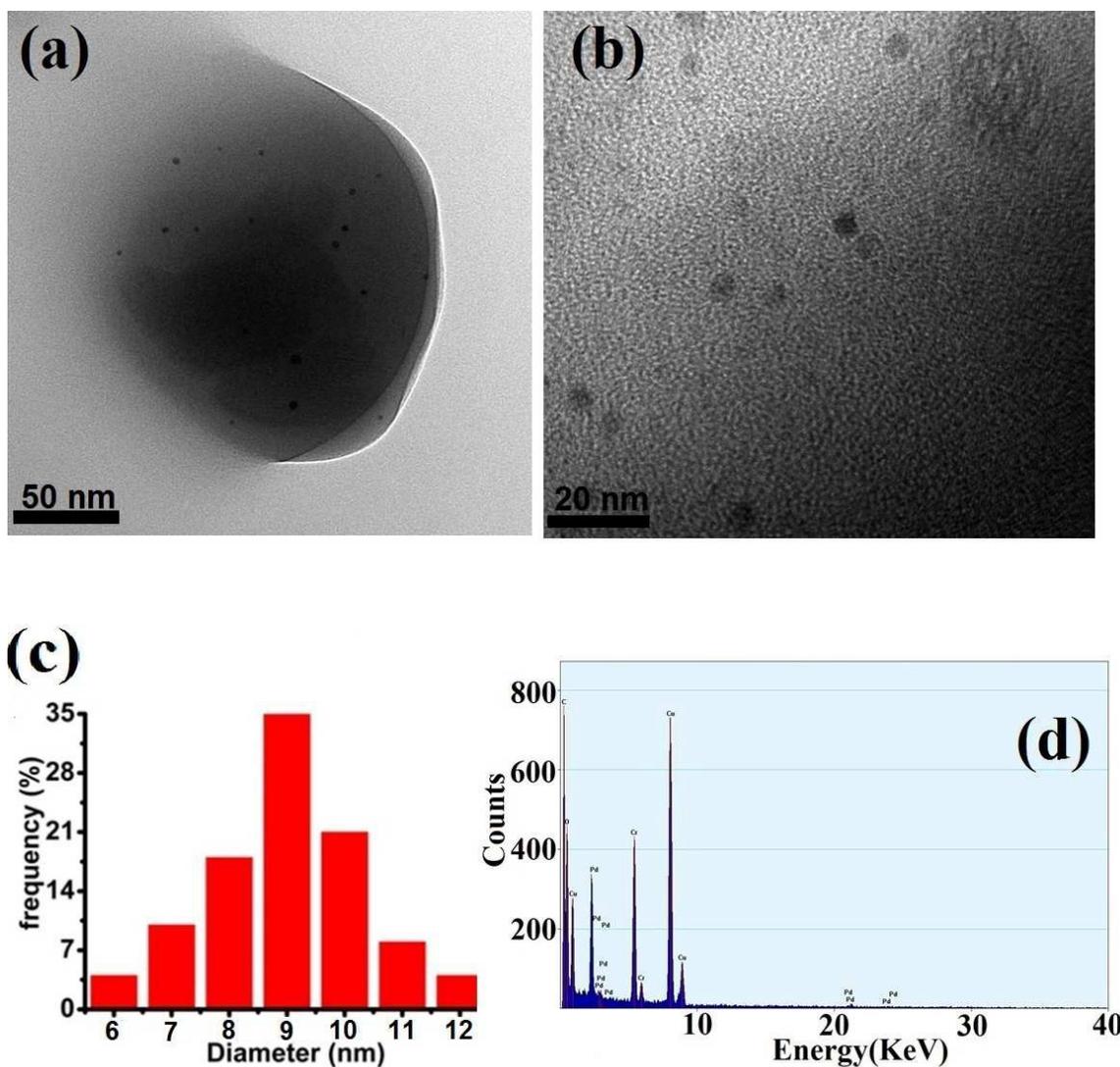


Fig. 4. (a-b) TEM images of 2 wt% Pd_{0.5}Cu_{0.5}/MIL-101 with different magnifications. (c) Particles size distributions histogram of 2 wt% Pd_{0.5}Cu_{0.5}/MIL-101 NPs. (d) EDX of 2 wt% Pd_{0.5}Cu_{0.5}/MIL-101

