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Letter

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Sub-Nanometer Gold Clusters on Amino-Functionalized Silica: An Efficient Catalyst for the Synthesis of 1,3-Diynes by Oxidative Alkyne Coupling

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ABSTRACT: Sub-nanometer (d = 0.8 ± 0.2 nm) gold particles homogeneously dispersed on amino-functionalized silica catalyze Glaser-type alkyne coupling, providing corresponding 1,3-diynes under mild conditions. Readily available λ^3-iodane PhI(OAc)$_2$ is used as the oxidant and 1,10-phenanthroline as additive. Ten symmetrical 1,3-diynes and three products of heterocoupling containing various functionalities are isolated in high yields. The catalyst can be recycled at least five times giving consistently high isolated yields and maintaining the size and distribution of gold clusters. This unique combination of stable sub-nanometer gold clusters and hypervalent iodine thus paves a hitherto unexplored avenue in organic synthesis employing heterogeneous gold catalysis.

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alkyne coupling, gold, heterogeneous catalysis, hypervalent iodine, subnanometer

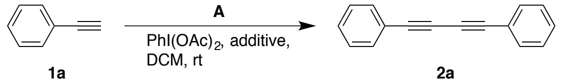
The chemistry of 1,3-diynes has been flourishing in the recent years[1] thanks to their growing importance as building blocks for the synthesis of pharmaceuticals,[2] optoelectronic materials,[3] and polymers.[4] Such compounds are usually prepared by Glaser-type oxidative coupling of the corresponding alkynes.[1a,1b,5] Frequently, the coupling is based on the use of Cu^{II} salts, typically Cu(OAc)$_2$ (Glaser-Eglinton coupling),[6] or CuI salts with ligands such as *N*,*N*,*N′*,*N′*-tetramethylethane-1,2-diamine (TMEDA) and oxygen (Glaser-Hay coupling).[7] Since heterogeneous catalysis is often preferred with regard to facile catalyst separation and recycling,[8] efficient heterogeneous catalysts, mainly based on Cu,[9] but also on Pd[9a] and Ni,[9a] have been developed for alkyne homocoupling. Typical drawbacks of such catalysts include their cumbersome or expensive preparation, high metal loadings, high amounts of base, and elevated reaction temperature. Notably, only some of these heterogeneous catalysts have been investigated in the coupling of two different alkynes (heterocoupling),[9b,h–j] which is still a challenging topic.[9a]

Interestingly, despite the profound interest in heterogeneous gold catalysis and its indisputable role in fine chemical synthesis,[10] Au-catalyzed alkyne coupling studies are scarce, with only a handful of homogeneously catalyzed examples reported.[11] In addition, 1,3-diynes have been observed as side-products in Sonogashira coupling catalyzed by Au/CeO$_2$[12] (Boronat et al. focused on the alkyne coupling itself[12c]) and Au/La$_2$O$_3$[13] (but not Au/SiO$_2$[14]) or in surface reactions performed under vacuum without isolating the products.[15] There is thus clearly room for the development of novel heterogeneous gold catalysts for alkyne coupling, which could overcome the drawbacks described above and provide the valuable unsymmetrical products of heterocoupling.

In early 2016, we disclosed a material featuring exceptionally small sub-nanometer (d = 0.8 ± 0.2 nm) gold particles supported on 3-aminopropyl-functionalized silicate SBA-15.[16] Literature comparison reveals that the particles are as small as Au$_{13}$[17] or even Au$_{11}$[17a,18] clusters. This material (further referred to as catalyst **A**) was soon found to be highly active and selective in dehydrogenation of formic acid[16] and transfer hydrogenation of various N-heterocyclic compounds.[19] Consequently, we wish to report here the use of the stable sub-nanometer gold particles of **A** in a practical and efficient method for oxidative alkyne coupling with good to excellent yields even for the heterocoupled products.

