

Hydrosilylation of 1-hexyne promoted by acetone solvated gold atoms derived catalysts

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Abstract

Supported gold nanoparticles, prepared by deposition of acetone solvated Au atoms on supports as carbon and γ -Al₂O₃, behave as valuable catalysts for the regioselective hydrosilylation of 1-hexyne with different silanes. The catalytic behaviour of gold-based systems is compared with the activity of supported platinum catalysts and a different affinity between the metals and the silanes is observed.

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1. Introduction

The hydrosilylation of carbon–carbon multiple bonds provides a very convenient route to the preparation of organo-silicon compounds which have found industrial application to photo resistors, semiconductors, adhesives, binders and represent an important class of reagents for organic synthesis [1]. A considerable number of organometallic complexes containing Pt, Pd, Ir, Ru, Rh, Ni [2] and also supported metals [3,4] have been employed as catalysts for the hydrosilylation of organic molecules, while gold has been thought to be chemically inert for long times. Only in 2000 Hosomi and co-workers [5] described the first example of silanes addition to aldehydes using a catalytic amount of a AuCl(PPh₃).

Considering the high affinity of Au for carbon–carbon triple bonds [6], we investigated the catalytic properties of supported gold nanoparticles in the hydrosilylation of acetylenes. Here we report our preliminary results on the hydrosilylation of terminal alkynes using Au/C and Au/ γ -Al₂O₃ as catalysts, and their comparison with the performances of highly regioselective platinum based catalysts.

2. Results and discussion

Gold nanoparticles were prepared using the metal vapour synthesis (MVS) technique [7]. According to the procedure early described by Klabunde [8], gold was vaporised under vacuum and deposited on the inside walls (cooled to –196 °C) of a glass reactor simultaneously with vapours of acetone. A deep purple solid matrix was obtained which gave, on melting, “gold atoms” solvated by CH₃COCH₃ molecules (0.3 mg

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Au/ml acetone). This solution was added to a proper amount of the support (carbon or γ -Al₂O₃) and stirred at room temperature until the liquid phase became colourless. The organic layer was then removed via syringe and the powdered catalyst was dried under vacuum at room temperature. A Au/C 0.1% w/w and a Au/ γ -Al₂O₃ 0.1% w/w species were thus obtained. HRTEM indicated that in both catalysts metal particles are well dispersed onto the support (representative images in Fig. 1), and exhibit a narrow size distribution with a mean diameter of 4.0 nm (histograms in Fig. 1).

As reference systems, Pt/C and Pt/ γ -Al₂O₃ MVS catalysts, having the same metal loading (0.1% w/w), and the metal particle size narrowly distributed around 2.0 nm, were used. We had previously reported [4] that these MVS platinum species were very good catalysts for a selective *syn* addition of hydrosilanes to unsaturated substrates.

1-Hexyne was chosen as model compound for the reaction of hydrosilylation and treated with several silanes having different steric and electronic properties. In a typical experiment, an excess of the alkyne was reacted with the hydrosilane at 70 °C in the presence of a catalytic amount of Au/C (0.1% w/w). The obtained results are described in Table 1 and compared with the data previously obtained using the MVS Pt/C catalyst [4].

As evident from the table, the gold promoted reaction resulted highly regio- and stereoselective. Indeed, the hydrosilylation of a terminal acetylene such as 1-hexyne can yield three isomeric products: β -(Z), β -(E) and α (Table 1, upper part) and their distribution markedly depends upon the nature of the catalyst. The MVS Au/C specie clearly favours the formation of the trans isomer β -(E) which is almost the only product obtained

(Table 1, entries 2–4). Moreover, the catalytic properties (expressed as specific activity) of the carbon supported gold nanoparticles were strictly related to the structure of the hydrosilane. Et₃SiH and Me₂PhSiH resulted the most reactive compounds, while very polarised silanes such as (EtO)₃SiH showed low conversion (34%) and chloro functionalised reagents (Cl₂MeSiH) yielded no products.

These data are in contrast with the well known affinity between platinum catalysts and chlorosilane [1,2]. Indeed using the Pt/C MVS catalyst (0.1% w/w) [4] a reverse order of specific activity was observed and Cl₂MeSiH was completely consumed after 2 h at room temperature (Table 1, entry 5). On the other hand, in the presence of aliphatic and aromatic silanes (Table 1, entries 7,8) longer reaction times were necessary to improve the conversion of the reagents and a considerable loss of regioselectivity was detected, i.e., the yield of the α -isomer increased until around a 20% of the product mixture.

