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Bifunctional Mesoporous Silica Catalyst for C–C Bond Forming Tandem Reactions

Krishna K. Sharma,[a][‡] Ankush V. Biradar,[b,c] Sayantani Das,[b] and Tewodros Asefa*[b,c]

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We report on the synthesis and catalytic properties of a class of hybrid organic–inorganic mesoporous bifunctional heterogeneous catalysts for efficient catalysis of two-step tandem reactions in one pot. With a solvent-assisted grafting method, two different catalytic groups, that is, an organoamine and a palladium–organodiamine complex, were immobilized onto high-surface-area mesoporous silica sequentially, by using their corresponding organosilanes in 2-propanol or toluene as the solvent in the first step and toluene as the solvent in the second step. Both MCM-41 and SBA-15 mesoporous silicas were used as support materials for the two catalytic groups, and the effect of different sequential grafting of the two organosilanes in 2-propanol or toluene on the structures and the catalytic properties of the resulting bifunctional catalysts were investigated. By using the resulting amine/Pd^{II}–diamine bifunctional mesoporous material as catalyst, the occurrence of two very important C–C bond forming reactions, that is, the Sonogashira and the Henry reactions, was demonstrated in one pot for the first time. Yields of approximately 100 % in 2.5 h for the Sonogashira reaction and approximately 100 % in 45 min for the Henry reaction were obtained in the presence of the bifunctional catalyst when the reactions were run individually. When the bifunctional catalyst was used to catalyze the Sonogashira–Henry reactions in tandem in one pot, a yield of up to approximately 60 % of the Sonogashira–Henry product in 5 h was obtained. The synthesis and use of such bifunctional catalysts for efficient catalysis of the tandem reaction is of importance in three significant ways: it prevents the unnecessary use of solvents and other chemicals required for the purification of the intermediate products of either individual reaction, eliminates some of the work-up procedures, and lowers the cost of synthesis of the final product.

Introduction

Since the first report on mesoporous silica in the early 1990s, the synthesis of various hybrid organic–inorganic mesoporous materials and their potential applications in chemistry, catalysis, biology, and engineering have been widely investigated.[1–5] Mesoporous materials have drawn considerable attention because of their high surface areas, uniform nanometer pores, and monodisperse pore-size distribution, and because they can easily be functionalized with various organic and organometallic species to tune their surface properties as well as their potential applications.[6–8] For instance, organopalladium complexes, which have been widely used to catalyze various C–C bond coupling reactions such as the Sonogashira, Heck, and Suzuki reactions,[9–18] can be tethered onto the surface amine groups of primary amine-functionalized mesoporous silica. These organopalladium complexes can also be supported on mesoporous materials by means of other ligands such as phosphanes and diamines.[11–16,20] The resulting materials can serve as active heterogeneous catalysts for various organic reactions. The use of such materials as heterogeneous catalysts in industrial processes results in more cost-effective catalysis, as they allow the rapid recovery and multiple uses of the relatively "expensive" active catalysts such as palladium complexes. Consequently, mesoporous materials functionalized with palladium or other metal complexes hold great promise for use as efficient catalysts for various organic reactions.[9,11–16,22–27]

Similarly, numerous types of homogeneous and heterogeneous catalysts for the Henry reaction, which is another very important C–C bond forming reaction, have been reported.[28] Different types of amine groups that are tethered onto mesoporous silica support material have also been successfully used to catalyze the Henry reaction.[29–36] In our recent work, we showed that a solvent-assisted grafting synthetic method, involving the use of simple polar-protic solvents, can place organoamines in spatial isolation within

[a] Department of Chemistry, 111 College Place Syracuse University,
Syracuse, New York 13244, USA
[b] Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey
610 Taylor Road, Piscataway, New Jersey 08854, USA
Fax: +1-732-445-5312
E-mail: tasefa@rci.rutgers.edu
[c] Department of Chemical and Biochemical Engineering, Rutgers, The State University of New Jersey
98 Brett Road, Piscataway, New Jersey 08854, USA
Fax: +1-732-445-5312
[‡] Current Address: Department of Chemical Engineering, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139, USA
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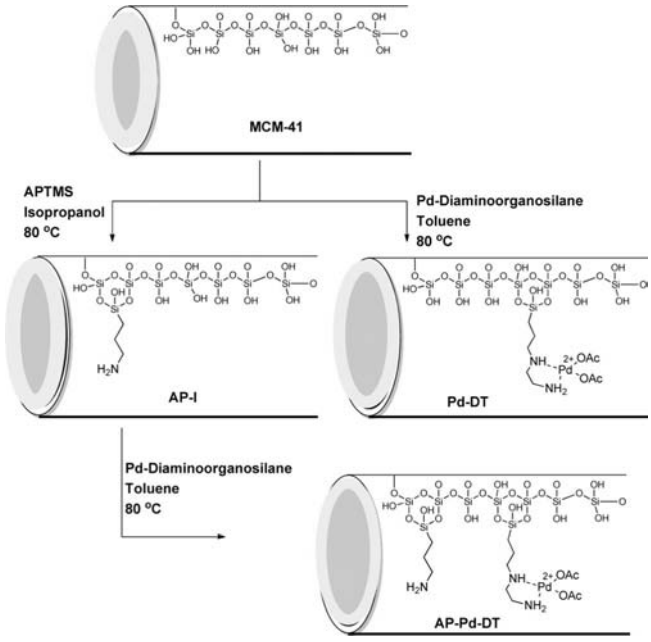
the pores of mesoporous silica material and can result in efficient catalytic activities in the Henry and aldol condensation reactions.[29–31] In fact, these materials superseded any previously reported mesoporous catalysts in terms of catalytic activity in the C–C bond coupling Henry and aldol condensation reactions.

