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Carbonylative Sonogashira coupling of terminal alkynes with aryl iodides under atmospheric pressure of CO using Pd(II)@MOF as the catalyst†

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A novel, highly efficient, and phosphine-free heterogeneous palladium-MOF catalytic system for the carbonylative Sonogashira coupling of terminal alkynes with aryl iodides was developed. The catalyst could efficiently promote the carbonylative coupling reaction under atmospheric pressure of CO, affording the corresponding aryl α,β-alkynyl ketones in good to excellent yields. Besides high activity and selectivity, the proposed catalytic system features a broad substrate scope for both alkynes and aryl iodides. Moreover, the heterogeneous catalyst was recyclable, showed negligible metal leaching, and could be reused at least five times without significant loss in catalytic efficiency under the investigated conditions.

Introduction

α,β-Acetylenic carbonyl derivatives (ynones) are important structural units found in many biologically active molecules, natural products, and pharmaceuticals.[1] They are extremely versatile intermediates for the synthesis of heterocyclic derivatives such as pyrimidine,[2] quinolone,[3] furan,[4] pyrazole,[5] pyrrole,[6] and flavone.[7] Traditionally, ynones are synthesized *via* the coupling of acyl halides with alkynyl organometallic reagents[8] or terminal alkynes.[9] Although acyl halides have shown good reactivity in this transformation, they suffer from inherent problems such as low stability and limited commercial availability.[10]

An alternative route for ynones is the Pd-catalyzed Sonogashira-type carbonylation of terminal alkynes with aryl halides in the presence of carbon monoxide.[11] Since the first example of carbonylative Sonogashira coupling reaction was reported,[11a] significant efforts have been devoted to the improvement of the original work of Tanaka *et al.* during the past three decades.[12] Among the developed methodologies for the carbonylative Sonogashira coupling, homogeneous Pd catalysts (usually with the addition of homogeneous phosphine ligands) have been shown to be the most efficient catalytic systems for ynones. However, these homogeneous systems are normally not reusable and it is difficult to separate the expensive palladium catalysts from the reaction mixture.[9f]

Heterogenization of the homogeneous palladium catalyst is an attractive solution to these problems. In this respect, a few phosphane-free heterogeneous palladium catalysts, such as commercial Pd/C, Pd/Fe_3O_4, and Pd complexes grafted on MCM-41 silica, have been developed for the carbonylative coupling reactions.[13,14] Indeed, the reusability of the expensive Pd catalysts was mostly achieved; however, their catalytic efficiencies are not satisfactory and still need to be largely improved. In particular, a high CO pressure is always required to achieve efficient carbonylative coupling for the preparation of ynones.

Here, we report a novel and highly efficient heterogeneous palladium-MOF system for carbonylative Sonogashira coupling of terminal alkynes with aryl iodides. To the best of our knowledge, this work represents the first example of a highly active heterogeneous catalyst for the synthesis of ynones *via* carbonylative Sonogashira coupling under atmospheric pressure of CO without the addition of any phosphine ligands. Besides high activity and selectivity to the target products, the proposed catalytic system features a broad substrate scope for both alkynes and aryl iodides. Furthermore, the catalyst is reusable and shows negligible metal leaching under the investigated conditions.

MOFs are a new class of porous materials that have shown interesting catalytic properties in a number of chemical transformations.[15] In particular, functionalization of MOFs with active metal species has been demonstrated to be a very useful approach to optimize MOFs for specialized catalytic applications.[16] Recently, we have reported the use of the uncoordinated 2,2′-bipyridine (bpy) moieties in MOF-253 for the immobilization of CuI as an efficient heterogeneous catalyst for the *O*-arylation of phenols or alcohols with aryl

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† Electronic supplementary information (ESI) available: Experimental details, catalyst characterization and reaction results, and spectra data of the products. See DOI: 10.1039/c4cy00488d

halides under ligand-free conditions.[17] Herein we extend the methodology to the heterogenization of palladium species by using a different MOF, ZrMOF-BIPY ($Zr_6O_4(OH)_4(bpydc)_6$, bpydc = 2,2′-bipyridine-5,5′-dicarboxylate) as a support, which also features uncoordinated bpy moieties in the MOF framework.[18] A careful literature survey shows that so far there is no report of employing MOFs as catalysts for carbonylative Sonogashira-type coupling reactions, although MOFs supported Pd nanoparticles (*e.g.*, Pd/MOF-5) for the Sonogashira coupling of terminal alkynes with aryl halides have been reported.[19]