We started our investigations by mixing phenylacetylene (**1a**) with catalyst **A** in reagent-grade dichloromethane (DCM) – no reactivity was detected during 18 h at ambient temperature (Table 1, entry 1). Adding hypervalent iodine-based oxidant PhI(OAc)$_2$[11b,c,20] to the reaction mixture did not promote

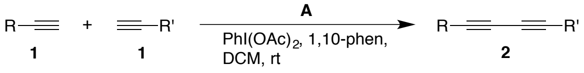
Table 1. Screening the reactivity of A with alkyne 1a, oxidant PhI(OAc)$_2$, and various basic additives.[a]

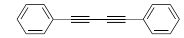
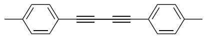
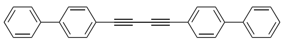
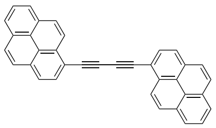
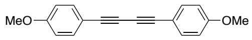
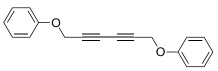
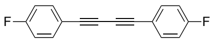
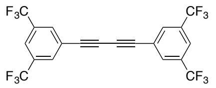
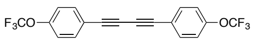
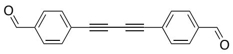
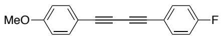
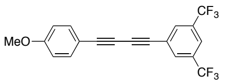
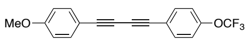


entry	additive	conversion (%)[b]
1[c]	--	0
2	--	0
3	1,10-phen	99
4[d]	pyridine	0
5[d]	benzo[*h*]quinoline	0
6[d]	triethylamine	0
7[d]	TMEDA	0
8	2,2′-bipyridine	48
9	2,2′-bipyridine[e]	68

[a]Reaction conditions: substrate **1a** (0.03 mmol), catalyst **A** (1 mol% Au vs. substrate), PhI(OAc)$_2$ (0.045 mmol, 1.5 equiv), additive (0.012 mmol, 0.4 equiv), DCM (0.40 mL), rt, 18 h. [b]Determined by GC-MS. [c]Reaction without PhI(OAc)$_2$. [d]Reaction time of 6 h; 0.4 and 1.0 equiv tested, giving the same result. [e]1 equiv.

Table 2. Screening of alkynes 1a–j in oxidative coupling catalyzed by A.[a]



entry	1	2		yield (%)[b]
1[c]	**1a**	**2a**		96
2[c]	**1b**	**2b**		98
3	**1c**	**2c**		94
4	**1d**	**2d**		89
5[c]	**1e**	**2e**		92
6	**1f**	**2f**		97
7[c]	**1g**	**2g**		98 (92)
8	**1h**	**2h**		84
9	**1i**	**2i**		90
10	**1j**	**2j**		93
11[d]	**1e**+**1g**	**2eg**		80
12[d]	**1e**+**1h**	**2eh**		60
13[d]	**1e**+**1i**	**2ei**		60

[a]Reaction conditions: substrate **1** (0.3 mmol, 1 equiv), catalyst **A** (5 mol% Au vs. alkyne **1**), 1,10-phenanthroline (0.12 mmol, 0.4 equiv), PhI(OAc)$_2$ (0.45 mmol, 1.5 equiv), DCM (4 mL), rt, 18 h. [b]Yield of isolated products (2 mmol scale in parentheses). [c]1 mol% Au vs. substrate. [d]Amount of **1g–i**: 2 equiv vs. **1e**; amount of **A**: 3.3 mol% vs. both alkynes together.

the coupling reaction (Table 1, entry 2). Gratifyingly, however, when using the oxidant together with 1,10-phenanthroline (1,10-phen) as additive,[11c] we suddenly observed full conversion to the target 1,3-diyne (diphenyldiacetylene, **2a**) (Table 1, entry 3). Replacing additive 1,10-phen with pyridine, benzo[*h*]quinoline, triethylamine, or TMEDA[7,21] yielded no product (Table 1, entries 4–7). On the contrary, reactions using 2,2′-bipyridine proceeded with moderate conversion to **2a** (Table 1, entries 8 and 9). Full conversion was achieved in 1,2-dichloroethane (DCE, Table S4, entries 1 and 2), but significantly lower reactivity was observed in DMF (17% conversion), THF (32%), 1,4-dioxane (63%), acetonitrile (72%), and chloroform (9%) (Table S4, entries 3–19). Varying the amount of 1,10-phen (Table S5, entries 1–5) dramatically influenced the reactivity, with the initially chosen 0.4 molar equivalents being optimal (Table S5, entry 4). The amount of PhI(OAc)$_2$ was found to provide best efficiency within 1–1.5 equivalents (Table S5, entries 4 and 6–9).

