

Hydrogenation over Supported Gold Catalysts

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Summary Gold on silica, or on γ -alumina, or on boehmite, prepared by thermal decomposition of impregnated chloroauric acid at 383—403 K, and by other methods, activates molecular hydrogen and catalyses the hydrogenation of mono-olefins, buta-1,3-diene, and but-2-yne.

According to the literature, gold does not activate molecular hydrogen below about 473 K,¹ nor is it a hydrogenation catalyst unless hydrogen atoms are supplied to the surface by dehydrogenation of an organic molecule (*e.g.* formic acid,² or by discharge of protons,³ or by diffusion from within.⁴ We have found that by impregnating either silica gel (Davidson 70), γ -alumina (Degussa), or boehmite (Caywood Wharton Refractories Ltd.) with HAuCl_4 (Specpure; Johnson Matthey Chemicals Ltd.) in aqueous solution, and drying the product at 383—403 K, decomposition to mauve products containing metallic gold occurs within 48 h provided the gold concentration does not exceed about 1% w/w (see Table 1 for details). Materials

having higher gold concentrations require reduction in hydrogen at 370—520 K, or in hydrazine solution at about 310 K, and are then red or brown in colour. We have examined by electron microscopy all the $\text{Au}/\gamma\text{-Al}_2\text{O}_3$ catalysts listed in Table 1, as well as the 5% and 0.05% Au/SiO_2 catalysts. All contained gold particles up to 50 nm in size; particles as large as this are not commonly encountered in supported metal catalysts. There was no discernible trend of mean particle size with metal concentration.

Treatment of Au/SiO_2 (5% w/w) at 368 K with D_2 produces HD and H_2 ; repetition of the treatment leads to extensive exchange of the silica hydroxy-groups (5×10^{21} H atoms exchanged per g catalyst).

Gold-catalysed hydrogenation and isomerization of pent-1-ene have been studied in a continuous-flow reactor at 373 K; turnover numbers obtained with two catalysts, and the conditions used, are shown in Table 1. The hydrogenation activity of Au/SiO_2 catalysts passes through a minimum

at 1% Au; some difficulty has been experienced in reproducing the activity of these catalysts, and those which are active show a decrease in conversion with time through the formation of carbonaceous residues. Au/ γ -Al₂O₃ catalysts are less active in hydrogenation. Of the Au/SiO₂ and Au/ γ -Al₂O₃ catalysts studied, only those having 5% Au catalyse double-bond migration.

TABLE 1. Apparent turnover numbers* for pent-1-ene hydrogenation over supported gold catalysts

% wt. Au	Apparent turnover number × 10 ³	
	Au/SiO ₂	Au/ γ -Al ₂ O ₃
5.0	0.40 ^a	0.15 ^a
1.0	0.01 ^a	0.02 ^b
0.25	0.87 ^a	0.01 ^b
0.05	11.9 ^b	0.03 ^b
0.01	72.3 ^b	0.00 ^b

* Average activities (0.2 g catalyst, 373 K, pent-1-ene (161 ± 7 N m⁻²) and hydrogen (101 kN m⁻²), flow rate 10 cm³ min⁻¹) were measured after 60 min and converted to an apparent turnover number (number of pentane molecules formed per second/total number of gold atoms).

^a Reduction in hydrogen.

^b Decomposition in air.

The reaction of C₂H₄ with D₂ takes place on 5% Au/SiO₂ at 368 K (ca. 12 kN m⁻² of each reactant, static system), but is accompanied by exchange of hydrogen atoms in the catalyst, and the resulting mass balance is poor; however, after their complete exchange, satisfactory mass balances are obtained. All possible deuteriated ethylenes and ethanes appear at both 368 and 448 K, their distribution at

448 K closely resembling that shown by Pt/Al₂O₃ at 423 K.⁵

Hydrogenation of buta-1,3-diene and of but-2-yne occurs over 1% Au/boehmite between 400 and 490 K (H₂, 26 kN m⁻²; hydrocarbon, 13 kN m⁻²; static system); the products are solely n-butene isomers (see Table 2). 1% Au/ γ -alumina is also active for hydrogenation of buta-1,3-diene. A comprehensive study of this substance's reaction with D₂ has been performed with these catalysts.

TABLE 2. Distribution of n-butene isomers formed by hydrogenation of buta-1,3-diene and of but-2-yne over 1% Au/boehmite

Reactant	<i>cis</i> - But-2-ene	<i>trans</i> - But-2-ene	But-1-ene
	But-2-ene	But-2-ene	
Buta-1,3-diene	20%	20%	60%
But-2-yne	80%	10%	10%

We are at a loss to understand why these catalytic properties of gold have not been reported before, especially since the preparative methods we have used are in no way remarkable. We are sure that the observed activity is due solely to gold, since spectrographic analysis of the HAuCl₄ by its supplier failed to detect impurities other than Si (3 p.p.m.) and Fe, Cu, and Ag (totalling 1 p.p.m.). We believe that making the gold particles at 380–400 K either introduces a large number of defects which are active sites for hydrogen dissociation, or alternatively that activity resides in some very small particles not sensed by electron microscopy.

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