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Unsupported nanoporous gold catalyst for highly selective hydroamination of alkynes[†]

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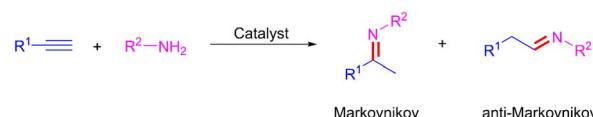
An efficient and highly selective heterogeneous catalyst system for hydroamination of alkynes was developed using unsupported gold nanopores (AuNPore) for the first time. The AuNPore-catalyzed highly regioselective hydroamination of alkynes proceeded smoothly without any additive and solvent under mild conditions (rt-50 °C) to yield Markovnikov imines in satisfactory to excellent yields. No gold leached from AuNPore during the hydroamination of alkynes. Moreover, the catalyst was easily recovered and reused without any loss of catalytic activity. A one-pot, two-step procedure using a single AuNPore catalyst has been devised to produce secondary amines derived from readily available alkynes and anilines with high atom efficiency.

Introduction

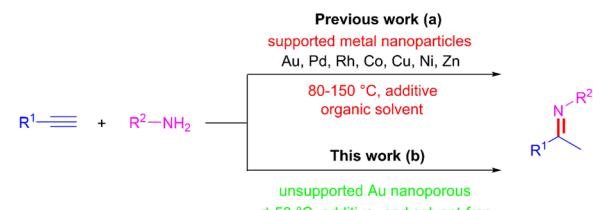
Nitrogen-based functionalities such as imines, enamines, and amines are ubiquitous structural motifs in biologically active molecules, fine chemicals, pharmaceuticals, or the agriculture industry.¹ Over the past decades, many methods such as reductive amination of the carbonyl compounds,² C–N cross-coupling,³ aminomercuration/demercuration of alkynes,⁴ and hydroamination of alkynes⁵ have emerged for their construction. Among these methods, the hydroamination of alkynes is the most convenient and promising synthetic route because of its 100% atom economy and easy access of the raw materials. However, the electronic repulsion between the electron-rich functional groups involved, namely the nitrogen lone pair and the π system of alkyne, as well as the regioselectivity towards the Markovnikov and anti-Markovnikov products, make this reaction challenging (Scheme 1).⁶ Therefore, many types of homogeneous⁷ and heterogeneous⁸ catalyst systems have been developed for the hydroamination of alkynes. Taking into consideration of the pharmaceutical process and potential industrial application, the use of recoverable and reusable

heterogeneous catalysts with a high catalytic activity for the hydroamination of alkynes would be more desirable. However, these catalysts still have the following considerable drawbacks: (i) high reaction temperatures (80–150 °C) and additives were required, (ii) organic solvent as reaction medium, (iii) poor yield and regioselectivity, (iv) metal nanoparticles needed specific carriers to prevent aggregation-induced catalytic deactivation, (v) leaching of metal, (vi) additional apparatus (microwave and light sources) may be indispensable (Scheme 2a). From the perspective of green chemistry and other practical concerns, the development of more environmentally benign and efficient catalyst systems, without any additive and solvent, under much milder conditions, for the hydroamination of alkynes is highly desirable.

In recent years, unsupported nanoporous metal material has attracted much attention because of their unique three-



Scheme 1 Possible imine products from hydroamination of terminal alkynes.



Scheme 2 Synthesis of Markovnikov imines.