Results and discussion

ZrMOF-BIPY was prepared according to the reported procedures.[18] ZrMOF-BIPY is isostructural to UiO-67 ($Zr_6O_4(OH)_4(bpdc)_6$, bpdc = *para*-biphenyldicarboxylate), as confirmed by PXRD measurements (Fig. 1). The activated ZrMOF-BIPY was soaked in an acetonitrile solution of $PdCl_2(CH_3CN)_2$ to afford Pd(II)@ZrMOF-BIPY. After modification with Pd (1.0 wt%), the crystallinity of the MOF was mostly maintained (Fig. 1). The intermolecular interaction between the bpydc ligand and Pd and their coordination environment were investigated by X-ray photoelectron spectroscopy (XPS). Both $PdCl_2(CH_3CN)_2$ and Pd(II)@ZrMOF-BIPY samples exhibited Pd $3d_{5/2}$ and Pd $3d_{3/2}$ bands at around 338 eV and 343 eV (Fig. 2), respectively, characteristics of divalent Pd cations.[20] However, the Pd 3d lines of Pd(II)@ZrMOF-BIPY were shifted by *ca.* 0.5 eV toward lower binding energies, as compared to the pristine $PdCl_2(CH_3CN)_2$. Such shifts reflected an increase in the electron density of Pd,[21] suggesting a strong coordination interaction between the bpydc ligand and the Pd atom in Pd(II)@ZrMOF-BIPY. The N 1s spectra (Fig. 3) showed two binding energies for the N 1s peaks of Pd(II)@ZrMOF-BIPY, which implied the presence of two types of coordination environments for N atoms. The small N 1s peak at a higher binding energy could not be attributed to the N atom in $PdCl_2(CH_3CN)_2$ because FT-IR analysis has shown that the characteristic absorbance band for a $C\equiv N$ bond at *ca.* 2340 cm^{-1} was absent (Fig. 4). The results confirmed that a small amount of the uncoordinated bpy units was bonded to Pd in Pd(II)@ZrMOF-BIPY. Elemental analysis indicated that the N : Pd molar ratio in Pd(II)@ZrMOF-BIPY was *ca.* 54.0, suggesting that *ca.* 3.7% of the bpydc ligands were coordinated with Pd(II). EDX analysis

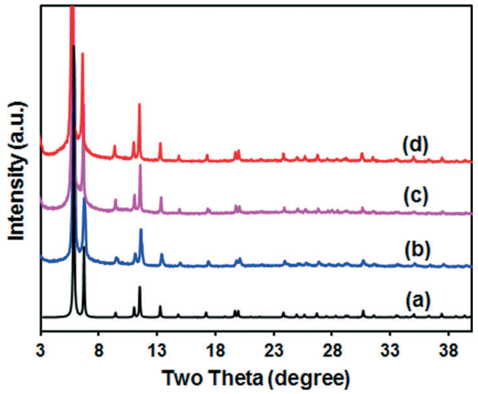


Fig. 1 Powder XRD patterns of the ZrMOF-BIPY samples: simulated UiO-67 (a); as-synthesized ZrMOF-BIPY (b); 1 wt% Pd(II)@ZrMOF-BIPY before (c) and after (d) catalytic reaction.

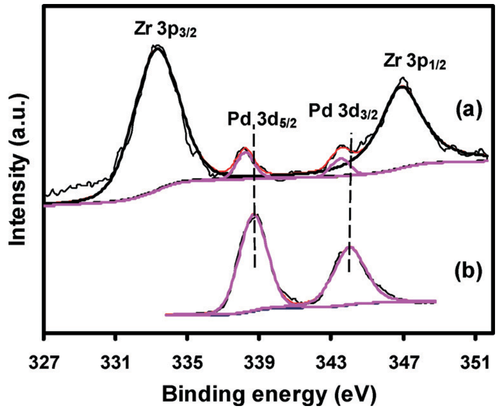


Fig. 2 XPS spectra of the Pd 3d region for (a) Pd(II)@ZrMOF-BIPY and (b) $PdCl_2(CH_3CN)_2$.