The Henry and Sonogashira catalytic reactions follow two different reaction mechanisms. While the Sonogashira reaction is an oxidative coupling between an aryl halide and an alkyne, the amine-catalyzed Henry reaction takes place between benzaldehyde or substituted benzaldehydes and a nitroalkane (or a nucleophile) by an ion-pair or imine mechanism.[34] For the Sonogashira coupling reaction, palladium is the most widely used catalyst, whereas for the Henry reaction, organoamines are often employed. As mentioned above, numerous methods have been used to immobilize palladium as well as amine groups on solid supports including mesoporous silicas.[11–14,16,20,27] Most importantly and in relevance to the work here, these two reactions, that is, the Sonogashira and the Henry reactions, are sometimes carried out one after another in order to generate various pharmaceutically and industrially valuable compounds.[37–39] However, catalyzing both reactions in one pot without isolating their intermediate products and at the same time controlling the selectivity of the reactions towards a particular product needs considerable effort. Although a mixture of two different catalysts in the homogeneous phase can be used to catalyze the two reactions in one pot, this method is rather complex; specifically, it is accompanied by multiple products, involves costly separation methods, and results in the loss of expensive catalysts such as palladium complexes.[15] Recently a successful "domino" type halogen exchange (HALEX)-Sonogashira reaction was successfully demonstrated by Thathagar and Rothenberg.[40] To the best of our knowledge, however, the catalytic transformation of two of the most important C–C bond-forming reactions, the Sonogashira and the Henry reactions, in one pot with a single bifunctional heterogeneous catalyst has not been demonstrated previously.

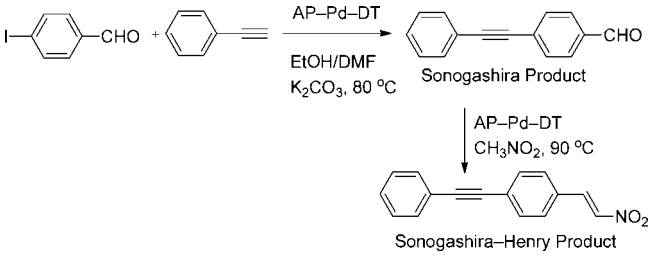
Here we report the synthesis of bifunctional mesoporous catalysts by immobilization of two catalytic groups, a Pd^{II}–diamine complex and a primary amine (-NH_2), onto mesoporous MCM-41 and SBA-15 silicas, and demonstrate their use as heterogeneous catalysts for the transformation of two-step Sonogashira and Henry reactions in one pot successfully without isolating the intermediate product.

Results and Discussion

The method for anchoring two catalytic groups, that is, a Pd^{II}–diamine complex and an amine (NH_2), onto the walls of mesoporous silicas (MCM-41 and SBA-15) in order to catalyze the Sonogashira and Henry reactions in tandem in a one-pot system is described in Scheme 1. The two active catalytic groups are conveniently placed next to one other without affecting the individual catalytic properties of each other. Furthermore, their catalytic activities in the two-step tandem reactions in one pot involving the Sonogashira and Henry reactions is demonstrated (Scheme 2).



Scheme 1. Schematic description of the synthesis of bifunctional amine/Pd^{II}–diamine catalyst (AP–Pd–DT) supported on mesoporous MCM-41 silica and the corresponding control catalyst containing only Pd^{II}–diamine catalyst (Pd–DT). In the synthesis of the materials, first 3-aminopropyltrimethoxysilane (APTS) in 2-propanol and then Pd^{II}–[*N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane] in toluene were grafted onto MCM-41, giving monofunctional catalysts AP-I and Pd–DT, respectively. AP-I was subsequently grafted with Pd^{II}–[*N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane] complex in toluene to afford the bifunctional catalyst AP–Pd–DT.



Scheme 2. The two-step-in-one-pot Sonogashira and Henry reactions catalyzed by a bifunctional amine/Pd^{II}–diamine catalyst, AP–Pd–DT.

To synthesize the bifunctional catalyst, AP–Pd–DT, first, primary amine groups were immobilized onto mesoporous silica (MCM-41) by using 2-propanol as the solvent. This produced primary-amine-functionalized mesoporous silica (AP-I). 2-Propanol was chosen here as the solvent to graft the primary amine groups onto mesoporous silica, because, according to our previous studies,[29,30] 2-propanol produces site-isolated organoamine catalytic groups, which are more efficient catalysts in the Henry reaction. Furthermore and most importantly, the grafting of mesoporous silica with organic groups in 2-propanol leaves the mesoporous

silica with ample amount of "ungrafted" surface, onto which secondary functional groups or catalytic sites can be anchored.[29,30] In the second step, the Pd^{II}–diaminoorganosilane complex was grafted on the leftover space on AP-I by using toluene as the solvent (Scheme 1). Toluene was used as a solvent in the second step in order to help the second organosilane graft well enough within the remaining relatively smaller leftover space on the mesoporous channel walls of AP-I. Unlike 2-propanol, toluene strongly favors the grafting of organosilanes onto mesoporous silica,[29,30] and this leads to enough density of the secondary functional group (in this case, the Pd^{II}–diamine complexes) even in the smaller available space.

This sequential grafting of the two different organosilanes by using two different solvents resulted in an optimum bifunctional mesoporous silica catalyst containing two different catalytic sites, that is, the primary amine (NH_2) and the Pd^{II}–diamine complex. Consequently, the catalyst was expected to catalyze the Sonogashira and the Henry reactions individually as well as in tandem in one pot.

Nitrogen gas adsorption/desorption measurements were used to characterize the mesoporous structure, the surface areas, pore diameters, and pore volumes of the materials, before and after each step of organosilane functionalization during catalyst synthesis. Figures 1 and 2 show the nitrogen gas adsorption isotherms and pore size distributions, respectively, of the parent material (MCM-41), the amine grafted sample (AP-I), the Pd^{II}–diamine-functionalized material (Pd–DT), and the bifunctional amine/Pd^{II}–diamine mesoporous catalyst (AP–Pd–DT). As expected, the mesoporous structures and other physical attributes of the materials such as surface areas, pore sizes, and mesopore volumes decreased slightly as more and more organosilanes were grafted within the pores of the mesoporous silica. The Brunauer–Emmett–Teller (BET) surface area, pore volume, and Barrett–Joyner–Halenda (BJH) pore diameter of MCM-41 were found to be 1161 m^2/g, 0.74 cm^3/g, and 24.2 Å, respectively. However, these values decreased successively as 3-aminopropyl groups and/or Pd^{II}–diamine complexes were placed within the mesopores. For instance, the BET surface area, pore volume, and BJH pore diameter of AP-I were 1065 m^2/g, 0.45 cm^3/g, and 21.9 Å, respectively. The BET surface area, pore volume, and BJH pore diameter of the amine/Pd^{II}–diamine functionalized sample (AP–Pd–DT) were even significantly lower with values of 509 m^2/g, 0.17 cm^3/g, and 21.7 Å, respectively. These results indicate that the latter samples have reduced BET surface area, pore volume, and BJH pore diameter with respect to the parent mesoporous material (MCM-41), owing to the presence of more grafted organic and organometallic groups in its mesopores.