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dimensional nanoporous structure, large surface-to-volume ratio, nontoxic nature, high recyclability, and simple recovery.⁹ Moreover, the bulk metallic feature of nanoporous metals could prevent the aggregation-induced catalytic deactivation and nanoporous metals without any supports may help to understand the intrinsic catalytic activity more easily by elimination of the support-effect.¹⁰ We have demonstrated that nanoporous metals are promising green heterogeneous catalysts for liquid-phase organic synthesis.¹¹ In the current study, we attempted the hydroamination of alkynes using unsupported gold nanopores (AuNPore) as the catalyst, which can be fabricated easily by selective leaching of Ag from an alloy foil of $\text{Au}_{30}\text{Ag}_{70}$ at chemical dealloying conditions. The highly regioselective hydroamination of alkynes proceeded smoothly under relatively low temperatures (rt-50 °C) to provide Markovnikov imines in good to excellent yields without any additive and solvent (Scheme 2b). Furthermore, a one-pot, two-step procedure using AuNPore catalyst has been devised to produce secondary amines derived from alkynes and anilines with high atom efficiency. The results are reported in the current work.

Experimental

Materials

Au (99.99%) and Ag (99.99%) were purchased from Tanaka Kikinzoku Hanbai K. K. and Mitsuwa's Pure Chemicals, respectively. Au/TiO₂ (1% wt/wt loading; average size of AuNPs is around 2–3 nm) were purchased from Strem. The starting materials were purchased from Energy Chemicals Co., Ltd. Solvents were purified by standard techniques without special instructions. All other reagents were used as received.

Catalyst preparation

The unsupported nanoporous gold (AuNPore) catalyst was prepared according to a method described previously.¹² Au (99.99%) and Ag (99.99%) were melted with electric arc-melting furnace under argon atmosphere to form Au/Ag alloy (30 : 70, in at%), which was rolled down to thickness of 0.04 mm. The resulting foil was annealed at 850 °C for 20 h. The foil was cut into small pieces (5 × 2 mm square). Treatment of the resulting chips (67.1 mg) with 70 wt% nitric acid (7.5 mL) for 18 h at room temperature in a shaking apparatus resulted in the formation of the nanoporous structure by selective leaching of silver. The material was washed with a saturated aqueous solution of NaHCO₃, pure water, and acetone, successively. Drying of the material under reduced pressure gave the nanoporous gold (Fig. S1†).

Catalyst characterization

SEM observation was carried out using HITACHI FE-SEM S4300 operated at an accelerating voltage of 10 kV. TEM was performed on a Tecnai G2 microscope operating at 120 kV. EDX analysis was carried out using EDAX Genesis with HITACHI FE-SEM S4300 operated at an accelerating voltage of 20 kV. The XPS measurements were carried out using an ESCALAB 250Xi spectrometer (Thermo Fisher Scientific Inc., UK) employing

monochromatic AlK α X-ray radiation. ICP-MS analysis was performed with Agilent ICP-MS HP 4500.

Typical procedure for hydroamination of phenylacetylenes

AuNPore (4.92 mg, 5 mol%), phenylacetylene (**1a**, 51.07 mg, 0.5 mmol), and phenylamine (**2a**, 55.55 mg, 0.6 mmol) were placed in a V-shaped vial reactor with a magnetic stir bar under N₂ atmosphere. The reaction mixture was stirred at 50 °C for 24 h and cooled down to room temperature. Then, the AuNPore was recovered by filtration, followed by washing with acetone, and the residual was purified *via* silica gel chromatography (eluent: petroleum ether/ethyl acetate = 5/1 with 10% of triethylamine) to afford imine (**3a**) as a yellow oil.

Results and discussion

Characterization of AuNPore catalyst

The scanning electron micrograph (SEM) in Fig. 1a clearly indicate the formation of three-dimensional (3D) nano-architecture constructed by hyperboloid-like ligaments. The ligament and nanopore channel were formed uniformly across the entire AuNPore with an average ligament size around 30 nm. The dealloyed material was found to comprise $\text{Au}_{>99}\text{Ag}_{<1}$ based on energy dispersive X-ray spectroscopy (EDX) analysis (Fig. 1b). The transmission electron micrograph (TEM) showed the structure of the AuNPore with bright nanopores and dark-contrast ligaments (Fig. 1c). Further, the high-resolution TEM (HRTEM) of freshly prepared AuNPore demonstrated that the topmost surface of these ligaments is not smooth but various steps and kinks are found representing low coordinated gold atoms as shown in Fig. 1d. The high density of low coordinated gold atoms on surface are proposed to be catalytically active sites in this catalyst. The lattice spacing was 0.235 nm corresponding to the (111) crystal plane of the AuNPore. The Au 4f 7/2