It is of interest to notice that the observed difference in specific activity between the Au/C catalyst and the Pt/C catalyst towards Et₃SiH and Me₂PhSiH should be even larger by taking into consideration the surface metal atoms, as Au particles (mean size 4.0 nm) have a lower surface/volume ratio than the Pt ones (mean size: 2.0 nm).

The peculiar catalytic behaviour of the Au catalyst appeared independent on the type of support. As reported in Table 2, a Au/ γ -Al₂O₃ catalyst exhibited exactly the same order of reactivity detected for Au/C, i.e., the best specific activities (6440–8000) were obtained using Me₂PhSiH and Et₃SiH (Table 2, entries 3,4). As already observed for the carbon supported gold nanoparticles (Table 1), the reaction proceeds with high

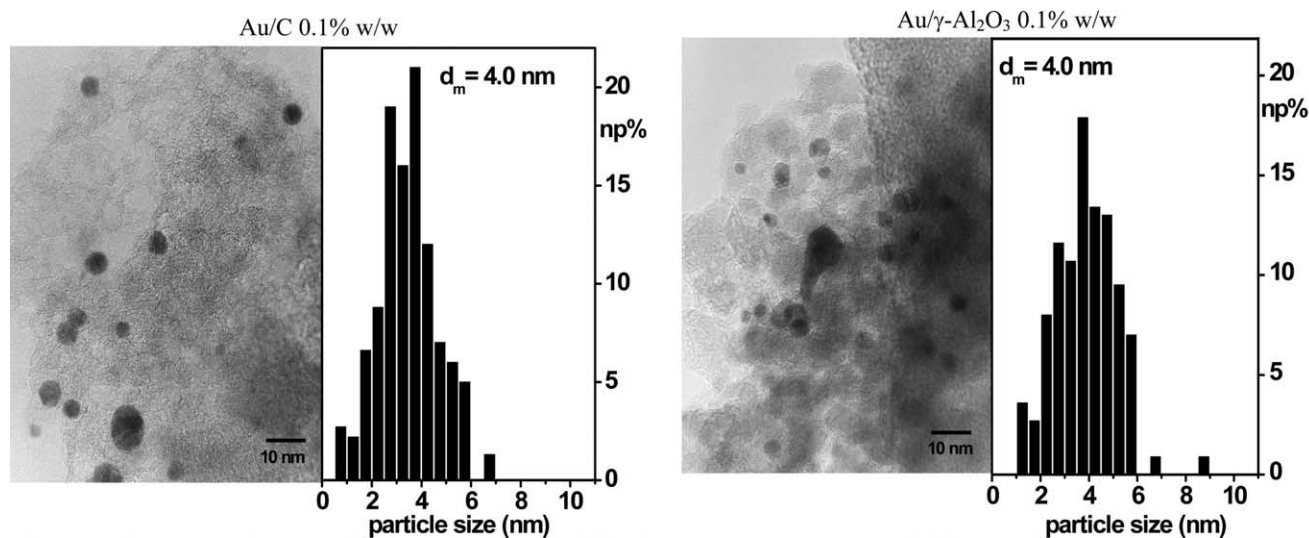


Fig. 1. Electron micrographs (original magnification 200,000 \times) and histograms of particle size distribution of Au/C 0.1% w/w and Au/ γ -Al₂O₃ 0.1% w/w.

Table 1

Hydrosilylation of 1-hexyne promoted by carbon supported catalysts^a

Entry	R ₃ SiH	t	Conv (%) ^b	Product distribution (%) ^c			Specific activity ^d
				β-(Z)	β-(E)	α	
Au/C (MVS) 0.1% w/w							
1	Cl ₂ MeSiH	1 h	0	–	–	–	–
2	(EtO) ₃ SiH	2 h	34	–	98	2	341
3	Et ₃ SiH	1 h	83	–	97	3	1662
4	Me ₂ PhSiH	15'	71	–	98	2	7012
Pt/C (MVS) 0.1% w/w							
5 ^{e,f}	Cl ₂ MeSiH	2 h	100	–	95	5	4166
6 ^f	(EtO) ₃ SiH	2 h	100	–	78	22	3571
7 ^f	Et ₃ SiH	7 h	85	–	86	14	867
8 ^f	Me ₂ PhSiH	4 h	68	–	79	21	2267

^a Experimental conditions: 1-hexyne = 8 mmol; silane = 2 mmol; catalyst = 1.5×10^{-4} – 3×10^{-3} mg-atom Au or Pt; 70 °C; all reactions carried out without solvents.

^b GC conversion of the silane.

^c Isomeric ratio derived from GC areas and ¹H NMR integrals of the olefinic protons.

^d Specific activity calculated as moles of silane converted/g-atom of metal per hour.

^e Reaction performed at 25 °C.

^f See [4].