When developing catalyst **A**, we also synthesized materials **B**–**D** consisting of larger gold particles supported on NH$_2$-SBA-15 or SBA-15 (Tables S1–S3).[16] While the catalyst featuring large gold nanoparticles on amino-functionalized silica (**B**) gave 35% conversion in 6 h (Table S6, entry 1), those on SBA-15 (**C**, **D**) were catalytically inactive (Table S6, entries 2 and 3). Similarly, test reactions with plain NH$_2$-SBA-15, SBA-15, and without catalyst gave no conversion (Table S6, entries 4–6). This implies that the alkyne coupling requires gold particles on the amino-functionalized support. Smaller particles exhibit considerably higher reactivity than large ones – this can be related to the number of accessible gold atoms and numbers of edge and corner sites, which are highest with the smallest particles.[22]

Optimized reaction conditions thus comprised catalyst **A** (1 mol% gold with respect to alkyne), 1,10-phen (0.4 equiv), oxidant PhI(OAc)$_2$ (1.5 equiv), reagent-grade DCM as solvent, and room temperature. To examine the scope of the oxidative homocoupling reaction catalyzed by **A**, structurally different alkynes **1a**–**j** were tested on a preparative scale (Table 2). As our preliminary screening with alkynes **1e**, **1f** and **1i** displayed slower reaction rates than with **1a** at room temperature, the catalyst loading was increased to ensure full conversion without the necessity of individual subtle optimization. The corresponding symmetrical 1,3-diynes **1a–j** were isolated in high yields and purity (Table 2, entries 1–10) even on a larger scale (Table 2, entry 7). In addition, products of heterocoupling of non-polar fluorinated alkynes **1g–i** with slightly more polar methoxy-substituted **2e** were obtained in good yields (Table 2, entries 11–13) under the same reaction conditions. Diyne **2eg** is known and has been isolated before at yields of 44% (20 mol% of CuBr$_2$ + ligand and pyrrolidine in DCM at rt),[23] 57% (10 mol% of CuI + pyrrolidine in ethyl lactate, 50 °C),[24] 75% (0.2 mol% of Na$_2$PdCl$_4$ + 2 mol% of CuI + ligand + Et$_3$N in DMF at rt),[25] 81% (1 mol% of Cu@silica + piperidine in DCM at rt),[9b] and 82% (6 mol% of Cu@MnO$_x$ in toluene at 105 °C).[9j] This shows that the yield of 80% (Table 2, entry 11) achieved with **A** under mild conditions is fairly competitive in relation to the literature examples.

Next, we investigated the recyclability of catalyst **A** in the homocoupling of **1b** on the preparative scale – after each cycle, the catalyst was filtered off, washed with DCM, dried, and weighed for the subsequent run because each time a small amount of **A** was inevitably lost due to manipulation. The filtrate and solvent from catalyst washing were combined and the product was isolated by column chromatography. Under these conditions, catalyst **A** was reused five times, delivering product **2b** in excellent yields (Figure 1). Z-contrast scanning electron microscopy (ZC-STEM) revealed that the sub-nanometer gold particles of **A** retained their size and homogeneous distribution even after five cycles (Figure 2).

The heterogeneous nature of the catalyst was tested by separating **A** from the reaction mixture after 1 h and 1.5 h and measuring the conversion of alkyne **1a** to product **2a** in the stirred filtrate. In both cases the conversion increased only by 1% within 24 h (Figure 3 left), which can be attributed to measurement uncertainty rather than catalytic activity of the liquid phase. An ICP-OES analysis of the filtrate showed gold concentration of about 1.3 ppm (= µg/g), which accounts for <1 % of the total gold content in the reaction. At 40 °C the leached amount of gold increased to 3.6 ppm, and therefore ambient temperature was preferred in the reactions described above so as to minimize the undesirable leaching.