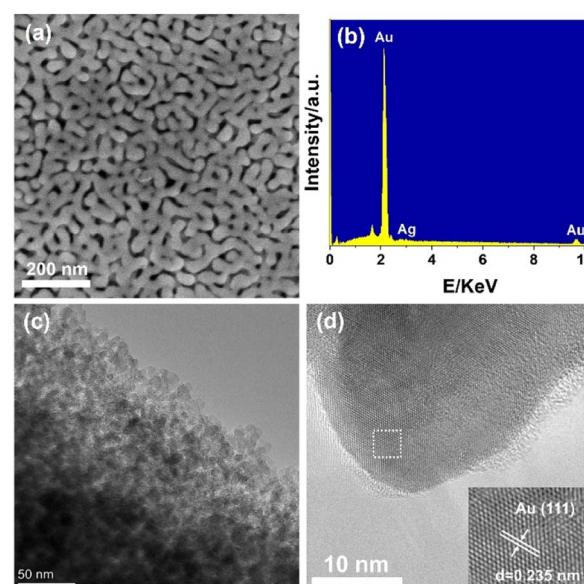


Fig. 1 (a) SEM image, (b) EDS analysis, (c) TEM image, (d) HRTEM image (inset: close-up views of the boxed regions) of fresh AuNPore.



peak was observed at 84.0 eV from the Au 4f X-ray photoelectron spectroscopy (XPS) measurements. This observation indicated that the oxidation state of Au in the AuNPore was Au(0) (Fig. S2†).¹³

Hydroamination of phenylacetylene catalyzed by AuNPore

The hydroamination of phenylacetylene (**1a**) in the presence of AuNPore (5 mol%) was chosen as a model in our preliminary studies to optimize the reaction conditions. The results are shown in Table 1. Toluene, ethanol (EtOH), water (H₂O), acetonitrile (CH₃CN), and tetrahydrofuran (THF) were initially tested at 50 °C for 24 h. Good conversion of **1a** and high yield of **3a** were observed (entries 1–5). Trace amounts of acetophenone (**4a**) were also obtained, probably due to hydrolysis of the imine **3a**. Notably, the best results were obtained without solvent, leading to 99% conversion of **1a** and 97% yield of Markovnikov product **3a** (entry 6). The conversion and yield decreased with decreases in both the catalyst amount and the temperature (entries 7 and 8, respectively). The conversion and yield also decreased with relatively short reaction time (entry 9). No reaction was observed in the absence of catalyst AuNPore or by using the precursor of AuNPore, Au₃₀Ag₇₀ alloy, in the hydroamination of **1a** (entries 10 and 11). The homogeneous AuCl also did not exhibit any catalytic activity (entry 12). Accordingly, we set the standard conditions as follows: AuNPore (5 mol%) and 50 °C for 24 h. Low conversion and yield were observed

Table 1 Screening of reaction conditions^a

| Entry | Solvent | Conversion ^b (%) | Yield ^b (%) | |
|-----------------|--------------------|-----------------------------|------------------------|----|
| | | | 3a | 4a |
| 1 | Toluene | 67 | 64 | 3 |
| 2 | EtOH | 87 | 85 | 2 |
| 3 | H ₂ O | 96 | 92 | 4 |
| 4 | CH ₃ CN | 82 | 80 | 2 |
| 5 | THF | 57 | 56 | 1 |
| 6 | — | 99 | 97(94) | 2 |
| 7 ^c | — | 83 | 82 | 1 |
| 8 ^d | — | 83 | 81 | 2 |
| 9 ^e | — | 87 | 86 | 1 |
| 10 ^f | — | NR ^j | — | — |
| 11 ^g | — | NR ^j | — | — |
| 12 ^h | — | NR ^j | — | — |
| 13 ⁱ | — | 63 | 61 | 2 |

^a Reaction conditions: phenylacetylene (**1a**, 0.5 mmol), phenylamine (**2a**, 0.6 mmol), AuNPore (5 mol%), and solvent (2 mL) at 50 °C for 24 h. ^b Determined by ¹H NMR and GC-MS analysis; the value in parenthesis indicates isolated yield. ^c 3.0 mol% of AuNPore was used.

