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Additional Information

Glass wool: novel applications as support for heterogeneous catalysis

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Supporting Information Placeholder

ABSTRACT: Glass wool has been used as support for different metal and metal oxide nanoparticles, namely Pd, Co, Cu, Au and Ru. The supported nanostructures were proved to act as catalyst for different test reactions, opening the opportunity to develop inexpensive and manageable heterogeneous catalysts with excellent potential for flow photochemistry applications.

INTRODUCTION

Heterogeneous catalytic processes have several advantages over the equivalent homogeneous ones, specifically, easy catalyst separation, minimal product contamination¹ and the distinct possibility of reuse.² [REF] Quite frequently these catalysts are in the form of nanometric or micrometric powders decorated with active nanostructures such as metal or metal oxides.³⁻⁴ [CHECK THESE ONES] Although they are easy to separate after batch reactions, they may not be ideal for flow chemistry, a strategy that enables easy scale up of reactions.⁵ With this in mind, we explored the possibility of using fibrous materials as catalyst supports, as they would be easy to separate after batch reactions and have the potential for flow chemistry applications where a static catalyst would act on flowing solutions, also facilitating photocatalytic processes. Glass wool is inexpensive, readily available with a variety of surface properties and easy to modify to provide physical or chemical affinity towards many catalytic materials. Glass wool (GW) is widely employed for thermal and noise insulation in homes, appliances and instrumentation. In chemistry, GW is commonly used as filter, packing material in GC columns, purge traps and adsorbent beds.⁶ There are some examples where GW is used as an attachment surface for bactericidal studies.⁷ Some concerns about the inert nature of the glass wool were noted many years ago by Hayes and Macdonald, but no further

studies were found in literature.⁸ A more recent work shows an example of GW used as heterogeneous catalyst, although under very high temperature conditions.⁹ Apart from these examples, is hard to find GW uses other than the ones mentioned above.⁶

In this contribution we report on a number of metal and metal oxides nanostructures supported on commercially available, sometimes modified, GW and how they perform on a variety of catalytic processes. We explored individual reactions emphasizing the use of classic reactions with diverse novel materials. Not surprisingly, the successful examples provided in this article were accompanied by many failed attempts. In our effort to facilitate future uses of these materials, we describe several unsuccessful experiments in the SI. Sometimes the difference between failure and success rests on subtle surface modifications.

In catalysis the term support is used with a wide range of meanings, from the passive support that simply restricts the mobility of the active catalyst, to cases where the support is an integral part of the catalyst and its performance; frequently this is the case with semiconductors, such as TiO₂. Further, in the case of photocatalysis the absorption and scattering properties of the support are also important. Our work on glass wool was initiated with the assumption that this support would be of the passive type; we have found that while this is frequently true, there are exceptions where GW is catalytically active to the extent that in some examples further derivatization is not required.

The following sections deal with the performance of a few types of GW, different strategies for its modification, the derivatization with various metal and metal oxides, and their performance in representative classic catalytic processes. The characterization of new material and its application in wide variety of organic transformations will be discussed along with their impact on selectivity, efficiency and reusability toward

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the development of potential and commercial heterogeneous photocatalysts.

RESULTS AND DISCUSSION

Non-silanzed (NS-GW) and silanzed (S-GW) glass wool were decorated with different metal and metal oxides nanoparticles, namely Au, Pd, Ru, Co and Cu, utilizing photoinduced and chemical methods as described in the SI. The optimal synthetic method was chosen based on the shown catalytic activity and stability of the new materials prepared. Thus, GWs were subjected to different pre-treatments before incorporating the metal/metal oxide nanoparticles in order to increase their interaction with the GW surface. Figure 1 shows how the materials look like before and after different surface modifications.