The mesoporous structure in the catalysts was further confirmed by transmission electron microscopy (TEM). Representative TEM images of the bifunctional catalyst AP–Pd–DT, showing highly ordered mesoporous structure, are presented in Figure 3.

The thermogravimetric traces (Figure 4) showed a weight loss below 100 °C for all the samples due to the loss of water adsorbed on the materials. The weight loss from AP-I in the range 175 °C to 600 °C was due to the loss of 3-aminopropyl groups, residual surfactants, and some surface

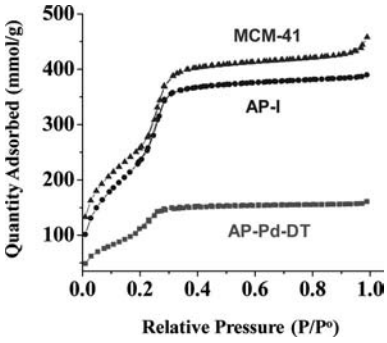


Figure 1. Nitrogen gas adsorption isotherms for MCM-41, AP-I, and AP–Pd–DT.

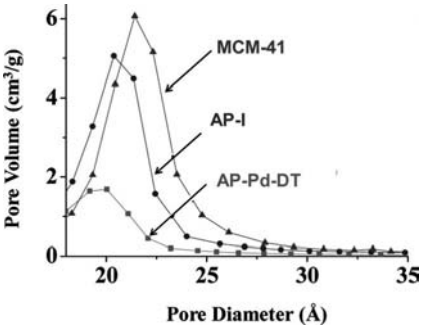


Figure 2. Pore-size distribution for MCM-41, AP-I, and AP–Pd–DT.

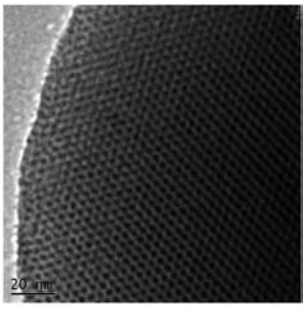


Figure 3. Transmission electron microscope (TEM) image of AP–Pd–DT. Scale bar: 20 nm.

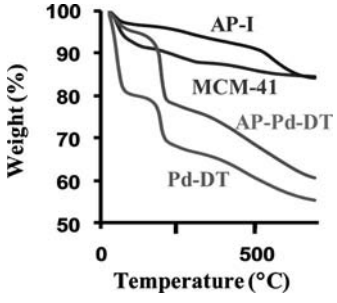


Figure 4. Thermogravimetric traces of MCM-41, AP-I, Pd–DT, and AP–Pd–DT.

silanol groups. In AP–Pd–DT and Pd–DT samples, significant weight losses in the range 175 °C to 210 °C and in the range 250 °C to 600 °C were observed. The first weight loss was most likely due to the loss of the acetate/water ligands anchored on the Pd^{II} ions, and the second was probably due to the loss of organodiamine (and propylamine) groups. The exact amount of aminopropyl groups and palladium in the materials was determined by elemental analyses. Elemental analysis of AP-I gave C 8.43, H 2.99, and N 2.57%. Pd–DT was found to contain C 15.13, H 4.31, N 4.78%, while AP–Pd–DT was found to possess C 19.86, H 3.99, N 6.06%. ICP-AES analysis of AP–Pd–DT gave Pd 16.7%, which confirmed the presence of palladium in the bifunctional catalyst (AP–Pd–DT); the amount of palladium was calculated to be 1.6 mmol Pd/g sample.

Performing the Sonogashira and Henry reactions together in a one-pot system can be a fairly complicated process. The Sonogashira reaction requires a homogeneous base such as K_2CO_3 for abstracting alkyne protons of the phenylacetylene reactant and to make the reaction go to completion. However, homogeneous bases such as K_2CO_3 can also catalyze or participate in the base-catalyzed Henry reaction and give the nitroalcohol product. This means that K_2CO_3 could potentially interfere with any intended Sonogashira–Henry (dehydrated) tandem product.

Thus, as a control experiment, we conducted the Henry reaction between *p*-hydroxybenzaldehyde and nitromethane in the presence of K_2CO_3 (homogeneous catalyst). The reaction gave approximately 90% conversion of *p*-hydroxybenzaldehyde in 30 min; however, it predominantly yielded 1-(4-hydroxyphenyl)-2-nitroethanol (a nitroalcohol) as product. In addition to *p*-hydroxybenzaldehyde, the catalytic activity of K_2CO_3 on *p*-iodobenzaldehyde, that is, the reactant involved in the tandem reaction with its iodo and aldehyde groups, was investigated. This reaction also gave 1-(4-iodophenyl)-2-nitroethanol (also a nitroalcohol) as product with a low reactant conversion of 38% in 2 h. Thus, this possibility of nitroalcohol formation by K_2CO_3 could further complicate the outcome of the Sonogashira–Henry reaction if the two reactions were to be performed in tandem in a one-pot system in the presence of excess K_2CO_3, which is typically used in the Sonogashira reaction, and if the Sonogashira–Henry dehydrated product were the intended target. Besides giving the 1-(4-iodophenyl)-2-nitroethanol (nitroalcohol) product, K_2CO_3 catalyzes the Henry reaction more slowly[41] relative to our amine-functionalized-mesoporous-silica-catalyzed Henry reaction, which gives approximately 100% conversion into the nitrostyrene product in 15–20 min. This means that K_2CO_3 would potentially leave some unreacted the *p*-iodobenzaldehyde, which would further undergo the Sonogashira reaction to yield multiple unwanted products in the tandem reactions (see below).