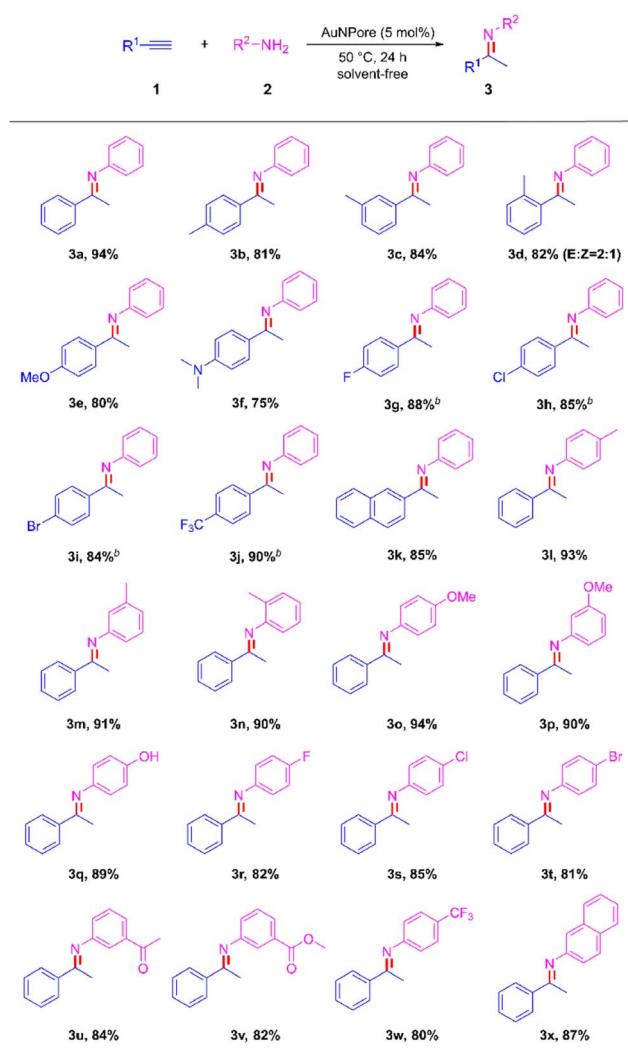
^d The hydroamination reaction was conducted at room temperature.

^e The reaction mixture was treated for 20 h. ^f The reaction was treated in the absence of AuNPore. ^g Au₃₀Ag₇₀ alloy was used. ^h AuCl was used. ⁱ Au/TiO₂ was used as the catalyst instead of AuNPore. ^j No reaction; starting material **1a** and **2a** were recovered.

when the Au/TiO₂ catalyst was used instead of the AuNPore catalyst (entry 13). This result clearly indicated that the activity of the AuNPore catalyst is higher than that of the commercially available catalyst. In all cases, the Markovnikov product was obtained exclusively. No isomeric anti-Markovnikov product could be detected by ¹H NMR analyses of the crude reaction mixtures.