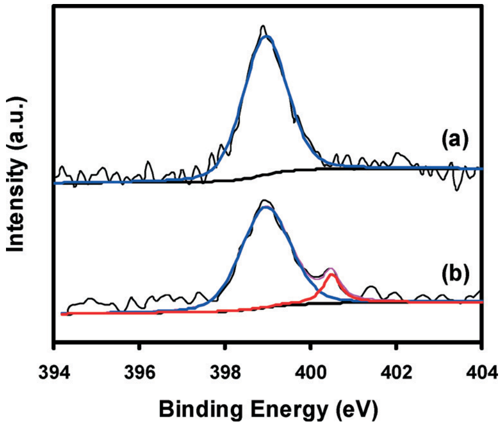


Fig. 3 XPS spectra of the N 1s region for (a) ZrMOF-BIPY and (b) Pd(II)@ZrMOF-BIPY.

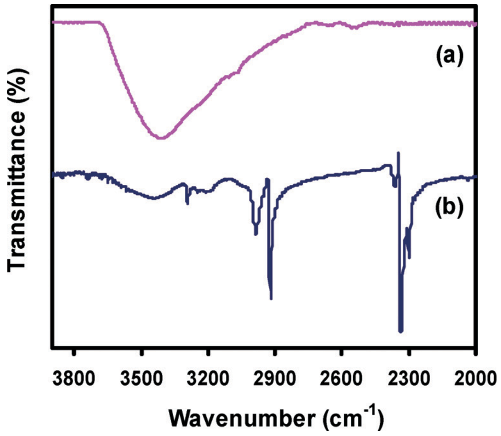
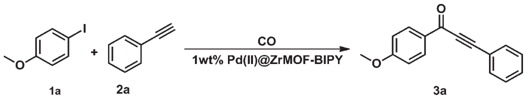


Fig. 4 FT-IR spectra of (a) Pd(II)@ZrMOF-BIPY and (b) $PdCl_2(CH_3CN)_2$.

showed that the atomic ratio of Pd : Cl was *ca.* 1 : 2 (see the ESI†), which indicated that all of the palladium remained in its dichloride form in Pd(II)@ZrMOF-BIPY.

For initial optimization of the reaction conditions, the carbonylative Sonogashira coupling reaction of 4-methoxyiodobenzene with phenylacetylene was selected as the model reaction, and the results are summarized in Table 1. First, the effect of solvents on the coupling reaction was investigated. It is well known that MOFs are not as stable as other porous materials such as zeolites, so we should pay special attention to the selection of reaction parameters when using MOFs for catalytic reactions. Therefore, we carefully examined the stability of ZrMOF-BIPY in various commonly used solvents before performing the reaction over the Pd(II)@ZrMOF-BIPY catalyst. It was found that the MOF material was stable in DMF, DMA, DMSO, acetonitrile, benzene, and toluene (Fig. 5), while its structure was destroyed when immersed in some solvents such as water, acetone, 1,4-dioxane, chloroform, and THF (see the ESI†). Using the appropriate solvents, the reactions were carried out at 373 K and 5 atm of CO pressure with 1 wt% Pd(II)@ZrMOF-BIPY as the catalyst and Et_3N as the base. It was observed that DMF was the best solvent among the five other solvents used, affording the desired product, 1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-one (**3a**) in quantitative yield (Table 1, entries 1–6).

Table 1 Carbonylative coupling of 4-methoxyiodobenzene with phenylacetylene under different reaction conditions[a]



Entry	Base	Solvent	CO (atm)	Conversion[b] (%)	Selectivity[b] (%)
1	Et_3N	CH_3CN	5	89	98
2	Et_3N	DMF	5	>99	>99
3	Et_3N	DMA	5	91	>99
4	Et_3N	toluene	5	13	>99
5	Et_3N	Benzene	5	20	98
6	Et_3N	DMSO	5	>99	77
7	—	DMF	5	5	>99
8	K_2CO_3	DMF	5	78	70
9	K_3PO_4	DMF	5	88	90
10	Cs_2CO_3	DMF	5	>99	>99
11	DABCO	DMF	5	80	>99
12	CH_3ONa	DMF	5	65	95
13	Cs_2CO_3	DMF	1	>99	>99
14	Et_3N	DMF	1	85	99
15[c]	Cs_2CO_3	DMF	1	—	—
16[d]	Cs_2CO_3	DMF	1	—	—
17[e]	Cs_2CO_3	DMF	1	>99	97
18[f]	Cs_2CO_3	DMF	1	>99	90
19[g]	Cs_2CO_3	DMF	1	95	99