Thus, to circumvent these problems associated with excess K_2CO_3 and to avoid the possibility of its participation as a homogeneous catalyst in the Henry reaction during the one-pot tandem Sonogashira–Henry reactions, the optimum or minimum amount of K_2CO_3 required to complete the Sonogashira reaction had to be determined from a series of experiments. Furthermore, since K_2CO_3 is "toxic" and may be hard to recover from the reaction, its use in the minimum possible amount in heterogeneous catalysis would have an added benefit. To the best of our knowledge, the optimum mol-% of K_2CO_3 needed to perform the Sonogashira reaction in reasonable time without leaving K_2CO_3 behind in the reaction mixture has not been reported before. All previous studies of Sonogashira reactions employed excess amounts of base or K_2CO_3, often much more than the stoichiometric ratios.[15,23,25]

Thus, a series of Sonogashira reactions using different mol ratios of K_2CO_3 with respect to 0.5 mmol phenylacetylene and 0.5 mmol iodobenzene were performed. Various mol ratios of K_2CO_3 with respect to one of the reactants, that is, phenylacetylene or *p*-iodobenzaldehyde, as both of them are limiting reactants, were used. This included K_2CO_3/phenylacetylene ratios of 2:1, 1.6:1, 1.4:1, and 1:1. Of these, the 1.6:1 of was found to be the optimum ratio for the Sonogashira reaction as it gave approximately 100% reactant conversion in a reasonably short time (about 3 h) in the presence of Pd–DT and AP–Pd–DT catalysts, and it barely left any more K_2CO_3 behind to possibly affect the successive Henry reaction. The 1:1 mol ratio of K_2CO_3 to phenylacetylene was found to be insufficient in order to convert all of the phenylacetylene reactant in the Sonogashira reaction in reasonable times of 3–5 h. In contrast, the 2:1 mol ratio was found to be slightly in excess, which means that, although it resulted in the completion of the Sonogashira reaction, it also gave the Henry reaction product, immediately after the addition of both nitromethane and *p*-hydroxybenzaldehyde into the reaction mixture. Since the 1.6:1 mol ratio of K_2CO_3/phenylacetylene was able to completely drive the Sonogashira reaction to completion in 3 h without catalyzing the Henry reaction upon addition of the nitromethane and *p*-hydroxybenzaldehyde afterwards, it was used as the optimum mol ratio in the subsequent studies of tandem reactions.

However, because the Henry reaction can be catalyzed by K_2CO_3, this reaction would still compete for the optimum K_2CO_3 available for the Sonogashira reaction. Thus, performing the two reactions in sequence in the one-pot system was necessary in order to obtain the intended tandem products in higher yield. Indeed, when the Henry reaction took place before the Sonogashira reaction, it deprived the Sonogashira reaction of the K_2CO_3 and led to lower yields in the tandem process (see Supporting Information). Furthermore, the Henry reaction with K_2CO_3 yielded predominantly the nitroaldol product and also left a significant amount of unreacted *p*-iodobenzaldehyde. An when combined with the Sonogashira reaction, the reaction mixture of the Henry reaction with K_2CO_3 further led to multiple types of Sonogashira–Henry tandem products and other side products (see Supporting Information). Attempts to obtain even a tandem Sonogashira–nitroalcohol product by using excess K_2CO_3, which is large enough to catalyze both the Henry and the Sonogashira reactions, also failed to give reasonable yields (Figures S1 and S2). However, these issues

were easily avoided by simply changing the order of addition of the reactants in the one-pot reaction. By performing the Sonogashira reaction to completion with the bifunctional AP–Pd–DT catalyst in the presence of the optimized amount of K_2CO_3, followed by the addition of nitromethane into the same reaction mixture, the formation of such multiple products was prevented, and the Sonogashira–Henry dehydrated tandem product was predominantly formed.

For the first part of the study, various reference monofunctional mesoporous catalysts, that is, AP-I and Pd–DT, were synthesized by using MCM-41 as a support material. The catalytic properties of these materials as well as MCM-41 were then tested and the results were used as reference for demonstrating the importance and the ability of our bifunctional mesoporous catalyst (AP–Pd–DT) to catalyze the two reactions efficiently in one pot (Table 1). The mesoporous silica (MCM-41), which lacks primary amines or palladium complexes, catalyzed neither the Sonogashira reaction nor the Henry reaction, as expected. The amine-grafted catalyst (AP-I) gave 90% yield in 15 min for the Henry reaction, which is in accordance with our previously reported results.[29,30] However, the AP-I catalyst did not catalyze the Sonogashira reaction, also as expected (Table 1). The catalytic activity of the Pd^{II}–diamine functionalized sample (Pd–DT) was then tested in both the Henry and the Sonogashira reactions individually. Pd–DT, which lacks free primary amine groups but has diamine groups that are complexed with Pd^{II}, failed to give any Henry reaction product up to 12 h. It, however, catalyzed the Sonogashira reaction efficiently, giving approximately 100% Sonogashira product in 2.5 h for the reaction between aryl halide and phenylacetylene. These results indicate that both the amine (AP-I) and the palladium–diamine grafted catalyst (Pd–DT) alone can catalyze the respective individual reactions efficiently, but not both.