Scope of the substrates

The catalytic activity of AuNPore was further examined with terminal alkynes and anilines under the aforementioned conditions (Scheme 3). The hydroamination of aromatic alkynes **1b–1f** bearing an electron-donating group such as methyl, methoxy or dimethylamino group proceeded smoothly to afford the corresponding imines **3b–3f** in good yields (75–84%). The sterically hindered *ortho*-substituted aryl alkynes **1d** exhibited high reactivity, which indicated that electron-donation in the *ortho*-position was tolerated well despite the



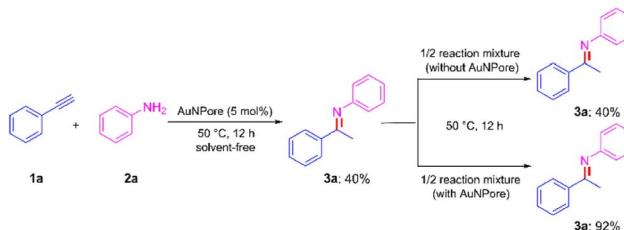
Scheme 3 AuNPore-catalyzed hydroamination of terminal alkynes and anilines^a. ^bReaction conditions: AuNPore (5 mol%), **1** (0.5 mmol), **2** (0.6 mmol), at 50 °C for 24 h. Isolated yield. ^cThe hydroamination reaction was conducted at room temperature.



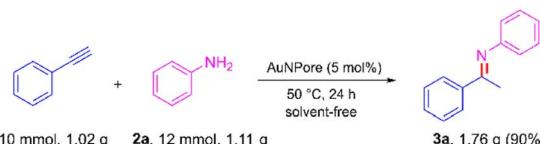
increased steric bulk. The product **3d** contained a 2 : 1 ratio of E : Z isomers. This behavior was attributed to the E/Z interconversion caused by the *ortho*-effect.¹⁴ The substrates **1g–1j** bearing an electron-withdrawing group fluoro (F), chloro (Cl), bromo (Br) or trifluoromethyl (CF₃) at the *para*-position exhibited higher reactivity than the substrates bearing an electron-donating group in the hydroamination reaction. The products **3g–3j** were obtained in high yields (88%, 85%, 84% and 90% respectively) at room temperature. The hydroamination of 2-naphthalene acetylene (**1k**) under the standard reaction conditions gave the corresponding imine **3k** in 85% yield. Subsequently, various anilines were tested with phenylacetylene under the standard set of reaction conditions. The hydroamination of the substrates **1l–1q** bearing an electron-donating group such as methyl, methoxy or hydroxy group proceeded smoothly to afford the corresponding imines **3l–3q** in high yields (89–94%). Similarly, the steric hindrance did not affect the catalytic performance as the bulky aniline (**1n**) bearing the methyl group at the *ortho*-position. Aniline substrates **1r–1w** bearing a strong electron-withdrawing group halogen (F, Cl, Br), acetyl (CH₃CO), methoxycarbonyl (CH₃OOC) or trifluoromethyl (CF₃) at the *para* or *meta* position, respectively, exhibited relatively low reactivity for completion of hydroamination compared with that of anilines **1l–1q**. The desired products **3r–3w** were obtained in 80–85% yields. The hydroamination of **1x** proceeded well under the standard reaction conditions to produce the corresponding imine **3x** in 87% yield. These results described above indicate that the reactivity of phenylacetylenes and anilines were influenced by the electronic property of substituents in substrates.

Leaching studies of AuNPore catalyst

We next examined the leaching test to clarify whether the AuNPore-catalyzed reaction proceeds heterogeneously or not (Scheme 4). The hydroamination of **1a** was performed under standard conditions for 12 h. At this stage, **3a** was formed in 40% yield. Then, half of the reaction mixture was transferred to another reaction vessel, and it was continuously stirred in the absence of a solid catalyst for 12 h. As we expected, no change in the yield of **2a** was observed. By contrast, **2a** was obtained in 92% yield from the reaction of residual containing the AuNPore catalyst. The inductively coupled plasma-mass spectrometry (ICP-MS) measurements were also used to confirm that no Au leached from the AuNPore catalyst (detection limit of 0.01 ppm).



Scheme 4 Leaching test of AuNPore catalyst in the hydroamination of **1a**.



Scheme 5 AuNPore-catalyzed gram-scale hydroamination of **1a**.

