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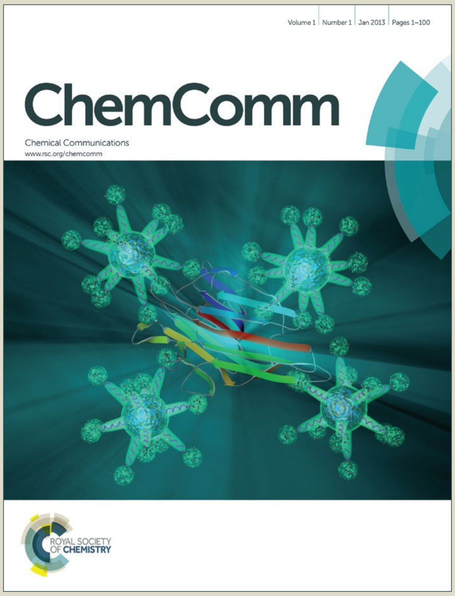

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ARTICLE TYPE

Pd-Cu_2O nanocomposite as an effective synergistic catalyst for selective semi-hydrogenation of terminal alkynes only

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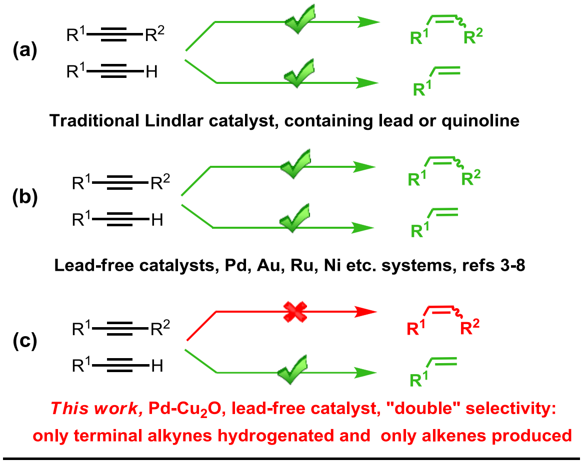
A new type lead-free catalyst of Pd-Cu_2O nanocomposite was developed for highly selective semi-hydrogenation of alkynes. With unprecedented selectivity for the semi-hydrogenation of terminal alkynes to alkenes, we show for the first time the catalyst only hydrogenated terminal alkynes, i.e. not hydrogenated internal alkynes.

Selective semi-hydrogenation of alkynes to alkenes, without further reduction to alkanes, is of great significance in the polymer and fine chemical industries.[1] The most famous catalyst for this reaction is Lindlar catalyst (Pd/$CaCO_3$ modified by $Pb(OAc)_2$ or Pd/$BaSO_4$ with excessive addition of quinoline) (Scheme 1a).[2] The presence of Lead species and quinoline leads to harmful wastes and heavy metal residual in the products. In addition, isomerization of the (*Z*)-alkene to the (*E*)-alkene, shift of the double bond, over-reduction to the alkane, and poor stability were frequently observed with the Lindlar type catalysts.[1b]

During the past years, several lead-free heterogeneous catalysts, including Pd-based alloys (such as PdAg, PdCu, PdGa, PdSn...),[3] Au,[4] Ru,[5], Fe,[6] and Ni[7] have been developed as alternatives to Lindlar catalyst. For example, Jin *et al.* reported an impressive nanoporous Au catalyst for selective hydrogenation of alkynes. They found that amine additives were important for the activity and selectivity of the catalyst.[8] Lee *et al.* prepared an interesting core/shell silica microspheres containing Pd and $CuFe_2O_4$ nanoparticles for selective semi-hydrogenation of arylacetylenes.[9] Although up to 99 % selectivity to alkenes was obtained under optimal conditions, the alkene selectivity decreased with prolonged reaction time. In addition, there was no selectivity against terminal alkynes and internal alkynes (Scheme 1b). All alkynes can be hydrogenated.