Table 1. Relative catalytic efficiencies for the individual and tandem Sonogashira and Henry reactions in the presence of K_2CO_3 or various mesoporous catalysts synthesized from MCM-41 by grafting various organosilanes on it.[a]

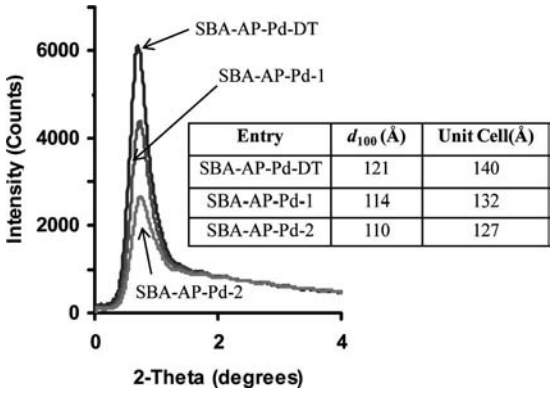
Catalyst	Reaction	Time	% Conversion[d]
MCM-41	Sonogashira[b]	24 h	ca. 0
	Henry[b]	24 h	ca. 0
API	Sonogashira[b]	24 h	ca. 0
	Henry[b]	15 min	95[d]
K_2CO_3	Sonogashira[b]	24 h	ca. 0
	Henry[b]	2 h	38[e]
Pd–DT	Sonogashira[b]	2.5 h	ca. 100
	Henry[b]	12 h	ca. 0
AP–Pd–DT	Sonogashira[b]	2.5 h	ca. 100
(*Bifunctional catalyst*)	Henry[b]	45 min	ca. 100[d]
	Sonogashira–Henry tandem[c]	**5 h**	***60***[f]

[a] The reactions were performed with 30 mg of catalyst. For the Sonogashira reaction, phenylacetylene (0.5 mmol), *p*-iodobenzene (0.5 mmol), and K_2CO_3 (0.8 mmol) were used. For the Henry reaction, *p*-substituted benzaldehyde (0.5 mmol) in CH_3NO_2 (5 mL) was used. The Sonogashira reaction was performed at 80 °C, while the Henry reaction was performed at 90 °C. In case of the Sonogashira–Henry tandem reaction, the Sonogashira reaction was performed at 80 °C until the reaction reached completion, and the temperature was then raised from 80 to 90 °C, before adding nitromethane. [b] When the reaction was performed individually. [c] The two reactions were performed in tandem in one pot. [d] This result reflects also the % yield of the *p*-iodo-β-nitrostyrene product. [e] This result reflects also the % yield of the nitroalcohol product. [f] The yield was lower than approximately 100.0%, because of the formation of some tandem Sonogashira–nitroaldol product (ca. 15%) and the loss of some of the *p*-iodobenzaldehyde reactant as benzaldehyde (ca. 25%).

Thus, the AP-I catalyst was prepared and further grafted with Pd^{II}–diamine complex in toluene yielding the bifunctional mesoporous catalyst, AP–Pd–DT, which contained both the primary amine and the Pd^{II}–diamine complex (Scheme 1). To demonstrate the catalytic activity of AP–Pd–DT in the tandem reactions, *p*-iodobenzaldehyde was purposely chosen as substrate, because it has both functional groups necessary to perform the Sonogashira and the Henry reactions in a one-pot system. AP–Pd–DT gave approximately 100% conversion for the Sonogashira reaction between *p*-iodobenzaldehyde and phenylacetylene in 2.5 h. After confirming the completion of the Sonogashira reaction (ca. 100 conversion of phenylacetylene) by GC and GC–MS, nitromethane was added into the reaction mixture. Nitromethane served both as a solvent and as a nucleophile for the Henry reaction. This reaction gave approximately 100% conversion of the *p*-substituted benzaldehyde, with a yield of 60% for the Sonogashira–Henry dehydrated tandem product (see Scheme 2). Thus, the bifunctional hybrid heterogeneous catalyst catalyzed not only the oxidative C–C coupling, or Sonogashira reaction, between *p*-iodobenzaldehyde and phenylacetylene but also the Henry reaction between the *p*-substituted benzaldehyde group and nitromethane to give *p*-substituted nitrostyrene. Furthermore, the catalyst transformed these two reactions in one pot, without isolation of the intermediate product.

To determine the effects of the pore size of the bifunctional mesoporous materials and the relative density of their catalytic groups, additional bifunctional catalysts were prepared. By using mesoporous SBA-15, which has higher pore diameter than MCM-41, as a support material, three more catalysts were synthesized for this investigation. The first sample was prepared by following the same procedure as that for the synthesis of AP–Pd–DT. The resulting material was labeled as SBA–AP–Pd–DT. The other two samples were prepared by following slightly different grafting sequences in order to produce materials with different structures (see Experimental Section for details of the syntheses). The second material was prepared by grafting the primary amine groups by using APTS in toluene instead of APTS in 2-propanol. (Please note that both AP–Pd–DT and SBA–AP–Pd–DT involved grafting of APTS in 2-propanol in the first step.) This was followed by grafting Pd^{II}–diaminosilane with toluene as a solvent. This generated a catalyst labeled as SBA–AP–Pd–1. The third catalyst, denoted as SBA–AP–Pd–2, was prepared from SBA-15 support by first grafting the Pd^{II}–diaminosilane in toluene, followed by the grafting of the primary amine in toluene. As shown below, these materials had slight differences in their structures/

composition as characterized by powder X-ray diffraction (XRD) (Figure 5), UV/Vis spectroscopy (Figure 6), X-ray photoemission spectroscopy (XPS) (Supporting Information), and thermogravimetric analysis (Figure 7).



Entry	d_{100} (Å)	Unit Cell(Å)
SBA-AP-Pd-DT	121	140
SBA-AP-Pd-1	114	132
SBA-AP-Pd-2	110	127

Figure 5. Powder X-ray diffraction (XRD) patterns of bifunctional catalysts SBA–AP–Pd–DT, SBA–AP–Pd–1, and SBA–AP–Pd–2. The inset contains the *d*-spacing and unit cell values of the materials.

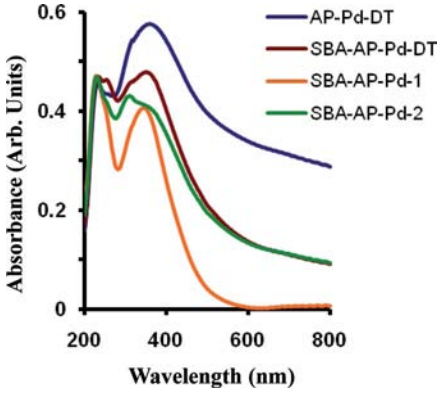


Figure 6. UV/Vis absorption spectra of SBA–AP–Pd–DT, SBA–AP–Pd–1, and SBA–AP–Pd–2 bifunctional catalysts. The spectrum for AP–Pd–DT (from MCM-41) is also included for comparison.