The resultant green palladium-copper/metal-organic framework composites, designated as Pd-Cu/MIL-101, have been isolated. The PXRD patterns of Pd-Cu/MIL-101 exhibited the characteristic diffractions for Pd-Cu NCs as well as MIL-101 (Fig. 2 & Fig. S1, ESI†). Fig. 3 shows the isotherms of N₂ on MIL-101 and Pd-Cu/MIL-101 catalysts at 77 K, from which the textural properties were determined, and the results are summarized in Table S1, ESI†. The decrease in the amount of N₂ adsorption and the pore volume of Pd-Cu/MIL-101 indicated that cavities of the host framework are either occupied by the dispersed Pd-Cu NPs or blocked by the Pd-Cu NCs. The transmission electron microscopy (TEM), and corresponding energy-dispersive X-ray spectroscopic (EDX) analyses (Fig. 4; Fig. S2-S5, ESI†) of 2 wt% Pd-Cu/MIL-101 observations revealed the uniformity of the Pd-Cu NCs in the MIL-101 framework for all the samples. The Pd-Cu NCs size distribution

histogram of 2 wt% Pd-Cu/MIL-101 showed that the sizes of the Pd-Cu NCs were about 5.5-11 nm (Fig. 4 & Fig. S2-S5, ESI†). The EDX spectra indicated the presence of Pd, and Cu in the catalyst. The Pd:Cu atomic ratio determined by EDX analysis and inductively coupled plasma-mass spectrometry (ICP-MS) analysis is almost consistent with the ratio of precursors (Table S1, ESI†).

Reductive conversion of Cr(VI) to Cr(III)

The comparative catalytic performances of bimetallic Pd-Cu NCs as well as Pd-Cu/MIL-101 NPs have been investigated for the reduction of Cr(VI) in aqueous solution using formic acid at room temperature. Potassium dichromate (K₂Cr₂O₇) was chosen as a representative Cr(VI) compound. The progress of the catalytic reaction was monitored using UV-visible absorption spectroscopy in the wavelength range of 220-600 nm at room temperature. Cr₂O₇²⁻ exhibits a strong absorption

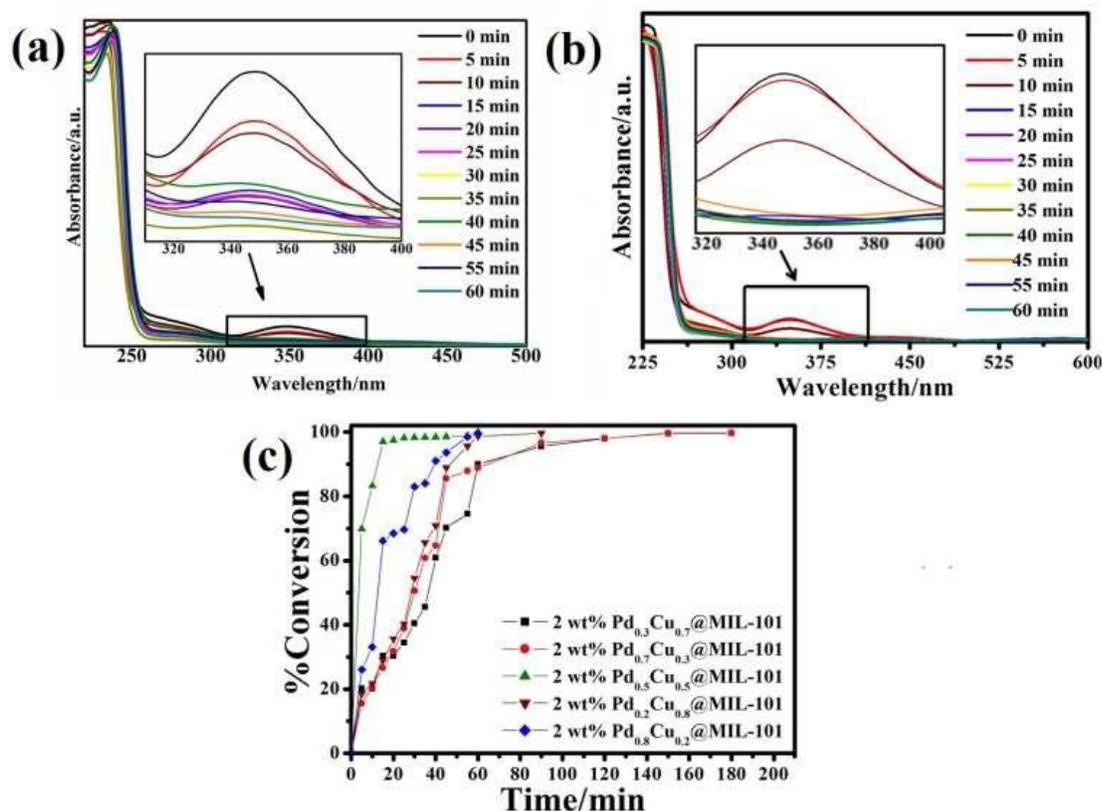
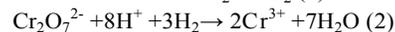
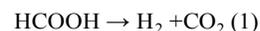