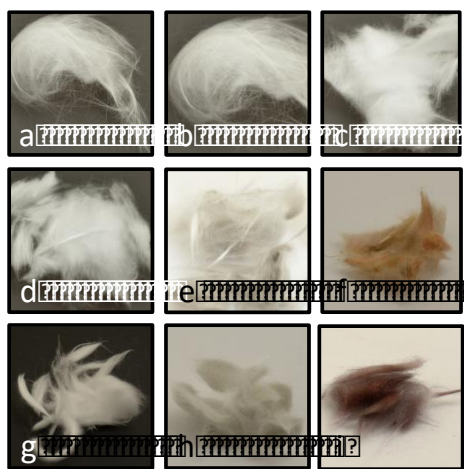


Figure 1. Pictures of different materials used in this work: a) pristine S-GW, b) pristine NS-GW, c) HCl-treated S-GW, d) APTES-functionalized NS-GW, e) Pd@S-GW, f) Au@NS-GW, g) Cu@NS-GW, h) Co@S-GW, i) Ru@NS-GW and j) Au@NS-GW.

Cu@NS-GW, g) Co@S-GW, h) Ru@NS-GW and i) Au@NS-GW.

In order to determine whether or not these new materials would perform as catalyst we selected different reactions based on some of our previous reports.^{4, 10-12} Scheme 1 summarized the tested reactions that were successfully catalyzed utilizing the different materials synthesized. Conditions explored for each reaction vary from thermal control to photo-induced catalysis. Table 1 shows a summary of the reactivity of different GW-based materials toward different organic transformation. In order to discuss their activity we divided the following sections according to the organic transformation under study. Notice that here we focused on the reactions that were catalyzed by the use of a GW-based material, while all the unsuccessful trials are compiled in the SI.

Last but not least, the material becomes easy to separate from the reaction vessel simply using regular twizers, Figure 2.



Figure 2. Picture showing easy removal of the material from the reaction vessel utilizing a pair of twizers.

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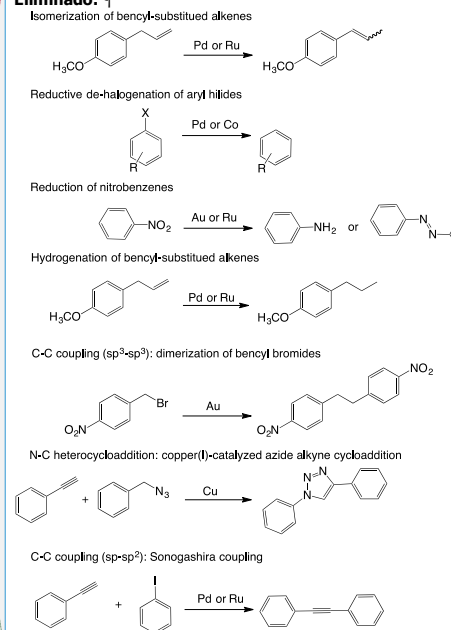
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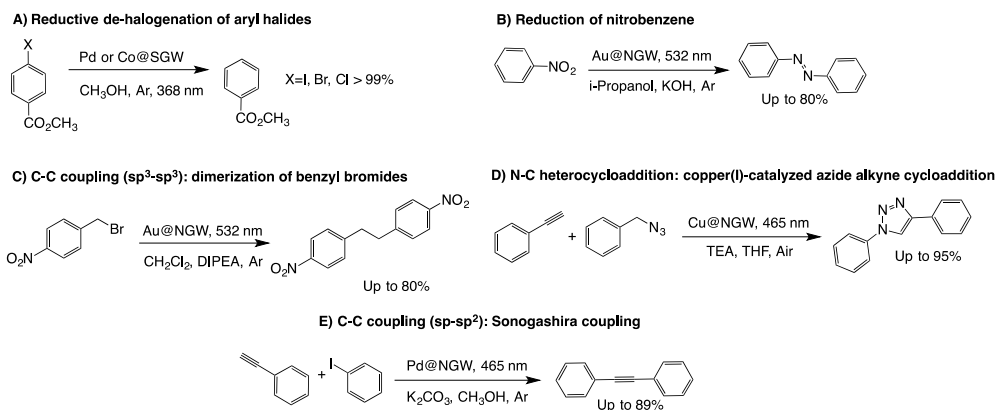
Bajado hacia abajo[1]: Scheme 1. Different reactions tested with the modified glass wool materials.

