Oriented Au(111)/Graphene: an efficient catalyst for coupling reactions

V.I. Parvulescu[a],* N. Candu[a], S.M. Coman[a], C. Teodorescu[b], A. Primo[c], H. Garcia[c],*

[a]*Department of Organic Chemistry, Biochemistry and Catalysis, University of Bucharest, 030018 Bucharest, Romania*
[b]*National Institute of Materials Physics, 077125 Magurele-Ilfov, Romania*
[c]*Instituto de Tecnología Química CSIC-UPV, Universitat Politécnica de Valencia, 46022 Valencia, Spain*
**Corresponding author: +00404100241, E-mail address: vasile.parvulescu@chimie.unibuc.ro*

Abstract: Au has been deposited onto few-layers graphene ($\overline{\text{fl-G}}$) as oriented $\overline{\text{Au}}$(111) flat (3-6 nm thick, 20-40 nm lateral dimension) nanoplatelets. The characterization of these materials has been carried out by several techniques HRTEM, FESEM, AFM, XPS and Raman spectroscopy. This material exhibits a strong Au-graphene interaction compared to analogous graphene supported Au nanoparticles obtained through other preparation routes. The oriented Au nanoplatelets on graphene exhibited a very high activity in several coupling reactions and good recyclability.

Keywords: oriented Au(111)/graphene, AuNPs on graphene, cross coupling reactions.

1. Introduction

Cross coupling reactions are among the most versatile transformations in modern organic synthesis, they allowing an efficient assemble of molecules with access to important used chemicals as therapeutical drugs, pesticides or specialty chemicals[1]. Important specificities for these transformations are their capability to afford high yields, the compatibility with a large number of functional groups and the mild reaction conditions[2,3]. Most of these cross coupling reactions are catalyzed under homogeneous conditions by Pd, either as metal complexes or as nanoparticles (NPs)[4]. To date, the replacement of Pd with other transition metals led to less general and efficient catalysts to promote these coupling reactions[5]. Both the support nature and the size of the metal particles are very important in these reactions.

Based on this state of the art, the present study aimed to investigate the role of graphene as support for Au and to provide a rationalization of the relative reactivity of aryl halides in catalysis considering the influence of the preferential crystal morphology, facet orientation and strong grafting of these metal nanoparticles on the graphene sheet. Another aspect of our studies is to show that 111-facet oriented Au supported on G exhibit, in spite of their much large particle size, enhanced catalytic activity in catalytic coupling reactions (Ullmann, C-N, oxidative coupling and Suzuki-Miyaura) compared to analogous graphene supported Au nanoparticles obtained by *in situ* Au^{3+} reduction on preformed G sheets.

2. Experimental

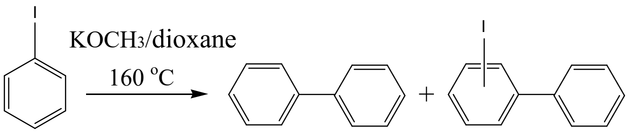
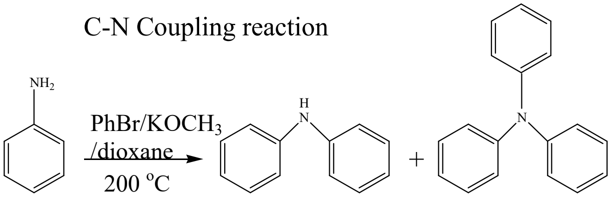
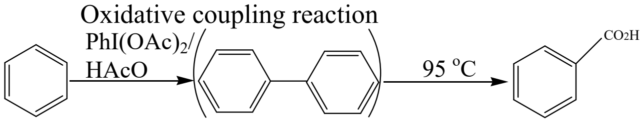
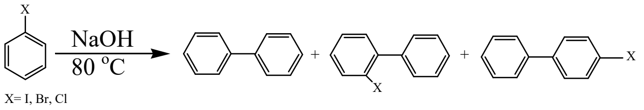
Few-layers graphene (fl-G) supports were produced from sodium alginate using a reported procedure[6,7]. Metal NPs deposition has been carried out from ($HAuCl_4$, 0.2 mg) that was added to the suspension of ethylene glycol containing fl-G and the metal reduction was then performed at 120 °C for 24 h under vigorous magnetic stirring (500 rpm). The Au/G was recovered by filtration and washed thoroughly with water and with acetone and dried at 110 °C. The synthesis of ($\overline{\text{Au}}$/fl-G) started from 0.5 g of chitosan (Aldrich) that was dissolved in water by adding acetic acid (0.23 g). The viscous solution (500 μL) was cast as nanometric film on quartz plates (2 x 2 cm^2) spinning at a rate of 4000 rpm during 1 min. Then, the resulting chitosan film was immersed in a $HAuCl_4$ solution (0.01 mM) during 1 min to adsorb Au. Analysis of gold was determined by ICP-OES (Agilent Technologies, 700 Series) and indicated a metal content of 3.2 $ngAucm^{-2}$. Reactions were carried as reported[6,7]. Analysis of the reaction products was done by GC-MS and ^1H and ^{13}C NMR spectroscopy, and the catalysts characterized by Raman, HRTEM, FESEM, AFM and XPS.