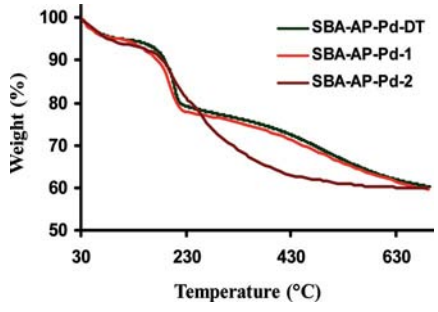


Figure 7. Thermogravimetric traces for bifunctional catalysts SBA–Pd–DT, SBA–AP–Pd–1, and SBA–AP–Pd–2.

The XRD patterns of these new catalysts (Figure 5) showed the typical (100) Bragg reflection of SBA-15-type materials, which is indicative of the presence of ordered mesostructures in the materials. The *d*-spacing values of the (100) Bragg reflection corresponded to 121, 114, and 110 Å for bifunctional catalysts SBA–AP–Pd–DT, SBA–AP–Pd–1, and SBA–AP–Pd–2, respectively.

These SBA-15-based bifunctional catalysts were further characterized by UV/Vis absorption spectroscopy (Figure 6). The UV/Vis spectrum of the bifunctional catalyst from MCM-41, that is, AP–Pd–DT, was included for comparison. All the samples showed strong absorption bands at approximately 350–370 nm and a second band at approximately 225 nm. These absorption bands can be assigned to typical metal–ligand charge transfer (MLCT) transitions in Pd^{II}–diamine complexes, which seem to exist in different forms as $Pd(N)_2(OAc)_2$ and $[Pd(N)_2(OH_2)(OAc)]OAc$, respectively, in our samples.[42,43] The presence of a slight difference in the intensity of the two bands in the MCM-41-based catalyst (AP–Pd–DT) relative to that of the bands in the three SBA-15-based bifunctional catalysts can also be observed.

In addition, the presence of the catalytic groups (Pd and amine) was characterized by X-ray photoemission spectroscopy (XPS). Representative XPS spectra are shown in the Supporting Information (Figures S3 and S4). The XPS of AP–Pd–DT shows a peak at 399.8 eV, which is the characteristic binding energy for N1s. Furthermore, the spectrum contains a strong peak at 532.1 eV and a weaker peak at 535.0 eV. The first peak corresponds to siloxane (Si–O–Si) oxygen atoms of SBA-15 in the sample, while the second peak corresponds to the oxygen atoms of residual silanol groups (Si–OH).[44,45] Furthermore, the spectrum has two peaks at 337.8 and 342.9 eV. These binding energies correspond to Pd $3d_{5/2}$ and $3d_{3/2}$, respectively, of Pd^{II} complexes having two N ligands and two O ligands. These peak assignments were consistent with those reported for other similar materials previously.[46,47] Similarly, the XPS spectrum of catalyst SBA–AP–Pd–DT showed a peak at 399.4 eV corresponding to N1s, and a peak at 531.7 eV and a shoulder at 534.7 eV, which correspond to O1s. In addition, the spectrum showed peaks at 337.4 and 342.8 eV corresponding to $3d_{5/2}$ and $3d_{3/2}$, respectively. No significant difference was observed between the XPS spectra of AP–Pd–DT and SBA–AP–Pd–DT.

The TGA traces for SBA–AP–Pd–DT, SBA–AP–Pd–1, and SBA–AP–Pd–2 are shown in Figure 7. The results showed a loss of approximately 5–6 wt.-% water in the temperature range 30 to approximately 100 °C in all the samples. Furthermore, a weight loss in the temperature range of approximately 175–220 °C was observed, which corresponds to acetate ions bound to Pd^{II}–diamine complex. An additional weight loss in the temperature range of approximately 240–630 °C, mainly associated with the loss of organoamine groups, is also exhibited. Interestingly, the TGA traces of the samples prepared by different grafting sequences, that is, SBA–AP–Pd–DT and SBA–AP–Pd–1 as opposed to SBA–AP–Pd–2, revealed slight differences in their weight loss patterns (Figure 7). The sample that was functionalized with the Pd^{II}–diaminosilane complex in the first grafting step (i.e. SBA–AP–Pd–2) showed a weight loss after approximately 240 °C, more quickly than the ones

grafted with Pd^{II}–diamine complex in the second grafting step (i.e. SBA–AP–Pd–DT and SBA–AP–Pd–1). This is possibly because of the fact that the Pd^{II}–diamine complexes can be grafted in more accessible locations in the mesoporous channels when they are grafted in the first grafting step than in the second. The Pd^{II}–diamine complexes in more accessible locations will in turn have a greater chance to come off or decompose at higher temperatures. On the other hand, the organosilanes grafted in the second step may end up in the microporous or corrugated leftover porous structures that SBA-15 type materials typically have,[48,49] making them decompose rather slowly.

The presence of the organoamine and palladium catalytic groups in the bifunctional catalysts was further corroborated by elemental analyses and ICP-AES, respectively (Table 2). Furthermore, the ICP-AES results indicated that the SBA-15-based bifunctional catalysts contained 1.1–1.3 mmol Pd/g of sample, which was slightly lower than the 1.6 mmol Pd/g obtained for AP–Pd–DT.

Table 2. Chemical compositions of SBA-15-based amine/Pd^{II}–diamine bifunctional mesoporous catalysts SBA–Pd–DT, SBA–AP–Pd–1, and SBA–AP–Pd–2.[a]

Sample	Wt.-% N (mmol/g)	Wt.-% Pd (mmol/g)
SBA–AP–Pd–DT	5.3 (3.8)	13.4 (1.3)
SBA–AP–Pd–1	5.4 (3.9)	11.7 (1.1)
SBA–AP–Pd–2	5.4 (3.9)	11.2 (1.1)

[a] The wt.-% N and wt.-% Pd were obtained by elemental and ICP-AES analysis, respectively.