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Scheme 1. Different reactions tested with the modified glass wool materials. Only the reaction that were successfully catalyzed are listed here.

Table 1. Summary of the reactivity of different GW-based materials toward different organic transformations

Entry	Material	Reaction	% Conversion	% Yield	Conditions
i	Co@SGW		100	>99	Table 2, i
ii	Pd@SGW	Reductive de-halogenation	100	>99	Table 2, v
iii	SGW		37	37	Table 2, viii
iv	Ru@SGW* (or Ru@NGW*)	Reduction of nitro compound	??	66 ^c	Table 3,
v	Au@SGW*		68	?	
vi	Au@SGW*	C-C coupling (sp ³ -sp ³)	77	64	
vii	SGW*		36	26	
viii	Cu@NGW (or Cu@NGW*)	N-C heterocycloaddition	100	94	
ix	Cu@Charcoal		??	21	
x	NGW*		ND	ND	
xi	Pd@NGW*	C-C coupling (sp-sp ²) (Sonogashira)	100	90	
xii			ND	ND	
xiii	NGW*		0	ND	

Reductive de-halogenation of aryl halides

De-halogenation processes are usually dictated by the C-halogen bond strength; thus, C-Cl bonds are harder to break than C-Br bonds and those than C-I bonds, which is reflected in harsher reaction conditions to achieve de-halogenation.¹³⁻¹⁴ Recent reports on dehalogenation processes involved the use of either high pressure conditions (H₂, 30 bar),¹⁵ or toxic and expensive iridium complexes.¹⁶ Here we per-

formed photodehalogenation of methyl 4-halogenobenzoate catalyzed by GW-based materials (Table 2). The reaction proceeds to completion under UVA light irradiation in the presence of K₂CO₃ base within 1-3 h depending on the catalyst material and the aryl halide. Notice that no homocoupling product is detected in any case. With X=I or Br, all GW-based materials show photocatalytic activity, although more time is needed for the reaction to proceed when only untreated GW is used. To our delight, the dehalogenation of the aryl chloride was successfully catalyzed

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with the supported CoNPs, while Pd and bare GW showed lower reactivity compared to the former one. Additionally, the new material Co@GW showed a great reusability where after 3 cycle a 100 % yield of reductive compound was achieved within 4 h of irradiation of methyl 4-chlorobenzoate (table Si).

Table 2. Light induced reductive dehalogenation catalyzed by GW-based materials



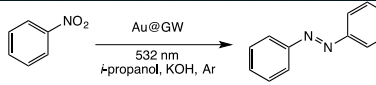
X (1)	Catalyst	Time (h)	% 2 Yield ^d	
i	I-	Co@SGW	0.25	>99
i	I-	^b Co@SGW	24	15
iii	I-	^c Co@SGW	0.25	XX
iv	I-	^c Co@SGW	1	>99
v	I-	Pd@SGW	0.25	>99
v	I-	SGW	0.25	XX
vii	I-	SGW	1	XX
viii	I-	SGW	5	>99
viii	I-	none	24	ND
vii	Br-	Co@SGW	1	95
vii	Br-	Co@SGW	2	>99
viii	Br-	Pd@SGW	1	88
viii	Br-	Pd@SGW	2	>99
ix	Br-	SGW	7	XX
ix	Br-	SGW	5	>99
x	Cl-	Co@SGW	1	80
x	Cl-	Co@SGW	2	93
x	Cl-	Co@SGW	3	>99
xi	Cl-	Pd@SGW	7	30
xi	Cl-	Pd@SGW	20	>99
xii	Cl-	SGW	24	37

Reaction conditions: 0.2 mmol of substrate 1, 0.36 mmol of K₂CO₃, 5 mL methanol, 60 mg catalyst. ^aYields were determined by GC-FID using 4-stilbene as external standard. ^bUnder dark at 47°C. ^cUnder Air. ^d