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), catalyst (1 mol% Pd), base (0.5 mmol), solvent (2 mL), 373 K, 3 h. [b] Conversions and selectivities were determined by GC-MS analysis. [c] No catalyst was used. [d] ZrMOF-BIPY was used as the catalyst. [e] 0.5 wt% Pd(II)@ZrMOF-BIPY was used. [f] 2 wt% Pd(II)@ZrMOF-BIPY was used. [g] **1a** (10 mmol), **2a** (11 mmol), catalyst (0.2 mol% Pd), base (10 mmol), solvent (6 mL), 373 K, 6 h.

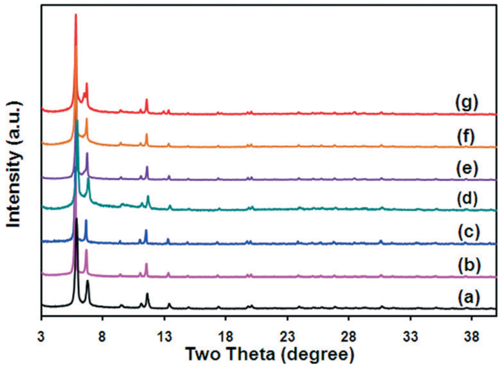


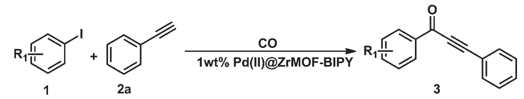
Fig. 5 PXRD patterns of ZrMOF-BIPY (a) as-synthesized and after exposure to a variety of solvents at 393 K for 24 h: (b) DMA, (c) DMF, (d) DMSO, (e) acetonitrile, (f) benzene, (g) toluene.

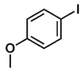
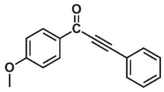
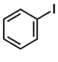
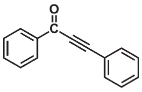
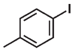
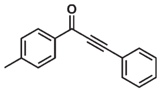
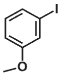
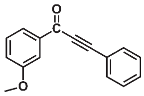
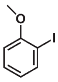
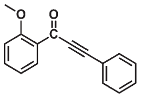
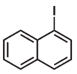
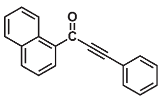
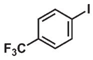
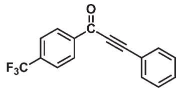
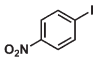
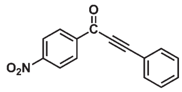
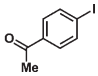
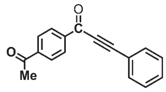
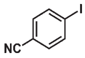
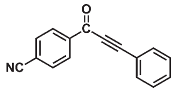
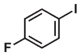
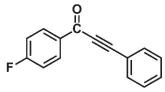
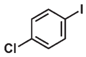
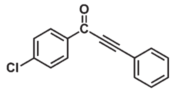
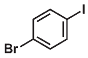
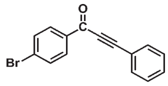
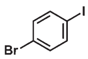
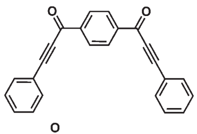
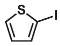
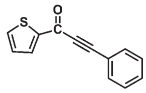
Using DMF as the solvent, we further investigated the influence of bases on the carbonylative Sonogashira coupling reaction. It can be seen that in the absence of a base, only a 5% yield of **3a** was obtained (Table 1, entry 7), indicating that a base was necessary for the coupling reaction to proceed. As with Et_3N, the use of Cs_2CO_3 as the base also furnished **3a** in quantitative yield under 5 atm of CO (Table 1, entry 10). Notably, Pd(II)@ZrMOF-BIPY retained its high activity and selectivity even though the CO pressure was lowered to atmospheric pressure with Cs_2CO_3 as the base (Table 1, entry 13), which was apparently superior to the result in the presence of Et_3N (Table 1, entry 14). Moreover, *ca.* 15% of the total Pd in the fresh catalyst was observed to have leached into the solution after reaction, leading to a much lower conversion (68%) and selectivity (73%) when reusing the catalyst under identical conditions as compared to the fresh one (Table 1, entry 14). Therefore, Cs_2CO_3 was selected as the base for the next reaction tests.