Usually, terminal alkynes are easily over-hydrogenated to alkanes because of their higher reactivity than internal alkynes.[10] Thus, selective semi-hydrogenation of terminal alkynes only to corresponding alkenes is quite difficult and challenging. In this work, we met this goal with a lead-free Pd-Cu_2O catalyst. As depicted in Scheme 1c, two impressive chemo-selectivities were observed. One was that when both internal alkynes and terminal alkynes are present, the catalyst selectively hydrogenated terminal alkynes only with internal alkynes intact. The other was the hydrogenation reaction produced corresponding alkenes only, i.e. no alkane was observed even at prolonged reaction time. Such “double” selectivity for terminal alkynes only and to alkenes only is unprecedented in chemo-selective hydrogenation research. Cu_2O played a crucial role in suppressing over-hydrogenation of terminal alkynes to alkanes as well as hydrogenation of internal alkynes.



Scheme 1 Selective semi-hydrogenation between internal and terminal alkynes with various catalysts.

Pd-Cu_2O catalyst was prepared by a two-step process. First, Fe_3O_4 and Cu nanoparticles were simultaneously coated onto the surface of MWCNTs through one-pot thermolysis of $Fe(acac)_3$ and $Cu(acac)_2$ in TREG to produce MWCNTs-Fe_3O_4-Cu (denoted as **M-1**, detail characterizations are listed in the Experimental Section, Fig. S1-S2, ESI†). Then MWCNTs-Fe_3O_4-Cu_2O-Pd nanocomposite (denoted as **M-2**) was obtained through in situ galvanic replacement reaction between Cu nanoparticles and $PdCl_4^{2+}$ ($E_{Cu^{2+}/Cu}$ = +0.337 vs $E_{PdCl_4^{2-}/Pd}$ = +0.620). The remaining Cu was then oxidized to Cu_2O in aqueous solution due to the presence of dissolved oxygen.[11] The typical XRD pattern of **M-2** was shown in Fig. S1b. The diffraction peaks of Cu_2O (JCPDS no.78-2076) can be clearly seen. However, no obvious peaks of Pd was observed, which may be ascribed to the small size and low content of Pd nanoparticles. The weight percentage of Pd in **M-2** was measured to be 1.67 wt% by inductively coupled plasma atomic emission spectroscopy (ICP-AES). FT-IR and XPS (Fig. S3-S4, ESI†) also confirmed the states of Cu_2O and Pd.

SEM and TEM images showed that the surface of **M-2** was coated with small particles uniformly (Fig. 1a and 1b). From the

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HRTEM image (Fig. 1c), lattice fringes with different distance could be seen, which can be ascribed to MWCNTs, Fe_3O_4, Cu_2O and Pd, respectively. The size of Pd was about 3 nm. EELS element mapping (Fig. 1d) further showed that Fe, O, Cu and Pd elements were uniformly dispersed on the surface of MWCNTs.

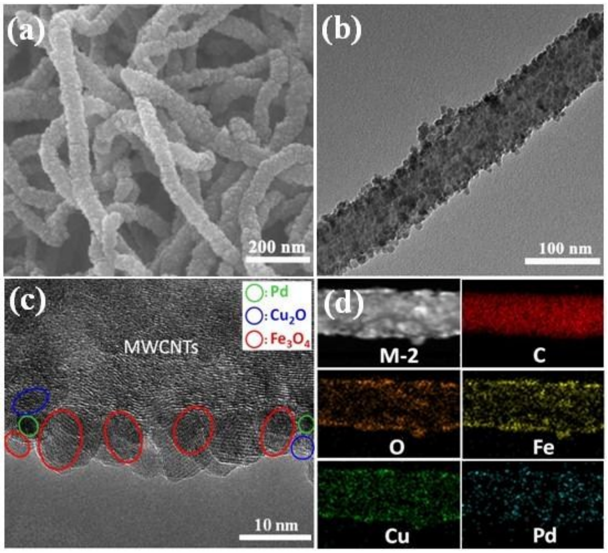


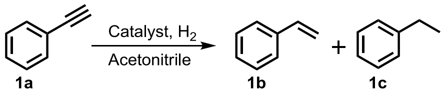
Fig. 1 (a) FE-SEM; (b) TEM; (c) HR-TEM images and (d) element mapping images of MWCNTs-Fe_3O_4-Cu_2O-Pd **(M-2)**.