Reduction of nitro compounds

The photoreduction of nitro compounds has been studied as a method to synthesize anilines derivatives under mild conditions.¹⁷⁻¹⁸ Although the azo compound might be one of the reaction intermediates, their formation under light conditions is rarely found as the reductive environment forces the reaction toward the correspondent amine.¹⁹ There are just a few examples where the azo compounds form under light irradiation.²⁰⁻²¹ Here we show that AuNPs deposited on GW can successfully perform this reaction within 7 h under green light irradiation (table 3). Briefly, the catalyst was mixed together with the nitro compound in *i*-propanol under inert atmosphere in the presence of KOH and irradiated with 532 nm LEDs. The formation of aniline was monitored by UV-Vis spectroscopy (Figure Sxxx). Table 3 summarizes the results found in the presence and in the absence of catalyst.

Table 3. Light induced reduction of nitrobenzene to azobenzene catalyzed by Au@GW



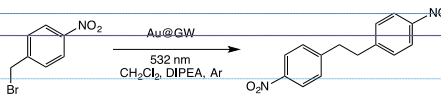
Catalyst	Time (h)	% Conversion ^a	% Yield ^a	
i	Au@SGW ^b	24	68	68
i	Au@SGW ^b	48	TBD	TBD
ii	Au@SGW ^b	24	TBD	TBD
iii	Au@SGW ^{bc}	24	ND	ND
iv	SGW ^c	24	ND	ND
xii	none	24	ND	ND

Reaction conditions: 0.3 mmol of substrate, 0.03 mmol of KOH, 5 mL *i*-propanol, 60 mg catalyst under Ar. ^aConversion and yields were determined by UV-vis spectroscopy. ^bUnder dark at 85°C. ^cUnder Air.

C-C coupling (sp³-sp³)

The reductive dimerization of benzyl bromides can be photoinduced using supported AuNPs and green light excitation. In our previous report,¹¹ we found that the reaction does not proceed if an inert support is used instead TiO₂, namely crystal nanodiamonds. Much to our surprise the same reaction proceeds with excellent yields if AuNPs are deposited on GW (Table 4). It is worthy to highlight that a noticeable product yield is obtained in the absence of catalyst under these irradiation conditions. These has been previously reported as a contribution from the UV contamination on the green light source.¹¹

Table 4. Light induced reductive dimerization of nitrobenzyl bromide catalyzed by Au@GW



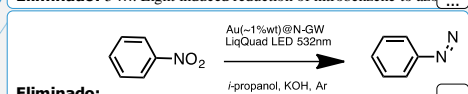
Catalyst	Time (h)	% Conversion	% Yield ^a	
i	Au@SGW ^b	5	77(58)	64(43)
ii	Au@SGW ^c	7	100(??)	80(??)
iii	Au@SGW ^{bc}	48	ND	ND
iv	SGW ^c	24	36	26
v	none	24	40	33

Reaction conditions: 0.1 mmol of substrate, 2 eq. of DIPEA, 30 mg of catalyst in 4 mL of CH₂Cl₂. ^aYields and conversions were calculated by ¹H-NMR using dimethyl sulfone as external standard. ^bValues between brackets from second cycle after 5h under the same conditions. ^cUnder dark at 30°C.

N-C heterocycloaddition (Click reaction)

We have recently report on the photocatalyzed click reaction using supported Cu₂O nanoparticles on TiO₂ and Nb₂O₅.¹² The reaction can proceed under both UV and visible light irradiation within 6 h. The unexpected reactivity of the material under visible light

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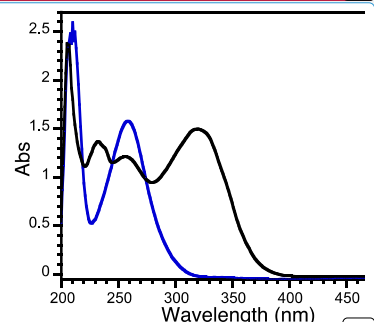
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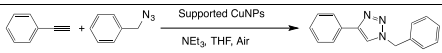
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suggests that the Cu_2O particles play an important role on the light harvesting. With this in mind, we decided to test the Cu_2O activity when deposited on GW (see SI for catalyst preparation details). The efficiency of the catalyst was compared to the reactivity of a commercial Cu@charcoal catalyst, which is one of the preferred catalysts to perform click chemistry under thermal conditions. As it can be seen in table 3, the new material showed great reactivity and high efficiency under both visible light irradiation or dark conditions at 55°C (temperature reached upon illumination). Unfortunately, the catalyst cannot be reused. (should we test Cu leaching?)