These results clearly indicated that the catalysis proceeded through a heterogeneous process.

Gram-scale reaction

To further explore the practical applicability of our method, the hydroamination of phenylacetylene was scaled up to the gram scale, and the result is shown in Scheme 5. When 1.02 g of **1a** and 1.11 g of **2a** were treated under standard conditions, 1.76 g of product **3a** was obtained with 90% yield. This result indicated that the gram-scale reactions also proceeded smoothly without loss of efficiency.

Reusability and recovery of AuNPore catalyst

Recycling tests of AuNPore catalyst were performed under the optimal conditions. The results are shown in Fig. 2. After each recycle, the AuNPore catalyst was simply washed with acetone for several times to remove the surface substances and then reused in the next run without further purification. After six recycles, high yield of **3a** was still obtained. The SEM image of AuNPore after six runs is shown in Fig. S3.† The result for the fresh one and that after six runs were essentially same, indicating that AuNPore catalyst is very stable and can be used repeatedly without loss of activity.

Catalytic synthesis of secondary amines through one-catalyst, one-pot, two-step process

To expand this reaction, we also investigated the reductive hydroamination reaction of alkynes with amines. In a typical reductive hydroamination reaction, the second reduction (hydrogenation) step is generally achieved by using either a separate catalyst system, such as ZnCl₂/NaBH₃CN,¹⁵ or a strong reducing agent, such as LiAlH₄.¹⁶ These procedures can

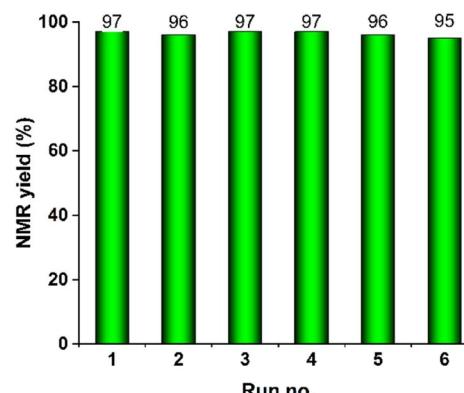
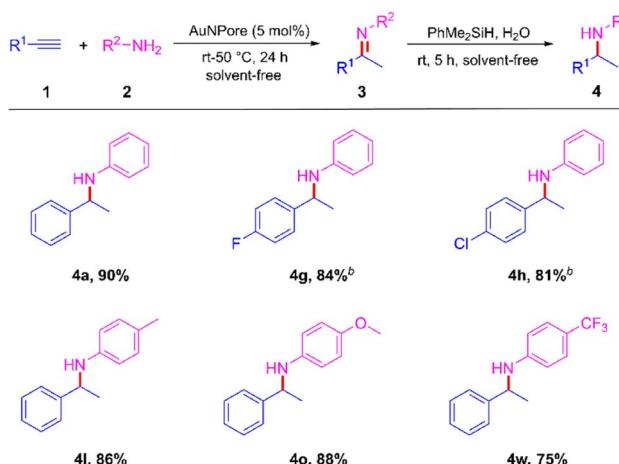


Fig. 2 Reusability of AuNPore for hydroamination of **1a**.

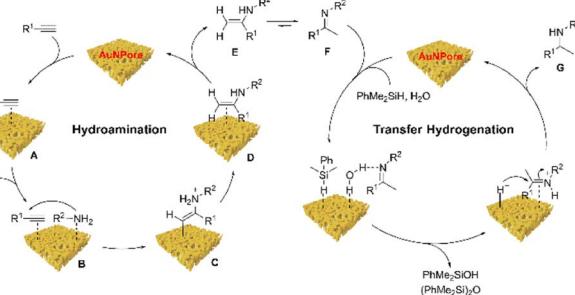




Scheme 6 AuNPore-catalyzed one-pot, two-step synthesis of secondary amine^a. ^aReactions were performed using AuNPore (5 mol%), 1 (0.5 mmol), 2 (0.6 mmol), at 50 °C for 24 h. Then, PhMe₂SiH (0.6 mmol) and H₂O (0.6 mmol) were added directly and the mixture continued to react at room temperature for 5 h. Isolated yield. ^bThe hydroamination reaction was conducted at room temperature.