The catalytic performance of **M-2** for the selective hydrogenation of phenylacetylene (**1a**) was first tested. Various solvents, including polar solvents and nonpolar solvents were explored, and acetonitrile showed the best result (Table S1, entry 8). Interestingly, when the reaction was carried out in green solvents, such as liquid CO_2 or super critical CO_2 ($SCCO_2$), satisfactory yields were also obtained (Table S1, entries 10 and 11). In these experiments, pure product can be readily obtained by releasing the compressed CO_2.[12]

The catalytic performance of **M-2** against commercial Pd/C and Lindlar catalysts were summarized in Table 1. In the control experiment using **M-1** (without Pd), no noticeable conversion of **1a** were observed, confirming that **M-1** alone was inactive for the hydrogenation and Pd was indispensable (Table 1, entry 1). Commercial Pd/C showed high activity for the conversion of **1a** as expected, but the selectivity was quite low (Table 1, entries 2-5). Although Lindlar catalyst showed 86 % conversion with 99 % selectivity after 1 h (Table 1, entry 6), the selectivity was lowered to 76 % when the reaction time was prolonged to 12 h (Table 1, entry 7). In sharp contrast, complete conversion (99 %) with high selectivity of 98% toward styrene was achieved in 1.5 h using **M-2** catalyst (Table 1, entry 8). No over-hydrogenation was observed even the reaction time was prolonged to 12 h after complete consumption of **1a** (Table 1, entry 9). Furthermore, **M-2** catalyst was easily recovered by centrifugation and reused for five times without significant loss of activity and selectivity (Table S2, ESI†).

The unique selectivity of **M-2** catalyst can be further extended to a wide range of terminal alkynes. Phenylacetylenes bearing electron-donating and electron-withdrawing groups were all selectively hydrogenated to the corresponding terminal alkenes with excellent selectivity (Table 2, entries 1-5). Though

Table 1 Hydrogenation of phenylacetylene with different catalysts.[a]

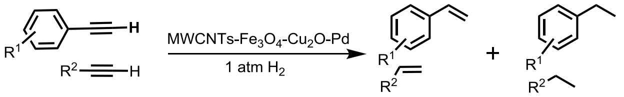


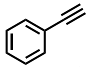
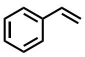
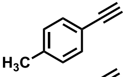
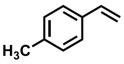
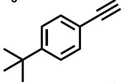
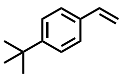
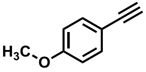
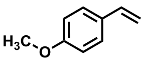
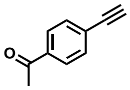
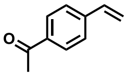
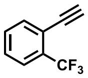
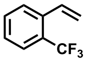
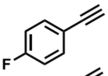
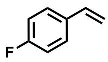
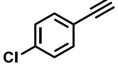
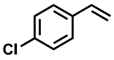
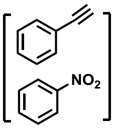
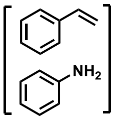
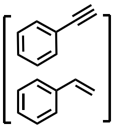
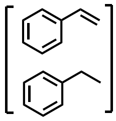
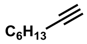
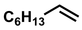
1a **1b** **1c**

Entry	Catalyst	Time/h	Conversion[a]	Selectivity
1	MWCNTs-Fe_3O_4-Cu (**M-1**)	4.0	<1%	—
2	Pd/C (5 wt%)	0.5	69%	98%
3	Pd/C (5 wt%)	1.0	99%	58%
4	Pd/C (10 wt%)	0.5	92%	98%
5	Pd/C (10 wt%)	1.0	>99%	38%
6	Lindlar catalyst (5 wt%)	1.0	86%	99%
7	Lindlar catalyst (5 wt%)	12.0	>99%	76%
8	MWCNTs-Fe_3O_4-Cu_2O-Pd (**M-2**)	1.5	>99%	98%
9	MWCNTs-Fe_3O_4-Cu_2O-Pd (**M-2**)	12.0	>99%	98%

[a] Reaction condition: Pd loading: 0.26 mol%, 1a (100 μL, 0.91 mmol) in 2.0 mL acetonitrile using the 1,3,5-trimethylbenzene as the internal standard, 1 atm H_2, 30 °C.