The catalytic activities of the SBA-15-based bifunctional catalysts in the Sonogashira and Henry reactions individually and in tandem were then investigated in the same way as for the AP–Pd–DT catalyst. All the three SBA-15-based bifunctional catalysts, that is, SBA–AP–Pd–DT, SBA–AP–Pd–1, and SBA–AP–Pd–2, were found to catalyze the the Sonogashira reaction effectively, giving approximately 100% conversion in 2.5 h (Table 3). In addition, they were also found to catalyze the Sonogashira and Henry reactions in tandem, affording the tandem products in 5 h with slight differences. Catalysts SBA–AP–Pd–DT and SBA–AP–Pd–1 gave slightly higher yields of approximately 60%, whereas catalyst SBA–AP–Pd–2 gave a yield of approximately 52% in 3.5 h. Further analysis of this product revealed that 59% of it was the Sonogashira–Henry dehydrated tandem product, while the rest was the Sonogashira–nitroalcohol tandem product. It can also be concluded that the SBA-15-based bifunctional catalysts did not show significant differences in catalytic activity among each other as well as when compared with the MCM-41-based bifunctional catalysts.

In addition, leaching tests for palladium was performed by taking the reaction mixture and analyzing it by ICP-AES. The result indicated that there was less than 0.19 ppm Pd in the reaction mixture after 5 h of catalytic reaction. This suggests that the Pd^{II} was barely leached into the reaction mixture and that the Sonogashira reaction was essentially catalyzed by the bifunctional solid catalyst.

The bifunctional catalyst has enabled us to omit the separation of the intermediate of either the Henry or the Sonogashira product from the reaction mixture and thus avoid unnecessary use of solvents and other chemical reagents to isolate the intermediate product. Thus, the use of the bifunctional catalyst can potentially cut the cost of preparation of the tandem product. Furthermore, unlike in many other studies in which K_2CO_3 was used in excess, here the optimum amount of K_2CO_3 was determined for the first time and employed without compromising the results and without leaving residual K_2CO_3 in the reaction mixture at the end of the reaction. In addition, the bifunctional catalyst was proven to catalyze the Sonogashira reaction without the presence of any toxic or expensive phosphane ligands or copper co-catalysts that are commonly used in Sonogashira reactions.[15,23,25]

Table 3. Relative catalytic efficiencies for the individual and tandem Sonogashira and Henry reactions in the presence of K_2CO_3 or various mesoporous catalysts synthesized from SBA-15 by grafting various organosilanes on it under different conditions (see Experimental Section for details).[a]

Catalyst	Reaction	Time	% Conversion[d]
SBA–AP–Pd–DT	Sonogashira[b]	3 h	ca. 100
	Henry[b]	2 h	ca. 100[d]
	Tandem[c]	3.5 h	ca. 59.6[e]
SBA–AP–Pd–1	Sonogashira[b]	3 h	ca. 100
	Henry[b]	2 h	ca. 100[d]
	Tandem[c]	3.5 h	ca. 58.2[e]
SBA–AP–Pd–2	Sonogashira[b]	3 h	ca. 100
	Henry[b]	2 h	ca. 100[d]
	Tandem[c]	3.5 h	ca. 52.1[e]

[a] The reactions were performed with 30 mg of catalyst. For the Sonogashira reaction, phenylacetylene (0.5 mmol), *p*-iodobenzene (0.5 mmol), and K_2CO_3 (0.8 mmol) were used. For the Henry reaction, *p*-substituted benzaldehyde (0.5 mmol) in CH_3NO_2 (5 mL) was used. The Sonogashira reaction was performed at 80 °C, while the Henry reaction was performed at 90 °C. In case of the Sonogashira–Henry tandem reaction, the Sonogashira reaction was performed at 80 °C until the reaction reached completion, and the temperature was then raised from 80 to 90 °C, before the addition of nitromethane. [b] When the reaction was performed individually. [c] The two reactions were performed in tandem in one pot. [d] This result reflects also the % yield of the *p*-iodo-β-nitrostyrene product. [e] This result reflects also the % yield of the nitroalcohol product. The yield was lower than approximately 100.0%, because of the formation of some tandem Sonogashira–nitroaldol product (ca. 15%) and the loss of some of the iodobenzene reactant as benzaldehyde (ca. 25%).

Conclusions

We have synthesized, by using a solvent-assisted post-grafting method, a bifunctional organic–inorganic hybrid mesoporous catalyst containing two different catalytic sites, that is, a Pd^{II}–diamine complex and a primary amine, next to each other within the channels of mesoporous silica. The bifunctional catalyst and the two catalytic groups are proven to be active catalysts for catalyzing two different C–C bond-forming reactions, that is, the Sonogashira and Henry reactions, in one pot. This is the first time that these two widely used C–C bond-forming chemical reactions were performed in tandem in one pot by using a single bi-

functional catalyst and without separating or purifying the intermediate products. The bifunctional catalyst gave 60% yield for the Sonogashira–Henry tandem product in 5 h by the two-step tandem reaction in one pot. The bifunctional catalyst also catalyzed both reactions, individually resulting in approximately 100% reactant conversion in 2.5 h in the Sonogashira reaction and approximately 100% reactant conversion in 45 min in the Henry reaction. Furthermore, the optimized or minimum amount of K_2CO_3 required to catalyze the Sonogashira reaction effectively without compromising the Henry reaction during the tandem reaction in the one-pot system was determined and utilized. The development of such bifunctional catalysts for tandem reactions would have implications such as reducing the cost of purification and separation of intermediate products in multi-step synthesis. Furthermore, soluble toxic copper compounds and phosphane-based ligands, which are typically used in the Sonogashira reaction, were not required here to successfully perform the two-step, one-pot tandem reaction.

Experimental Section

Materials: All materials and reagents were purchased and used as received. Toluene, ethanol, 2-propanol, dichloromethane, and *N*,*N*-dimethylformamide (DMF) were obtained from Fischer Scientific. Pd^{II} acetate, 4-hydroxybenzaldehyde, phenylacetylene, *p*-iodobenzaldehyde, K_2CO_3, tetraethyl orthosilicate (TEOS), and nitromethane were purchased from Sigma–Aldrich. 3-Aminopropyltrimethoxysilane (APTS) and *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AAPT) were obtained from Gelest, Inc. Poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) block copolymer (Pluronic® 123, average molecular mass ca. 5800) was obtained from BASF.