Under optimized conditions, blank runs and those using the parent MOF (without Pd grafting) showed no conversion in the reaction (Table 1, entries 15 and 16), confirming the need for a metal to perform the carbonylative Sonogashira coupling. We also investigated the effect of metal content and proved that 1 wt% Pd was the best catalyst with respect to conversion and selectivity (Table 1, entries 13, 17, and 18). An increase in Pd loading on the MOF led to a remarkable decrease in selectivity to the desired product **3a** (entry 18). We also investigated the carbonylative Sonogashira coupling at a much higher substrate/metal molar ratio (0.2 mol% Pd). The reaction also proceeded smoothly, furnishing a conversion of 95% with a good selectivity (~99%) to **3a** after 6 h of reaction (entry 19).

The scope of this novel heterogeneous Pd-catalyzed carbonylative coupling of phenylacetylene with a variety of aryl iodides was investigated. Aryl iodides containing an electron-donating group at the *para*, *meta*, and *ortho* positions afforded the corresponding substituted α,β-alkynyl ketones in excellent isolated yields (Table 2, entries 1–5). 1-Iodonaphthalene also underwent carbonylative coupling smoothly and afforded **3f** in 94% yield (entry 6). In general,

Table 2 Carbonylative coupling of phenylacetylene with various aryl iodides[a]



Entry	Substrate	Product	Yield[b]
1	 **1a**	 **3a**	97
2	 **1b**	 **3b**	98
3	 **1c**	 **3c**	95
4	 **1d**	 **3d**	95
5	 **1e**	 **3e**	92
6	 **1f**	 **3f**	94
7	 **1g**	 **3g**	92
8	 **1h**	 **3h**	86
9	 **1i**	 **3i**	91
10	 **1j**	 **3j**	87
11	 **1k**	 **3k**	92
12	 **1l**	 **3l**	93
13	 **1m**	 **3m**	92
14[c]	 **1m**	 **3n**	62
15	 **1o**	 **3o**	92

[a] Reaction conditions: **1** (0.5 mmol), **2a** (0.6 mmol), catalyst (1 mol%), Cs_2CO_3 (0.5 mmol), DMF (2 mL), CO 1 atm, 373 K, 3 h. [b] Isolated yield. [c] **1m** (0.5 mmol), **2a** (1.5 mmol), 373 K, 12 h.

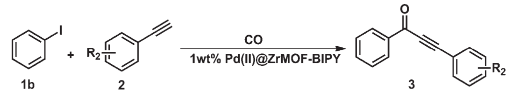
electron-deficient aryl iodides exhibited slightly lower activity than electron-rich ones (entries 7–13). Under optimized conditions, 4-fluoro, 4-chloro, and 4-bromo substituted iodobenzenes were selectively carbonylated at the iodo moiety to give the corresponding ynones in satisfactory yields (entries 11–13). However, when the reaction time is prolonged to 12 h, it was interesting to note that for the coupling of 4-bromoiodobenzene, both the iodo and bromo groups on the benzene ring could undergo carbon monoxide insertion, giving the double-coupling product **3n** in 62% yield (entry 14). Heteroaryl iodides, such as 2-iodothiophene, were also coupled with phenylacetylene smoothly to provide the desired ynones in excellent yields (Table 2, entry 15). It is noteworthy that only small amounts (*ca.* 1%) of the non-carbonylative coupling products were observed for all of the runs in Table 2. This could be related to the lesser reactivity of alkyne (compared with its corresponding alkynyl copper gate complex) in the absence of copper. Under these conditions, alkyne would react with the electron-deficient acylpalladium intermediates more easily than with aryl palladium iodide species, leading to the production of the carbonylative coupling reaction product.[10,12b,14a]