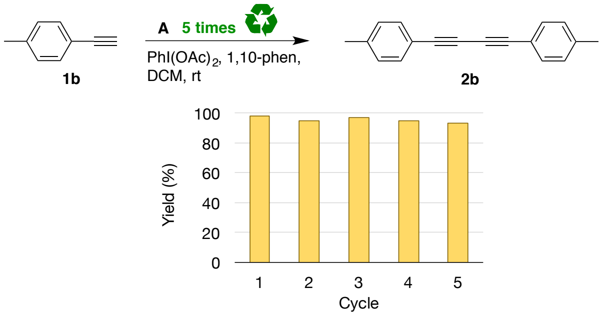


Figure 1. Isolated yields of diyne **2b** obtained from **1b** using catalyst **A** (5 mol%) and oxidant $PhI(OAc)_2$ (1.5 equiv) in DCM overnight in five cycles.

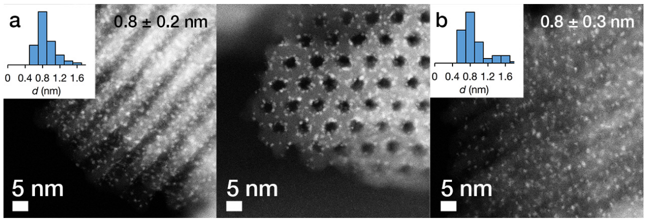


Figure 2. ZC-STEM images of material **A** – a) before performing catalysis, and b) after five consecutive uses as catalyst in homocoupling of **1b**. Particle size histograms, average particle size and standard deviation are included, as obtained from these images.

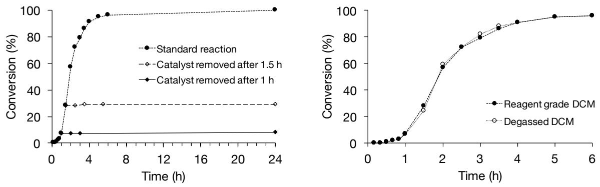


Figure 3. Time-conversion plots of homocoupling of alkyne **1a** using catalyst **A** and $PhI(OAc)_2$. *Left*: Standard run and runs after removal of **A**. *Right*: Comparison of reagent-grade and degassed DCM.

The reaction kinetics featured an induction period within the first hour, after which the reaction followed a first-order kinetic profile (Figure 3 right). Employing degassed solvent provided an identical kinetic curve (Figure 3 right), suggesting that oxygen is not required for the reaction like in the case of copper-catalyzed Glaser-Hay coupling.[1a,1b,5,7] When $PhI(OAc)_2$ was added after 1 h of stirring of all other reaction components, the induction period was still present, but adding the alkyne after stirring the other reactants for 1 h resulted in a faster onset of the reaction with the induction part being less pronounced (Figure S3). Also, the initial rate of the second catalytic cycle was notably higher compared to the first run (Figure S4).

The kinetic experiments, particularly the behavior of the induction period upon changing the reaction conditions, indicate that the catalyst undergoes some type of activation, presumably via partial oxidation of gold by reacting with the λ^3-iodane $PhI(OAc)_2$. Toste and co-workers showed that dendrimer-encapsulated gold clusters on SBA-15 are oxidized by $PhICl_2$ to Au^{III} species – as detected by X-ray photoelectron spectroscopy (XPS) measurements – that catalyzes diastereoselective cyclopropanation.[26] By means of XPS, we checked the oxidation state of the gold clusters in **A** before and after the catalytic reaction. The spectra (Figure 4) featured large Au 4f peaks, which could be separated into two doublets. The one at lower binding energy (red line), displaying the $4f_{7/2}$ and $4f_{5/2}$ at 85.0 and 88.6 eV, respectively, can be associated to gold nanoclusters (Au).[27] As compared to the binding energy of bulk gold (84.0 eV), this peak is positively shifted by 1.0 eV. This is a final state effect due to the sub-nanometer dimension of the gold clusters, which at d < 1.0 nm are no longer metallic[28] and can readily undergo redox processes.[29] The second doublet (blue line), whose peaks are found at 86.4 and 89.7 eV, suggests the presence of gold in a higher oxidation state (Au^{III}).[26,27c,d,30] Furthermore, the Au/Au^{III} ratio does not change after the reaction, in good agreement with the data about the stability of the catalyst (Figure 1 and 2), and indicates that exposure to oxygen leads to partial oxidation.[29]

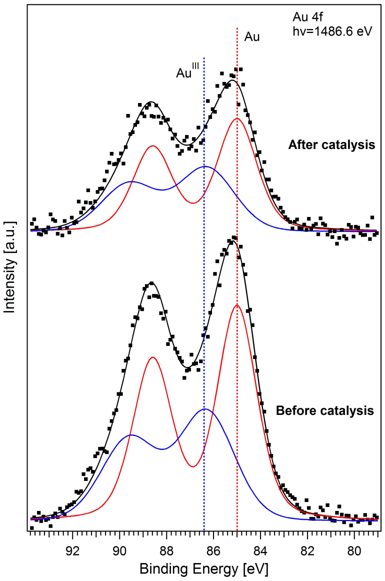


Figure 4. XPS spectra of material **A** before and after its use in catalysis.