Fig. 5. Catalytic reduction of Cr(VI) using excess of formic acid over 2 wt% Pd-Cu/MIL-101 (Pd-Cu = (a) Pd_{0.7}Cu_{0.3} (b) Pd_{0.5}Cu_{0.5}) and (c) Plot of conversion vs. time at room temperature as monitored using UV-Vis spectroscopy.

centred at 348 nm of the UV-visible spectrum due to a ligand (O²⁻) to metal (Cr(VI)) charge-transfer transition.^{33c} It can be seen that, without Pd-Cu NCs and Pd-Cu/MIL-101 NPs, the system incorporating only MIL-101 to the aqueous solution of potassium dichromate and formic acid was inefficient for the reduction of Cr(VI), suggesting that the MIL-101 itself is catalytically inactive for this reaction (Fig. S6, ESI†). In order to explore the comparative catalytic properties of different Pd-Cu NCs and Pd-Cu NPs supported by MIL-101, we observed a difference in catalytic activity, that is, Pd-Cu/MIL-101 NPs was highly efficient catalysts compared to Pd-Cu NCs for the reduction of Cr(VI) in the presence of excess formic acid (Fig. 5 & Fig. S7, ESI†). Bimetallic catalytic systems show higher catalytic activities than single-metal catalytic systems, because of electron transfer across the metal-metal interface. The progress of the reaction was monitored using UV-Vis absorption spectroscopy. As shown in Fig. 5, the absorption of Cr(VI) at 348 nm decreased sequentially, accompanied by a change in color from yellow to colorless (Fig. S8, ESI†), with increasing reaction time which indicates the reduction of Cr(VI). The presence of Cr(III) as the reaction product was confirmed by addition of sodium hydroxide. Addition of excess sodium hydroxide to the resulting solution led to the formation of a green solution, of hexahydroxochromate(III) (Fig. S9, ESI†).^{44,58} In the presence of 2 wt% Pd-Cu/MIL-101 NPs catalysts, Cr(VI) could be completely, within the limit of

detection, reduced within 60 to 180 min at room temperature (Fig. 5), while in case of Pd-Cu NCs, it was 180 min to 300 min, respectively indicating that Pd-Cu/MIL-101 NPs were much more active catalysts as compared to Pd-Cu NCs. The catalytic activity of different Pd-Cu/MOF as well as Pd-Cu NCs were tested for the reduction of Cr(VI) into Cr(III). Among them, the Pd_{0.5}Cu_{0.5}/MIL-101 NPs as well as Pd_{0.5}Cu_{0.5} NCs showed the best performance. It is reasonable to assume that formic acid was adsorbed on the surface of Pd-Cu NCs/NPs and there it decomposed to H₂ and CO₂ according to equation (1) (Fig. 6).⁵⁹ Thus the nascent hydrogen reduces Cr(VI) as shown in equation (2)