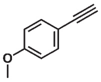
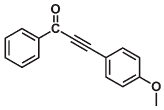
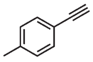
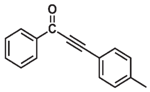
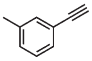
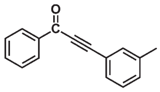
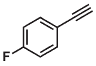
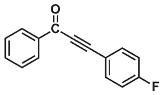
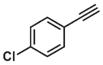
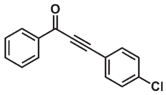
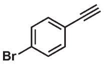
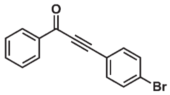
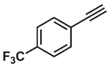
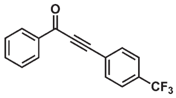
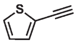
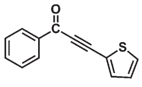
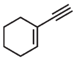
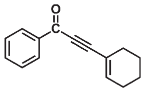
We also attempted to expand this catalytic system for the carbonylative coupling of aryl bromides. We tried several aryl bromides, such as bromobenzene, 4-bromobenzaldehyde, 4-bromoanisole, and 4-bromotoluene. However, no desired coupling products were found even though the reaction time was prolonged to 24 h under the optimized conditions. Aryl bromides or chlorides have been reported to be poor substrates for carbonylative Sonogashira coupling, because the dissociation energy of the sp^2-C–Cl or sp^2-C–Br bond is comparatively higher than that of sp^2-C–I.[22] So far, there is no report on the carbonylative Sonogashira coupling of aryl bromides or chlorides using phosphane-free heterogeneous catalytic systems.[11b–d]

We further investigated the carbonylative coupling reactions of various substituted phenylacetylenes with iodobenzene. All phenylacetylenes bearing an electron-withdrawing group or an electron-donating group on the aromatic ring were coupled with iodobenzene to afford the desired ynones in excellent isolated yields (Table 3, entries 1–7). The Pd(II)@ZrMOF-BIPY catalyst was also active in the carbonylative coupling of heterocyclic acetylenes, giving the corresponding ynones in excellent yields (Table 3, entry 8). The reaction with 1-ethynylcyclohex-1-ene (**2j**) provided the carbonylated products **3x** in 88% isolated yield (Table 3, entry 9).

In a final set of experiments, we evaluated the reusability of the Pd(II)@ZrMOF-BIPY catalyst in the carbonylative Sonogashira coupling reaction because it is crucial to confirm that the highly active catalyst is recyclable. It can be seen from Table S1 and Fig. S5 (see the ESI†) that the catalyst could be reused five times without apparent loss of activity and yield. The results were in accordance with AAS experiments for which only traces of Pd (less than 0.2% of the total palladium) were detected in the solution collected by hot filtration after reaction, as well as with the PXRD patterns of

Table 3 Carbonylative coupling of iodobenzene with various alkynes[a]



Entry	Substrate	Product	Yield[b]
1	 2b	 3p	96
2	 2c	 3q	92
3	 2d	 3r	90
4	 2e	 3s	91
5	 2f	 3t	90
6	 2g	 3u	93
7	 2h	 3v	82
8	 2i	 3w	90
9	 2j	 3x	88

[a] Reaction conditions: **1a** (0.5 mmol), **2** (0.6 mmol), catalyst (1 mol%), Cs_2CO_3 (0.5 mmol), DMF (2 mL), CO 1 atm, 373 K, 3 h. [b] Isolated yield.

the catalyst after the fifth run which showed no apparent changes in the crystallinity of the ZrMOF-BIPY material (Fig. 1). TEM images (Fig. S3†) showed that no apparent Pd aggregation could be observed after reaction. XPS analysis of the reused catalyst confirmed that palladium remained in its divalent form and was still coordinated to the bpy unit (Fig. S4†). The Pd content in the recovered catalyst was almost identical to the fresh one. Moreover, the reaction with the solution after hot filtration at approximately 30% conversion essentially stopped, strongly suggesting that the reaction proceeded mostly on the heterogeneous surface (Fig. 6).

