

Stabilization and recovery of gold catalysts in the carbene transfer reaction to alkenes within ionic liquids

María J. Sabater*, Avelino Corma*, Irene Domínguez, Tania Ródenas,
 *Instituto de Tecnología Química, UPV-CSIC, Universidad Politécnica de Valencia, Avenida
 los Naranjos s/n, 46022 Valencia, Spain.
 e-mail: mjsabate@itq.upv.es, acorma@itq.upv.es

Introduction

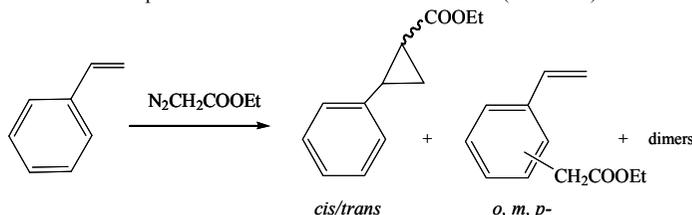
Transition metal catalyzed transfer of carbene units from diazo compounds to alkenes constitutes a powerful tool in organic synthesis to obtain cyclopropane derivatives, which are important intermediates for the construction of relatively complex molecules. It has been recently described in the literature that a gold(I)-based catalyst can be an efficient and chemoselective catalyst for this reaction [1]. We present here that Au(I) and Au(III) salts (KAuCN₂ and NaAuCl₄ and respectively) can catalyze the cyclopropanation of alkenes by ethyl diazoacetate (EDA) within ionic liquids (ILs), being stabilized against formation of inactive gold metal agglomerates.

Materials and Methods

To a stirred solution of alkene (3 mmol), 8%mol of catalyst NaAuCl₄ (or 5% mol KAuCN₂) and the ionic liquid (3 ml), EDA was added (1 mmol). The resulting mixtures were stirred at room temperature for 24h. After completion of the reaction, the reaction mixtures were extracted with diethyl ether. The organic extracts were analyzed by gas chromatography.

Results and Discussion

NaAuCl₄ and KAuCN₂ are active catalysts for cyclopropanation of alkenes with EDA, affording in many cases high yields of *cis/trans* cyclopropanecarboxylates and minor amounts of aromatic addition products and fumarate and maleate dimers (Scheme 1).



Scheme 1 Carbene transfer reaction from EDA to styrene catalyzed by NaAuCl₄ and KAuCN₂.

These gold salts rapidly decompose and agglomerate when working in organic solvents, resulting in less active and less selective gold metal particles. With ionic liquids such as 1-butyl-3-methylimidazolium hexafluorophosphate and 1-octyl-3-methylimidazolium hexafluorophosphate (commonly abbreviated as [BMIM] PF₆ and [OMIM] PF₆ respectively) as solvents, NaAuCl₄ and KAuCN₂ undergo a reductive transformation to Au(0) to afford gold nanoparticles, which remain stabilized in the ionic liquid behaving as an authentic metal

nanoparticle reservoir. The catalysts can be recovered and reused in subsequent runs. It has been found that cyclopropanation reaction is sensitive to gold particle size [2], with the smallest gold particles affording the highest yields of cyclopropanecarboxylates.

Table 1 Cyclopropanation reaction of styrene with EDA catalyzed by Au(III) and Au(I) salts in different solvents.

Catalyst	Solvent	styrene conv(mol%)	Yield(mol%)		
			<i>cis/trans</i>	<i>o-,m-,p-</i>	<i>dimers</i>
NaAuCl ₄	CH ₂ Cl ₂	96	25/39	25	10
NaAuCl ₄	toluene	91	32/40	26	2
NaAuCl ₄	[BMIM] PF ₆	98	32/62	2	2
NaAuCl ₄	[OMIM] PF ₆	86	1/83	2	--
KAuCN ₂	[BMIM] PF ₆	100	32/46	22	--

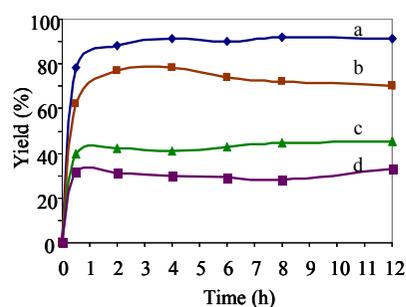


Figure 1 Plot showing the yield of cyclopropanes versus time in the cyclopropanation reaction of styrene with EDA catalyzed by gold(0) nanoparticles in [BMIM] PF₆. Z-average particle size: a) 8nm, b) 22 nm, c) 79 nm and d) 102 nm.

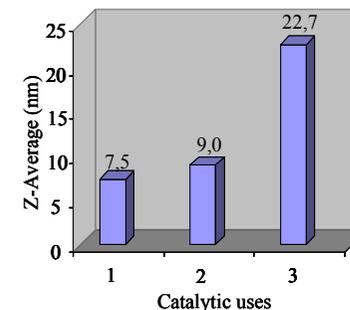


Figure 2 Comparative Z-average of gold nanoparticles after successive reuses in the cyclopropanation reaction of styrene catalyzed by NaAuCl₄ in BMIM PF₆.

Significance

The stability and performance of NaAuCl₄ and KAuCN₂ is much higher in ionic liquids than in typical organic solvents. Indeed it is possible to obtain stable gold metal nanoparticles that are active in the cyclopropanation reaction. A clear dependency of the product selectivity with the size of the gold particle is observed for *cis+trans* cyclopropanes.

References

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