According to Sadik et al., the Cr₂O₇²⁻ can be reduced to Cr(III) by bubbling H₂ gas. But this reaction is found to be very slow.^{44b} In our case, we have not used H₂ gas in any stage of the catalytic reaction thus it is expected that nascent hydrogen generated by the decomposition of HCOOH in the presence of Pd-Cu NPs/NCs is responsible for such a significant increase in the rate of the reaction. The recyclability of the different Pd-Cu/MIL-101 catalysts were examined in the reduction of Cr(VI) under the optimized conditions. After the catalytic reaction, the catalyst was isolated from the liquid

Table 1: Synthesis of 3-phenylpropionic acid from CO₂ and Phenylacetylene with catalysts Pd-Cu and Pd-Cu/MIL-101.^a

Entry	Catalyst (mg)	Solvent	Yield(%) ^b	Alkyne Dimerization Yield(%) ^b	TON ^c
1.	MIL-101(100 mg)	DMF	20	10	-
2.	No catalyst	DMF	0	0	-
3.	Pd _{0.5} -Cu _{0.5} (100 mg)	DMF	40	30	339
4.	Pd _{0.2} -Cu _{0.8} (100 mg)	DMF	55	25	396
5.	Pd _{0.8} -Cu _{0.2} (100 mg)	DMF	10	45	97
6.	Pd _{0.3} -Cu _{0.7} (100 mg)	DMF	50	25	382
7.	Pd _{0.7} -Cu _{0.3} (100 mg)	DMF	20	40	187
8.	Pd _{0.5} -Cu _{0.5} /MIL-101(100 mg)	DMF	65	10	550
9.	Pd _{0.2} -Cu _{0.8} /MIL-101(100 mg)	DMF	96	No	691
10.	Pd _{0.8} -Cu _{0.2} /MIL-101(100 mg)	DMF	56	15	544
11.	Pd _{0.3} -Cu _{0.7} /MIL-101(100 mg)	DMF	85	10	648
12.	Pd _{0.7} -Cu _{0.3} /MIL-101(100 mg)	DMF	60	20	560
13.	Pd _{0.2} -Cu _{0.8} /MIL-101(100 mg)	CH ₃ CN	70	25	503
14.	Pd _{0.2} -Cu _{0.8} /MIL-101(100 mg)	DMSO	80	15	575
15.	Pd _{0.2} -Cu _{0.8} /MIL-101(100 mg)	NMP	75	20	539
^e 16.	Pd _{0.2} -Cu _{0.8} /MIL-101(100 mg)	DMF	0	30	-
^d 17.	Pd _{0.2} -Cu _{0.8} /MIL-101(100 mg)	DMF	20	25	143

^aReaction conditions: Phenylacetylene (1.0 mmol), catalyst, Cs₂CO₃ (1.5 mmol), CO₂ (1.0 atm), 25°C, solvent (5 mL), 24 h.^bYield of isolated product.^cIn absence of CO₂.^dK₂CO₃.^eTON = mole of product per mole of catalyst.

phase by centrifugation, thoroughly washed with ethanol, and then reutilized as catalyst in subsequent runs under identical reaction conditions for up to five runs (Fig. S10, ESI[†]).

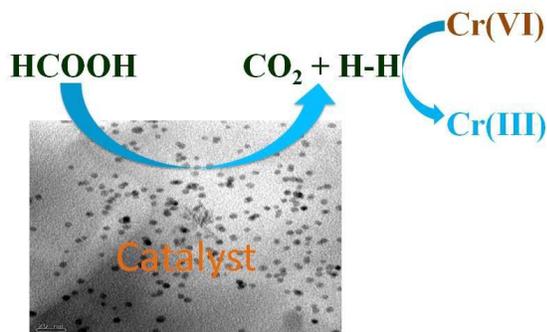


Fig. 6. Schematic representation of the reductive conversion of Cr(VI) to Cr(III) using HCOOH in the presence of catalyst.