create troublesome experimental procedures and require extra chemicals and solvents, and the strong reducing reagents can lead to a decrease in the chemoselectivity toward functional groups that are sensitive to reducing conditions. Therefore, the development of a one-pot method that uses a single catalyst for a reductive hydroamination reaction that occurs under mild reaction conditions would be highly worthwhile. During the investigation of the catalytic activity for the dissociation of various chemical bonds in the last decade, we have disclosed that the Si-H bond is readily activated by AuNPore, reacting with water to produce silanols and H₂,¹⁷ which was successfully extended to the selective reduction of unsaturated chemical bonds.¹⁸ Herein, considering the high product yield in hydroamination of alkynes as well as the fact that AuNPore catalyst can catalyze transfer hydrogenation of unsaturated chemical bonds with hydrosilanes as reductants, we envision a one-catalyst, one-pot, two-step process in which the initial imine formed in the hydroamination of alkynes is subsequently reduced to secondary amine. If the proposed process would take place with high efficiency and selectivity under mild conditions, it would be an interesting general catalytic process for the formation of secondary amines. The process is shown in Scheme 6. As anticipated based on the catalytic activity of AuNPore, we have been able to obtain different secondary amines **4** in one-catalyst, one-pot, two-step reactions without isolation of the imine intermediates **3** at room temperature under solvent-free conditions.

On the basis of our experimental outcomes, a plausible catalytic cycle is proposed to account for the present one-catalyst, one-pot, two-step reaction (Scheme 7). The initial step involves the generation of a AuNPore-activated alkyne intermediate **A**. The amine reagent coordinates to the electron-deficient intermediate **A**, forming intermediate **B**, which then undergoes a nucleophilic attack by the nitrogen of the amine resulting in the formation **C**. Intermediate **C** experiments



Scheme 7 Proposed mechanism for one-catalyst, one-pot, two-step synthesis of secondary amine.

a proton transfer to form a AuNPore-alkene species **D**, which releases the active AuNPore catalyst and the enamine **E**. After a tautomerization process, the imine product **F** is obtained. Then, PhMe₂SiH and H₂O were adsorbed onto the surface of the AuNPore catalyst. The hydrogen bond forms between imine **F** and water followed by the reaction of hydrosilane and water to give [AuNPore-H]⁻ and protonated imine species, in which the latter reacts subsequently with hydride on AuNPore to form the corresponding secondary amine **G** and regenerates the AuNPore catalyst.

Conclusions

In conclusion, we have demonstrated for the first time that the unsupported AuNPore is an efficient heterogeneous catalyst for the regioselective hydroamination of alkynes. Good to excellent yields of Markovnikov imines were obtained with excellent regioselectivities under low temperature without using any additive and solvent. The AuNPore catalyst could be easily recovered and reused several times without any loss of activity. Furthermore, the AuNPore is able to selectively catalyze the formation of secondary amines through a simple, one-catalyst, one-pot, two-step reaction that involves one hydroamination step followed by transfer hydrogenation. The unique features of the AuNPore catalyst system (no additive, no solvent, low temperature, high regioselectivity, good functional group tolerance, high stability, and no leaching) render this catalyst useful for laboratory and industrial applications.

Author contributions

Conceptualization, J. L., Y. L. and M. B.; methodology, Y. L.; analysis and validation, Y. W., Y. L. and H. L.; resources, J. L. and Y. L.; writing-original draft preparation, Y. L. and Y. W.; writing-review and editing, J. L., M. B. and Y. Y.; visualization, P. L. and X. F.; supervision, Y. L.; and funding acquisition, J. L., M. B. and Y. L. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

There are no conflicts to declare.



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