Table 3 Heterogeneous photocatalytic click chemistry catalyzed by Cu@GW .

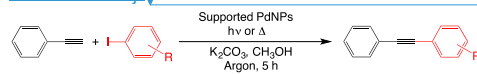


Catalyst	Condition	Time (h)	% Yield ^{a,b}
i Cu@GW	465 nm , 55°C	6	92 (95)
ii Cu@GW	Dark, 55°C	6	93 (94)
i Cu@GW	Dark, RT	6	8 (25)
i Cu@GW	Dark, RT	24	75
i Cu@Charcoal	Dark, 55°C	6	24
i Cu@Charcoal	Dark, 55°C	24	73
v GW	55°C	6	ND
v GW	55°C	24	2.8 (3)

Reactions conditions: 15 mg of catalyst, azide/alkyne/TEA (1:1:1), 6 h under air. ^aYields were calculated by $^1\text{H-NMR}$ analysis in CDCl_3 using caffeine as external standard. ^bValues between brackets are yields obtained after 6 h of reaction using supported Cu@NGW . ^cMixture of two isomers.

C-C coupling ($sp-sp^2$) (Sonogashira)

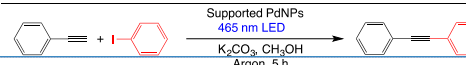
One of our recent reports demonstrated that PdNP-decorated materials such as TiO_2 , diamonds and Nb_2O_5 can selectively catalyze the cross-coupling of iodobenzene and phenylacetylene under both reflux and visible light irradiation (Scheme 2). (ref) We note that both new Pd@SGW and Pd@NGW catalysts selectively leads to the cross coupling product showing similar activity.



Scheme 2. Sonogashira C-C coupling catalyzed by supported PdNPs under mild conditions. (REF HERE)

Briefly, The selective cross coupling reaction of iodobenzene and phenylacetylene has been studied in methanol as solvent, potassium carbonate K_2CO_3 as base and supported PdNPs on activated and/or functionalized surface of GW. Table 1 summarizes the GW supported PdNPs screened for the optimization of light induced Sonogashira coupling under argon. The best conditions were found when PdNPs are grafted on the surface with an exposed active sites in which was confirmed by the XPS data the presence of Pd(o). The photocatalyst can be reused twice with good performance (Table SI). Control reactions in presence of GW and in absence of catalyst did not show any product after 24 h. The photocatalyst can be reused at least two times with excellent performance (See SI).

Table 1: Different Pd-decorated GW tested for the light-induced Sonogashira C-C coupling using visible light irradiation



Catalyst	time	% Conv	% Yield ^a
i none	24	0	ND
ii NGW	24	0	ND
iii Pd@NGW	5	100	89
iv Pd@NGW	5	0	ND

Reactions conditions: 1 eq. of Iodobenzene, 1.3 eq. of Phenylacetylene, 2 eq. of K_2CO_3 , 4 mL methanol, 60mg catalyst. ^aYields were determined by GC-FID using t-butylbenzene as an external standard. ^bUnder dark conditions, reaction was run at 42°C .

CONCLUSIONS

Here we show the versatility of the use of glass wool as very inexpensive and easy handling support. We demonstrated that despite the different nature of the glass wool utilized the efficacy of the material is similar. We have explored different glass surface activation methods and different metal loadings in our first attempt to prove this material is reliable and easy to use. We envision this as a first step towards an easy way to recover heterogeneous catalysts, and to improve the flow system setups.

ASSOCIATED CONTENT

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

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Notes

The authors declare no conflict of interest.

§CAMaR: Centre for Advanced Materials Research.

†CCRI: Centre for Catalysis Research and Innovation.

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