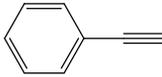
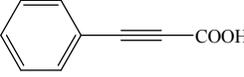
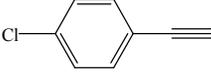
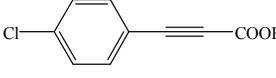
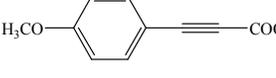
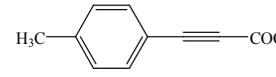
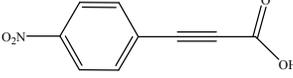
Conversion of CO₂ with terminal alkynes into propionic acids

The comparative catalytic activities of the different bimetallic nanocrystals (Pd-Cu) as well as nanocomposites (Pd-Cu/MIL-

101) were determined for the fixation of CO₂ with terminal alkynes into propionic acids. In the initial investigation, the carboxylation of phenylacetylene was selected as a model reaction to study the influence of various parameters on the reaction. Table 1 shows the generation of 3-phenylpropionic acid from CO₂ (1 atm) and phenylacetylene at room temperature in the presence of different Pd-Cu nanocrystals as well as Pd-Cu/MIL-101 nanocomposites. It can be seen that, the system incorporating MIL-101 or Cs₂CO₃ without bimetallic nanocrystals as well as nanocomposites, the catalytic systems gave 3-phenylpropionic acid in poor yields of 20% or 0%, respectively (entries 1 and 2) with 10 to 0% formation of homocoupling products. As shown in Table 1, we observed a difference in catalytic activity, that is, different nanocomposites Pd-Cu/MIL-101 exhibited higher catalytic activity compared to Pd-Cu nanocrystals. In the case of reaction between phenylacetylene and CO₂ in the presence of 100 mg of different Pd-Cu nanocrystals, the isolated yield of 3-phenylpropionic acid was 10-55% (entry 3-7), corresponding to TON of 97-396 with 25 to 45% formation of homocoupling byproducts. For 100 mg of different Pd-Cu/MIL-101 nanocomposites (entries 8-12), 3-phenylpropionic acid was obtained in good yields (56-96%), corresponding to TON of 544-691 with 10 to 20%

Table 2: Synthesis of propiolic acid derivatives from CO₂ and terminal alkynes with catalyst Pd_{0.2}Cu_{0.8}/MIL-101.^a

$$\text{R}-\text{C}\equiv\text{C} + \text{CO}_2 \xrightarrow[\text{HCl}]{\text{Pd}_{0.2}\text{Cu}_{0.8}/\text{MIL-101}} \text{R}-\text{C}\equiv\text{C}-\text{COOH}$$

Entry	Alkyne	Product	Yield(%) ^b	^c TON
1.			96	691
2.			98	705
3.			97	697
4.			97	697
5.			96	690

^aReaction conditions: alkyne (1.0 mmol), Pd_{0.2}Cu_{0.8}/MIL-101 (100 mg), Cs₂CO₃ (1.5 mmol), CO₂ (1.0 atm), 25°C, DMF (5 mL), 24 h.^bYield of isolated product.^cTON = mole of product per mole of catalyst.

formation of homocoupling byproducts. Catalyst Pd_{0.2}Cu_{0.8}/MIL-101 afforded the highest product yield, and the catalytic activity decreased in the following order: Pd_{0.2}Cu_{0.8}/MIL-101 > Pd_{0.3}Cu_{0.7}/MIL-101 > Pd_{0.5}Cu_{0.5}/MIL-101 > Pd_{0.7}Cu_{0.3}/MIL-101 > Pd_{0.8}Cu_{0.2}/MIL-101. Then, we studied the influence of other organic solvents on the catalytic system. We found that DMF as a superior solvent for this system compared to CH₃CN, NMP, and DMSO (entries 13-15) because DMF was a better solvent for both Cs₂CO₃ and CO₂ (DMF is a weak base) than the other organic solvents.^{47d} The yield dropped to 20% when the base was changed to K₂CO₃ under similar conditions (entry 17). This indicates that Cs₂CO₃ was a superior base for this direct carboxylation reaction of terminal alkynes with CO₂.^{47d,47e} With the optimized conditions (1.5 equiv Cs₂CO₃, 1 atm CO₂ DMF, 25°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 (96-98%), corresponding to TON of 690-705 when aromatic alkynes with either electron-donating (CH₃, OCH₃) or electron-withdrawing (Cl, NO₂) substituents were employed. As a heterogeneous catalyst, Pd-Cu/MIL-101 could not only be simply prepared, but also easily separated from the reaction solution by centrifugation. As shown in Fig. 7, catalyst Pd_{0.2}Cu_{0.8}/MIL-101 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 (Fig. 8 & Fig. S11, ESI[†]) showed that the framework of catalyst