Table 2

Hydrosilylation of 1-hexyne catalysed by γ -Al₂O₃ supported catalysts^a

Entry	R ₃ SiH	t	Conv (%) ^b	Product distribution (%) ^c			Specific activity ^d
				β-(Z)	β-(E)	α	
Au/ γ -Al ₂ O ₃ MVS (0.1% w/w)							
1	Cl ₂ MeSiH	1 h	0	–	–	–	–
2	(EtO) ₃ SiH	1 h	88.5	–	92	8	1770
3	Et ₃ SiH	15'	80.5	3	93	4	6440
4	Me ₂ PhSiH	15'	100	–	99	1	8000
Pt/ γ -Al ₂ O ₃ MVS (0.1% w/w)							
5 ^e	Et ₃ SiH	15'	52	–	88	12	4208

^a Experimental conditions: 1-hexyne = 8 mmol; silane = 2 mmol; catalyst = 10^{-3} mg-atom Au or Pt; 90 °C; all reactions carried out without solvents.

^b GC conversion of the silane.

^c Isomeric ratio derived from GC areas and ¹H NMR integrals of the olefinic protons.

^d Specific activity calculated as moles of silane converted/g-atom of metal per hour.

^e See [4].

regioselectivity, the β-(E) isomer being formed in major amount.

Once again, in the 1-hexyne silylation with Et₃SiH lower catalytic efficiency and regioselectivity were obtained by using the Pt/ γ -Al₂O₃ catalyst (Table 2, entry 5 vs. entry 3).

In conclusion, we have found that solvated gold atoms derived catalysts are very efficient for the hydro-

silylation of terminal acetylenes. High yields and almost 100% selectivity towards the β-(E) isomer formation make these gold systems a very good alternative to more expensive Pt-catalysts in the hydrosilylation reaction and a quite attractive specie for developing new synthetic processes.

Moreover, taking into account the opposite affinity of the gold and platinum derived catalysts towards the

different silanes, it is possible to control the chemoselectivity of the hydrosilylation process. Indeed if Me_2PhSiH or Et_3SiH are to be reacted with a carbon–carbon triple bond a gold catalytic system is requested, while a platinum catalyst must be used in the presence of Cl_2MeSiH .

3. Experimental

All the operation concerning the Metal Vapour Synthesis technique and the catalytic reactions were performed under argon atmosphere. Hydrosilanes and 1-hexyne were distilled and degassed before use. GLC analyses were performed with a DB1 capillary column ($30\text{ m} \times 0.52\text{ mm}$, $5\text{ }\mu\text{m}$) using He as the carrier gas and a flame ionisation detector (FID). ^1H NMR spectra were recorded with a Gemini 200 MHz instrument, in CDCl_3 solution using CHCl_3 as internal standard. The metal concentration in the MVS solution was determined by atomic absorption spectrometry in an electrochemically heated graphite furnace with a Perkin–Elmer 4100ZL instrument.

Electron micrographs were obtained by a Jeol 2000EX microscope. Before the introduction in the instrument, the samples, in the form of powders, were ultrasonically dispersed in isopropyl alcohol and a drop of the suspension was deposited on a copper grid covered with a lacery carbon film. Histograms of the particle size (d_m) were calculated by using the formula $d_m = \sum d_i n_i / \sum n_i$ where n_i was the number of particles of diameter d_i . At least 300 particles were considered for each sample.

3.1. General procedure for the preparation of the gold MVS supported catalyst

In a typical experiment, gold vapours, generated by resistive heating of an alumina crucible filled with ca. 500 mg of gold pellets, were co condensed at liquid nitrogen temperature with acetone (150 ml) in the glass reactor chamber of the MVS apparatus for ca. 30 min. The reactor chamber was then warmed at the melting point of the solid matrix and the resulting deep purple solution was siphoned at low temperature in a Schlenk tube affording a 0.3 mg Au/ml acetone solution, as determined by atomic absorption analysis.

10 ml (3 mg Au) of the gold/acetone solution were added to a suspension of C or $\gamma\text{-Al}_2\text{O}_3$ (3 g) in acetone (30 ml). The mixture was stirred for 24 h at room tem-

perature. The colourless supernatant solution was removed and the solid was washed with pentane and dried under reduced pressure.

3.2. General procedure for hydrosilylation of 1-hexyne

Catalytic runs have been carried out in Pyrex Carius tubes fitted with rotaflo taps. To a certain amount of Au/support were added via syringe 8 mmol (0.91 ml) of 1-hexyne and 2 mmol of the silane. The suspension was stirred for a chosen time at the reported temperature, filtered on celite and the filtrate evaporated under vacuum to remove the excess 1-hexyne. The crude products were characterised by GC analysis and ^1H NMR proton signals.

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