Literature points to three conceivable mechanistic pathways. The calculations done by Corma et al. on oxidized Au clusters on CeO_2[12c] show that two vicinal gold-activated alkyne molecules couple together on the gold surface, yielding the homocoupling product. The second one is based on homogeneous gold catalysis works,[11c,d] suggesting that geminal alkynyl moieties of an Au^{III} complex reductively eliminate to form the 1,3-diyne. While Peng and co-workers assume that the required bis(alkynyl)Au^{III} compound originates from a mono(alkynyl)Au^{III} species by reacting with another alkyne molecule,[11c] Corma et al.[11d] propose that an alkynyl-Au^{I} species is oxidized by Selectfluor to form a Au^{I}-Au^{III} digold complex that gives the bis(alkynyl)Au^{III} intermediate via transmetallation. The last scenario, proposed by de Haro and Nevado[31] and adopted by Zhu et al.,[11b] involves the formation of a gold-activated alkynyl(phenyl)iodonium salt[32] that reacts with another alkyne molecule to form a vinyl-gold intermediate that decomposes while producing the 1,3-diyne.

Our catalytic system requires the presence of 1,10-phen (or a similar chelate such as 2,2′-bipyridine), which can serve to stabilize gold clusters[33] and is a well-known ligand for square-planar complexes of Pd^{II}, Pt^{II}, Cu^{I} and also Au^{III}. Together with the facts that gold sub-nanoparticles are easily oxidized[29] and the material contains a significant portion of Au^{III}, as shown by XPS measurements, we incline to the notion that the reaction proceeds via the formation of the bis(alkynyl)Au^{III} species stabilized by 1,10-phen and subsequent reductive elimination, giving **A**. Oxidant $PhI(OAc)_2$ yields the catalytic oxidized gold in the course of the reaction.

In conclusion, we demonstrate a mild, robust, operationally simple and efficient method for the C_{sp}–C_{sp} coupling of terminal alkynes employing a hypervalent iodine-based oxidant and stable sub-nanometer gold particles supported on amino-functionalized silica. Ten structurally different 1,3-diynes, containing useful functional groups and structures such as fluorine, trifluoromethyl, trifluoromethoxy group, aldehyde, and intensively fluorescent pyrene, were isolated in excellent yields. The catalytic system was also applicable in heterocoupling, providing the unsymmetrical 1,3-diynes under the same conditions. The catalyst was perfectly recyclable owing to negligible gold leaching and clusters maintaining their sub-nanometer size. We infer that cationic gold is the active species, stabilized by $PhI(OAc)_2$ under reaction conditions. Glaser-type alkyne coupling catalyzed by a heterogeneous gold catalyst is not common, especially on the preparative scale. This work thus underlines the importance of heterogeneous gold catalysis in the synthesis of high value-added chemicals.

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Author Contributions

¶B.V. and J.V. contributed equally.

Notes

Any additional relevant notes should be placed here.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures and supplementary data (characterization of materials, supplementary results) as addressed in the text (PDF)