Table 2 Hydrogenation of terminal alkynes with M-2 catalyst.



Entry	Substrate	Time/h	Product	Conversion[a]	Selectivity
1		1.5		99%	98%
2		1.0		99%	99%
3		1.5		99%	98%
4		1.0		99%	97%
5		1.5		99%	99%
6		2.0		27%	99%
7		1.5		99%	99%
8		0.5		99%	98%
9[b]		4.0		99% 0%	98% —
10[c]		1.5		99% <1%	99% —
11		2.0		99%	99%

[a] Reaction condition: Pd loading: 0.26 mol%, substrates in 2.0 mL acetonitrile, 1 atm H_2, 30 °C. [b] 0.45 mmol **1a** and 0.45 mmol nitrobenzene was used. [c] 0.45 mmol **1a** and 0.45 mmol **1b** was used.

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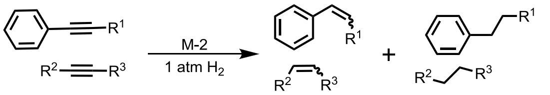
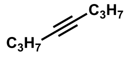
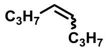
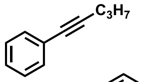
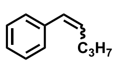
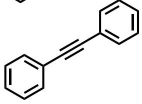
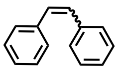
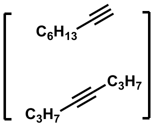
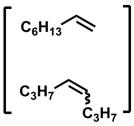
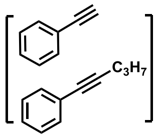
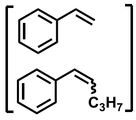
1-ethynyl-2-(trifluoromethyl) benzene showed relative low activity, high selectivity to alkenes was still maintained (99 %) (Table 2, entry 6). For the substrates with reducible functional groups, such as chloride, fluoride, and nitro moieties, the Pd-catalyzed de-halogenations reaction[13] and nitro-reduction reaction[14] were also avoided and corresponding olefins from the selective hydrogenation of alkynes were the only products (Table 2, entries 7-9). As shown in entry 9 of Table 2, when a mixture of phenylacetylene and nitrobenzene was used, only phenylacetylene was hydrogenated, while nitrobenzene was intact, showing excellent selectivity toward alkyne only. For a better illustration of the high selectivity of **M-2**, another experiment using a 1:1 mixture of phenylacetylene (**1a**) and styrene was carried out. The result showed that the only product was styrene with 99 % yield, indicating over-hydrogenation of styrene never occurred (Table 2, entry 10).

Another interesting finding was that **M-2** selectively catalyzes the terminal alkynes only, while leaving the internal alkynes untouched. As can be seen in Table 3, with either aromatic internal alkynes or aliphatic internal alkynes, the internal triple bond remained unchanged even when the reaction was prolonged to 12 h (Table 3, entries 1-3). The unique selective reaction of terminal alkynes was further demonstrated when terminal and internal alkynes were mixed together, in which only terminal alkynes were hydrogenated to the corresponding alkenes with 98 % selectivity, while the internal alkynes were unchanged (Table 3, entries 4-5). Such "double" selectivity for terminal alkynes only and to alkenes only has not been reported in the literatures.

Table 3 Hydrogenation of internal alkynes with **M-2** catalyst.[a]

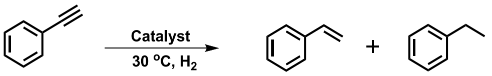


Entry	Substrate	Time/ h	Product	Conversion[a]	Selectivity
1		12.0		<1%	—
2		12.0		<1%	—
3		12.0		<1%	—
4[b]		2.0		>99% 2%	98% —
5[c]		19.0		99% <1%	99% —

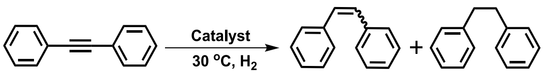
[a] Reaction condition: Pd loading: 0.26 mol%, substrates in 2.0 mL acetonitrile, 1 atm H_2, 30 °C. [b] 0.45 mmol 1-octyne and 0.45 mmol 1-octyne was used. [c] 0.45 mmol **1a** and 0.45 mmol 1-Phenyl-1-pentyne were used.