Synthesis of MCM-41 and Amine-Functionalized MCM-41 (AP-I): Mesoporous silica (MCM-41) was synthesized by the method reported previously.[29,30] Then, MCM-41 (500 mg) was grafted with APTS (3.68 mmol) in 2-propanol (250 mL) to give spatially isolated primary amine groups tethered on its mesoporous channel walls. This sample or catalyst was labeled as AP-I.[29,30]

Synthesis of Palladium–Diamine-Immobilized MCM-41 (Pd–DT): MCM-41 was grafted with Pd^{II}–diaminopropyltriethoxysilane complex in toluene. The Pd^{II}–diaminopropyltriethoxysilane was prepared in toluene by mixing a 1:1 mol ratio of Pd^{II} acetate (0.819 mmol) and [*N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane] (0.819 mmol) in toluene (5 mL) and stirring the solution for 2 h at room temperature. The Pd^{II}–aminoorganosilane solution was mixed with additional toluene (195 mL). The resultuing 200 mL of Pd^{II}–aminoorganosilane solution in toluene was then added into a round-bottomed flask containing MCM-41 (200 mg). The mixture was stirred at 80 °C for 5 h. The solution was filtered, and the solid material that contained the Pd^{II}–diamine complex was washed multiple times with ethanol and dried in an oven at 60 °C for 4 h. The resulting sample was labeled as Pd–DT.

Synthesis of Amine and Palladium–Diamine Complex (AP–Pd–DT) Containing Bifunctional Catalyst: Here AP-I was grafted with the Pd^{II}–diaminopropyltriethoxysilane prepared as described above. Briefly, AP-I (200 mg) was stirred with the Pd^{II}–diaminopropyltriethoxysilane solution in toluene (200 mL) at 80 °C for 5 h. The solution was filtered, and the solid product was washed with ethanol multiple times and dried in an oven at 60 °C for 4 h. The resulting material was labeled as bifunctional catalyst AP–PD–DT.

Synthesis of SBA-15 and Different SBA-15-Based Amine/Pd^{II} Bifunctional Catalysts

To determine the effect of pore size of the mesoporous materials, additional catalysts were prepared by using mesoporous SBA-15 parent material as support for the two catalytic sites. In addition, the effect of the relative density of the catalytic groups in the materials was investigated by varying the relative density of the catalytic groups through the synthesis.

SBA-15 mesoporous silica (SBA-15) was synthesized by the method reported previously.[31] Three different catalysts were prepared from SBA-15. The first sample was prepared in the same way as AP–Pd–DT above by grafting APTS (3.68 mml) in 2-propanol (250 mL) onto SBA-15 (500 mg) for 6 h at 80 °C to produce spatially isolated primary amine groups on the mesoporous channel walls of SBA-15. This sample or catalyst was labeled as SBA–AP–I. SBA–AP–I was then grafted with Pd^{II}–diaminopropyltriethoxysilane prepared as described above. Briefly, SBA–AP–I (200 mg) was stirred with the Pd^{II}–diaminopropyltriethoxysilane solution in toluene (200 mL) at 80 °C for 5 h. The solution was filtered, and the solid product was washed with ethanol multiple times and dried in an oven at 60 °C for 4 h. The resulting material was labeled as bifunctional catalyst SBA–AP–Pd–DT.

A second sample was prepared by grafting APTS (3.68 mmol) in anhydrous toluene (250 mL) onto SBA-15 (500 mg) for 6 h to produce more densely populated primary amine groups on the mesoporous channel walls of SBA-15 or a sample denoted as SBA–AP–T. This sample was then grafted with Pd^{II}–diaminopropyltriethoxysilane prepared as described above. Briefly, SBA–AP–T sample (200 mg) was stirred with the Pd^{II}–diaminopropyltriethoxysilane solution in toluene (200 mL) at 80 °C for 5 h. The solution was filtered, and the solid product was washed with ethanol multiple times and dried in an oven at 60 °C for 4 h. The resulting material was expected to contain less Pd^{II} and more primary amine groups and is labeled as bifunctional catalyst SBA–AP–Pd–1.

The third and final SBA-15-based catalyst was prepared by grafting Pd^{II}–diaminopropyltriethoxysilane solution in toluene (200 mL) on SBA-15 (200 mg) at 80 °C for 5 h. Then, APTS (3.68 mmol) in anhydrous toluene (250 mL) was grafted on the resulting material at 80 °C for 5 h. The solution was filtered, and the solid product was washed with ethanol multiple times and dried in an oven at 60 °C for 4 h. The resulting material was expected to contain more Pd^{II} and less primary amine groups and is labeled as bifunctional catalyst SBA–AP–Pd–2.

The Henry and Sonogashira Reactions Individually Performed: The Henry reaction was performed by using AP-I, Pd–DT, and AP–Pd–DT under the same conditions as reported before.[29,30] The progress of the reaction was monitored with TLC and ^1H NMR spectroscopy. For the Sonogashira reaction, iodobenzene (0.5 mmol) and phenylacetylene (0.5 mmol) were added into a 100 mL round-bottomed flask containing the catalyst (30 mg), K_2CO_3/phenylacetylene (1.6:1 mol ratio), and a mixture of ethanol/DMF (4:2 v/v) solvent. The mixture was stirred at 80 °C, and the progress of the reaction was monitored by GC and GC–MS.

The Tandem Sonogashira–Henry Reactions in One Pot: For the tandem Sonogashira and Henry reactions, phenylacetylene (0.5 mmol) and *p*-iodobenzaldehyde (0.5 mmol) were added into a solution containing ethanol/DMF (4:2 v/v), K_2CO_3/phenylacetylene (1.6:1 mol ratio), and AP–Pd–DT catalyst (30 mg). The solution was stirred at 80 °C while the reaction product was continually

monitored by GC and GC–MS. After confirmation of the completion of the Sonogashira reaction in about 2.5 h, the temperature of the reaction mixture was increased to 90 °C, and nitromethane (5 mL) was immediately added into the reaction mixture. The solution was further stirred while the Sonogashira product was consumed by the Henry reaction. The progress of this reaction was also monitored by GC, GC–MS, and TLC.

Supporting Information (see footnote on the first page of this article): Further experimental results, XPS and GC–MS spectra.

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