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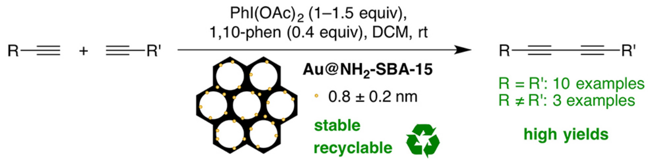
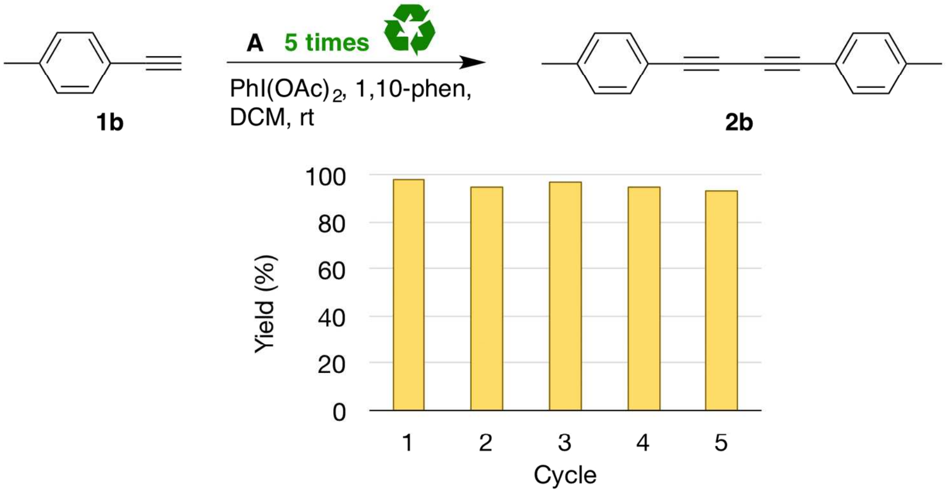
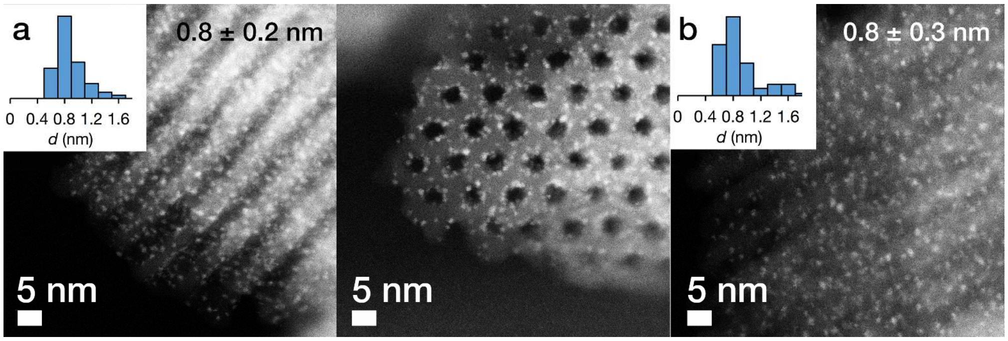

R
+
R'
PhI(OAc)2 (1–1.5 equiv),
1,10-phen (0.4 equiv), DCM, rt
Au@NH2-SBA-15
0.8 ± 0.2 nm
stable
recyclable
R
R'
R = R': 10 examples
R ≠ R': 3 examples
high yields



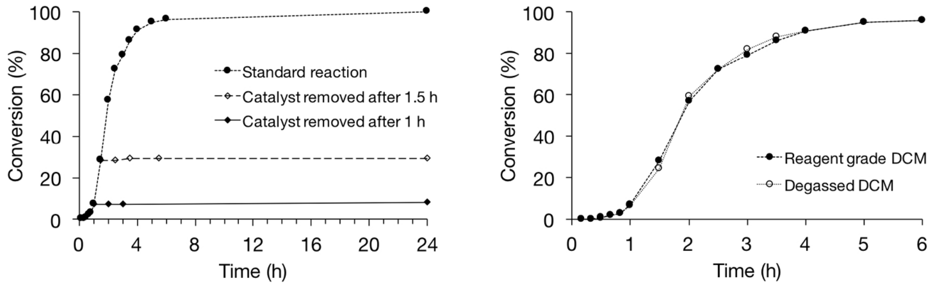
Isolated yields of diyne 2b obtained from 1b using catalyst A (5 mol%) and oxidant PhI(OAc)2 (1.5 equiv) in DCM overnight in five cycles.