Pd(II)@ZrMOF-BIPY after catalytic reaction was also characterized by scanning electronic microscopy (SEM) and energy dispersive spectroscopy (EDS). The SEM images recorded after the catalytic runs revealed that the morphology of the catalyst remained almost the same as that of the fresh one (Fig. 7). Interestingly, iodine was found in the catalyst after the catalytic reaction as confirmed by EDS analysis. We reasoned that iodine could be deposited on the catalyst surface from the oxidative addition of aryl iodides to the Pd center and subsequent reductive elimination of the products.

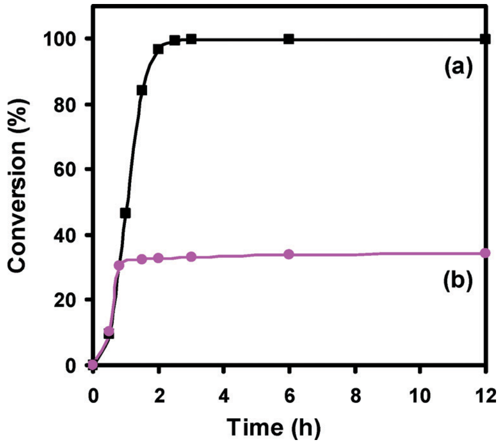


Fig. 6 Activity profile for the carbonylative Sonogashira coupling of 4-iodoanisole with phenylacetylene. Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), catalyst (1 mol%), Cs_2CO_3 (0.5 mmol), DMF (2 mL), CO 1 atm, 373 K. (a) With catalyst, and (b) with filtrate.

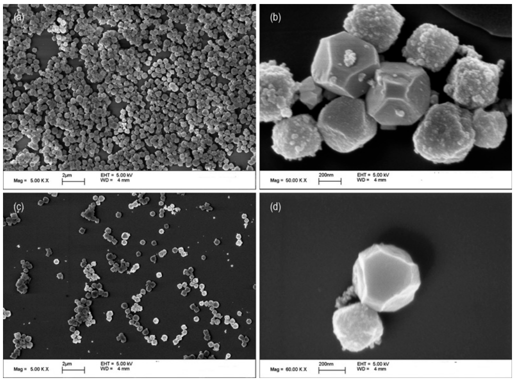


Fig. 7 SEM images of 1 wt% Pd(II)@ZrMOF-BIPY before (a and b) and after (c and d) catalytic reaction.

Conclusions

In summary, we have developed a novel and highly efficient Pd(II)@ZrMOF-BIPY system for the carbonylative Sonogashira coupling reaction of aryl iodides with terminal alkynes without the addition of phosphine ligands. The catalyst could efficiently promote the carbonylative coupling reaction under atmospheric pressure of CO to afford the corresponding aryl α,β-alkynyl ketones in good to excellent yields. Moreover, the heterogeneous catalyst is recoverable, shows negligible metal leaching, and could be reused at least five times without significant loss in catalytic activity and selectivity. The combination of high catalytic efficiency and substrate compatibility as well as good recyclability provides a practical and environmentally friendly procedure for the preparation of ynones.

Experimental

General information

^{1}H NMR and ^{13}C NMR data were obtained using a Bruker Avance III 400 spectrometer with $CDCl_3$ as solvent and tetramethylsilane (TMS) as an internal standard. The reaction products were quantified and identified by GC-MS analysis (Shimadzu GCMS-QP5050A equipped with a 0.25 mm × 30 m DB-WAX capillary column). Powder X-ray diffraction patterns of the samples were obtained using a Rigaku diffractometer (D/MAX-IIIA, 3 kW) with Cu Kα radiation (40 kV, 30 mA, $\lambda = 0.1543$ nm). XPS data were obtained using an Axis Ultra DLD spectroscope with Mono Al Kα (1486.6 eV, 10 mA × 15 kV) as an X-ray source. Atomic absorption spectroscopy (AAS) was carried out using a HITACHI Z-2300 instrument. The size and morphology were determined by scanning electronic microscope (SEM, 1530 VP of LEO) equipped with an energy dispersive X-ray detector (EDX, Inca 300 of Oxford).