In order to understand the origins of the high selectivity of **M-2** catalyst, MWCNTs-Fe_3O_4-Pd without Cu_2O (denoted as **M-3**, detail synthesis procedure and characterizations are listed in the Experimental Section, Fig. S1, S5-S6, ESI†) was prepared and tested. As shown in Table 4, for terminal alkynes hydrogenation, **M-3** catalyst showed excellent activity but very poor selectivity (< 1 %), similar to what was observed with commercial Pd/C catalyst. For internal alkyne 1,2-diphenylethyne, **M-3** catalyst showed 99 % conversion and poor alkene selectivity in 1.5 h. These sharply difference results of **M-2** vs **M-3** catalysts (with vs without Cu_2O) clearly demonstrated that Cu_2O played a critical role in suppressing over hydrogenation of terminal alkynes to alkanes as well as hydrogenation of internal alkynes. Together with the previous catalytic result of **M-1** (Table 1, entry 1), it suggested that the synergistic effect between Pd and Cu_2O was accounted for the unique selectivity. If without modifiers, Pd-containing catalysts will hydrogenate olefins very fast in many previous reports.[15]

Table 4 Selective hydrogenation between internal and terminal alkynes using **M-2** and **M-3** as catalysts, respectively.[a]



Catalyst	t/h	Conversion	Selectivity
(1) MWCNTs-Fe_3O_4-Cu_2O-Pd (M-2)	12	99%	98%
(2) MWCNTs-Fe_3O_4-Pd (M-3)	12	99%	<1%



Catalyst	t/h	Conversion	Selectivity
(3) MWCNTs-Fe_3O_4-Cu_2O-Pd (M-2)	12	<1%	—
(4) MWCNTs-Fe_3O_4-Pd (M-3)	1.5	99%	*Z*: *E*: *alkane* 46: 8: 46

[a] Reaction condition: 0.26 mol% Pd loading, 0.91 mmol alkynes in 2.0 mL acetonitrile, 1 atm H_2, 30 °C.

Roughly, two mechanisms were proposed for Pd-based catalysts in selective semi-hydrogenation of alkynes in the literatures. The major difference between them is that hydrogenation reaction occurred on different active sites. One is that hydrogenation of alkynes occurred on the surface of Pd, while other additive metals or supports acted as co-catalysts to lower the d-band energy of Pd and reduce the adsorption energy of alkenes, and/or to suppress the formation of β-palladium hydride (β-PdH) phase, which was considered to increase the conversion of alkynes to alkanes.[16] Another mechanism is that hydrogenation of alkynes occurred on the surface of additive metals or supports. In this mechanism, activated H atoms formed by Pd were transferred to other metals or supports through hydrogen spill over. For example, Sykes et al.[17] demonstrated that small quantity of Pd atoms on the Cu surface enhanced uptake of H_2, which can be dissociated on the Pd surface and then spill over to the bare Cu surface. The existence of Pd promoted the hydrogen uptake and subsequent desorption of alkene product from the Cu surface, resulting in high selectivity to alkenes.

However, nearly all of Pd-based catalysts involved in the above mechanisms research were Pd alloys (such as PdAg, PdCu, PdGa, PdSn...) or Pd supported on the bare Cu surface. No study about the synergistic effect between Pd and Cu_2O in selective hydrogenation of alkynes was reported. There may be a new reaction mechanism of this Pd-Cu_2O catalyst, which needs further investigation and will show in the future work.

In summary, we produced Pd-Cu_2O nanocomposite catalyst, which was a lead-free catalyst with better performance than conventional Lindlar catalyst. The catalyst showed unprecedented double selectivity in semi-hydrogenation of alkynes: only terminal alkynes were hydrogenated, and only corresponding alkenes were produced. Cu_2O played a vital role in suppressing over hydrogenation of terminal alkynes to alkanes as well as hydrogenation of internal alkynes. The synergistic effect between Pd and Cu_2O makes this catalyst can be used in wide range of selective semi-hydrogenation of alkynes.

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