327x176mm (144 x 144 DPI)



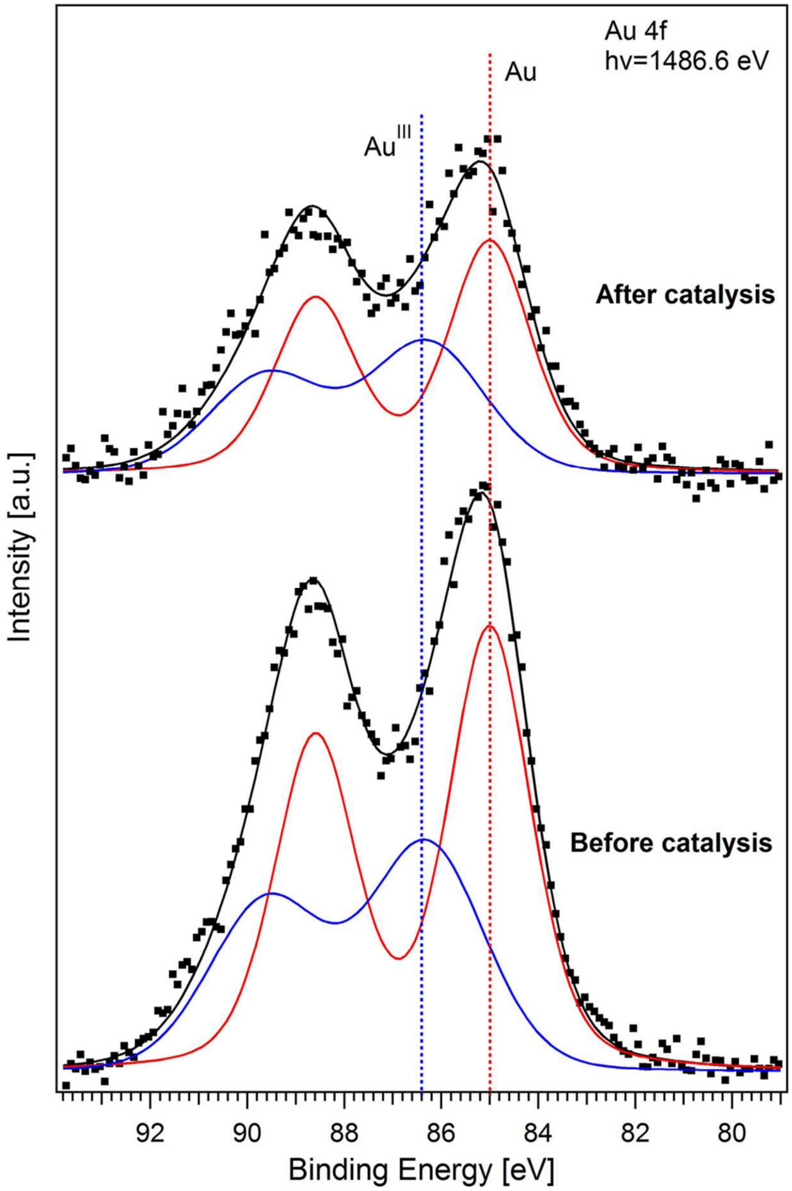
ZC-STEM images of material A – a) before performing catalysis, and b) after five consecutive uses as catalyst in homo- coupling of 1b. Particle size histograms, average particle size and standard deviation are included, as obtained from these images.

1083x361mm (72 x 72 DPI)



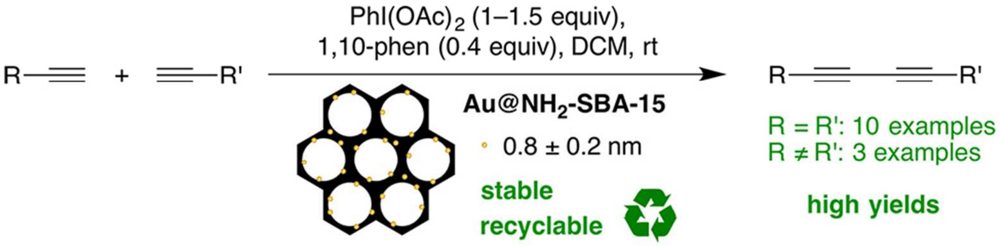
Time-conversion plots of homocoupling of alkyne 1a using catalyst A and PhI(OAc)2. Left: Standard run and runs after removal of A. Right: Comparison of reagent-grade and degassed DCM.

347x118mm (144 x 144 DPI)



XPS spectra of material A before and after its use in catalysis.

111x155mm (300 x 300 DPI)



TOC Graphic

82x20mm (300 x 300 DPI)