Synthesis of ZrMOF-BIPY

ZrMOF-BIPY was prepared according to the procedures developed by DeCoste *et al.* but with a change in the quantity of the organic linker.[18] Typically, $ZrCl_4$ (233 mg, 1 mmol) and 2,2′-bipyridine-5,5′-dicarboxylic acid (244 mg, 1 mmol) were dissolved in 50 mL of DMF at room temperature. The mixture was sealed in a 100 mL scintillation vial and heated to 393 K for 24 h. The resulting white microcrystalline powder was then filtered and washed with DMF, collected by filtration and finally dried at 423 K under vacuum for 12 h. Elemental analysis, calcd (%) for $Zr_6O_4(OH)_4(O_2C\text{–}(C_5H_3N)_2\text{–}CO_2)_6$: C, 40.56; H, 1.89; N, 7.88. Found: C, 40.58; H, 1.90; N, 7.87.

Stability of the MOF in different solvents

As-synthesized ZrMOF-BIPY (0.2 g) was soaked in solution (20 mL) of DMF, DMA, DMSO, acetonitrile, benzene, toluene, chloroform, THF, acetone, 1,4-dioxane, or water at 393 K for 24 h. The samples were filtered and dried under vacuum prior to analysis.

Synthesis of Pd(II)@ZrMOF-BIPY

Pd(II)@ZrMOF-BIPY was prepared by addition of ZrMOF-BIPY (212.4 mg) to a solution of $PdCl_2(CH_3CN)_2$ (5.2 mg, 0.2 mmol) in acetonitrile (25 mL) at 338 K for 24 h. After cooling to room temperature, the resulting solid was soaked in 15 mL of acetonitrile. After 24 h, the supernatant was decanted and replaced with fresh acetonitrile. The exchanging process was repeated two times, after which the powder was filtered and heated at 423 K for 12 h under vacuum. The molar ratio of $PdCl_2$ to bpy in ZrMOF-BIPY was *ca.* 0.037, as measured by atomic absorption spectrometry.

General procedure for the carbonylative Sonogashira coupling reaction

Aryl iodides (0.5 mmol), phenylacetylene (0.6 mmol), Pd(II)@ZrMOF-BIPY (0.005 mmol, 1 mol%), Cs_2CO_3 (0.5 mmol) and DMF (2 mL) were added to a Schlenk tube under CO atmosphere at room temperature. The tube was sealed and the mixture was stirred at 373 K for 3 h. After cooling to room temperature, the solid catalyst was isolated from the solution by filtration and washed with ethyl acetate. The supernatant was collected and added into 20 mL of water, subsequently extracted with ethyl acetate (3 × 20 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by silica gel chromatography using petroleum ether/ethyl acetate (8 : 1) as the eluent to afford the desired product.

Recycling of the Pd(II)@ZrMOF-BIPY catalyst

The recyclability of the Pd(II)@ZrMOF-BIPY catalyst was tested in the reaction of iodobenzene with phenylacetylene maintaining the same reaction conditions as described above, except that the recovered catalyst was used. The results of five runs are presented in Table S1.† Each time the reaction mixture was allowed to settle down at the end of reaction and the supernatant liquid was decanted. The solid was thoroughly washed with acetonitrile, dried, and then reused as the catalyst in the next run.

Heterogeneity of the catalyst

To verify whether the catalysis of Pd(II)@ZrMOF-BIPY is truly heterogeneous, the solid catalyst was hot filtered from the reaction solution after 50 min. The reaction was continued with the filtrate but with no solid catalyst for an additional 11 h. The solution in the absence of the solid catalyst did not exhibit any further reactivity. The results demonstrate that the reaction proceeds on the heterogeneous surface.

Time-conversion curves

The time-conversion measurements were performed in a 20 mL online Teflon-lined stainless-steel autoclave equipped with a sample connection. The autoclave was connected to a carbon monoxide gas cylinder, and the reaction pressure was controlled with a precise gas regulator. Aryl iodides (0.5 mmol), phenylacetylene (0.6 mmol), Pd(II)@ZrMOF-BIPY (0.005 mmol, 1 mol%), Cs_2CO_3 (0.5 mol), and DMF (2 mL) were added to the reactor. The autoclave was purged several times with CO to remove the air. Then the reactor was filled with CO at 1 atm and heated to the target temperature. 0.1 mL of liquid mixture was taken at each time interval. The mixture was centrifuged and the supernatant was analyzed by GC-MS.

Acknowledgements

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