3. Results and discussion

Table 1 compiles the results of the investigated Au/graphene catalysts in different coupling reactions. They demonstrate a very high versatility in these reactions preserving the activity in the presence of the different substrates and reaction conditions. Noteworthy, compared to supported AuNP catalysts, the

1.1.1 oriented Au led to much higher intrinsic activities affording TONs which were several order of magnitude higher. It is also important to notice these catalysts were recycled several times without any loss in the catalytic performances. The characterization of these catalysts by HRTEM, FESEM and AFM demonstrated that most of the platelets were located on valleys of the G film and preserved this location along the reactions. XPS analysis of the investigated catalysts offered arguments to explain the high catalytic activity. The binding energy values of the Au 4f peak in $\overline{\text{Au}}$/fl-G were shifted by 0.4 eV to higher values that may suggest the occurrence of a stronger gold–support interaction. XPS also explains the higher reactivity of coupling for chlorobenzene than for iodobenzene. Iodide causes catalyst deactivation, while no similar deactivation occurs in the case of chloride. Poisoning by iodide is the likely reason for the low activity of Au particles in the Suzuki-Miyaura coupling. (26 kJ/mol for PhI compared to 59 kJ/mol for PhCl).

Table 1. The comparative catalytic behavior of Au/fl-G and $\overline{\text{Au}}$/fl-G in catalytic coupling reactions

Catalyst	Catalytic reaction	Conversion %	Selectivity %	TON
$\overline{\text{Au}}$/fl-G film	Ullmann-like homocoupling of iodobenzene  1 2 3	0.3	83 to 2 16 to 3	3.7×10^5
Au/fl-G		0.2	100 to 2	79
$\overline{\text{Au}}$/fl-G film	C-N Coupling reaction  4 5 6	14.7	95.2 to 5 4.8 to 6	9.2×10^6
Au/fl-G		5.1	100 to 5	10
$\overline{\text{Au}}$/fl-G film	Oxidative coupling reaction  7 8 9	14.7	100 to 9	1.4×10^7
Au/fl-G		5.1	100 to 9	21.8
$\overline{\text{Au}}$/fl-G film	Suzuki-Miyaura coupling reaction  10 11 12 13	X=I ⇨ 2.4 X=Br⇨90.9 X=Cl⇨100	85.5 to 11 39.9 to 11 65.0 to 11	2.5×10^7 1.0×10^7 3.1×10^6
Au/fl-G		X=I ⇨ 51.3 X=Br⇨>99.9 X=Cl⇨81.7	81.4 to 11, 36.0 to 11 58.6 to 11	

4. Conclusions

The present investigation has shown that Au particles supported on G are able to promote various coupling reactions wherein chlorobenzene exhibits much higher reactivity than iodobenzene. Also, it has been found that strong grafting of Au on G and the preferential 111 facet orientation increases the activity compared to analogous samples of randomly oriented Pd NPs supported on G by several orders of magnitude. This approach can serve to develop more efficient coupling catalysts for organic syntheses.

References

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