Pd_{0.2}Cu_{0.8}/MIL-101 was well maintained after the catalytic reaction in DMF, which confirms the stability of the Pd_{0.2}Cu_{0.8}/MIL-101 catalysts during the reaction. Furthermore, the MOF matrix also plays several other important roles in achieving the excellent catalytic activity of Pd-Cu/MIL-101. Pd-Cu/MIL-101 can efficiently capture CO₂ around the catalytic centers in the framework to promote the activity of the catalyst to provide a favourable environment for the reaction of CO₂ 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 substrates⁶⁰ and therefore enhance the reactivity of catalyst Pd-Cu/MIL-101. The MOF structure stabilizes the whole material and leads to good regeneration properties. After supporting the channels of MIL-101, the terminal alkynes can coordinate to the Pd-Cu NPs and may be deprotonated by Cs₂CO₃ through acidifying the C(sp)-H bond to generate a palladium-copper acetylide intermediate. Afterwards, CO₂ inserts into the C-Cu bond to form the carboxylic acid products, as previously proposed.^{47c,47i}

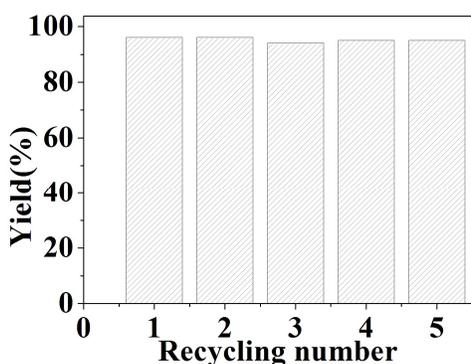


Fig. 7. The cycling performance with catalyst Pd_{0.2}Cu_{0.8}/MIL-101 for the carboxylation of terminal alkynes with CO₂.

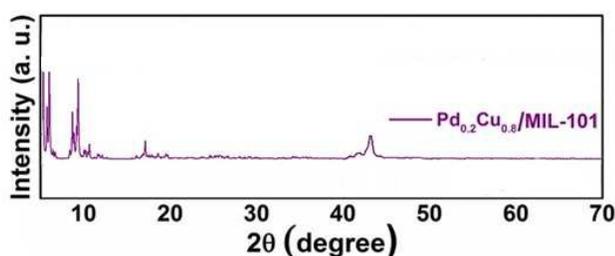


Fig. 8. PXRD pattern of catalyst Pd_{0.2}Cu_{0.8}/MIL-101 after the catalytic reaction for the carboxylation of terminal alkynes with CO₂.

Conclusions

In conclusion, we have successfully synthesized a series of Pd-Cu NCs supported on MIL-101 by the double solvents approach. We have also studied the comparative catalytic activity of Pd-Cu NCs and Pd-Cu/MIL-101 nanocomposites for the reduction of Cr(VI) to Cr(III) and for the transformation of CO₂ into carboxylic acids through C-H bond activation of terminal alkynes. The Pd-Cu/MIL-101 nanocomposites showed better performances than Pd-Cu nanocrystals. For the reduction of Cr(VI), Pd_{0.5}Cu_{0.5}/MIL-101 displayed much better catalytic efficiency compared to other Pd-Cu/MIL-101 nanocomposites. For the conversion of terminal alkynes into propiolic acids with CO₂, Pd_{0.2}Cu_{0.8}/MIL-101 exhibited highest catalytic efficiency compared to other Pd-Cu/MIL-101 nanocomposites. The present research may results in the development of novel high-performance heterogeneous bimetallic catalysts through the use of MOFs as supports.

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Graphical Abstract: Synopsis and Pictogram

Bimetallic Pd-Cu nanocrystals were supported on the zeolite-type metal-organic framework MIL-101 by a double solvents method to yield a series of Pd-Cu/MIL-101 nanocomposites. The resulting composites, Pd-Cu/MIL-101 represent the highly active MOF-supported metal catalysts for the reduction of Cr(VI) to Cr(III) using formic acid and conversion of terminal alkynes into propiolic acids with CO₂ at atmospheric pressure and room temperature.

