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Gold catalysis in chemical processing

Graham J. Hutchings*

Department of Chemistry, Cardiff University, P.O. Box 912, Cardiff, Wales CF10 3TB, UK

Abstract

It is now apparent that a potential role exists for Au catalysts in the field of chemical processing, in contrast to pollution abatement. This development is prompted by the observation that supported gold catalysts can be a catalyst of choice for some reactions. The recent literature concerning two of these reactions is briefly reviewed in this article, namely: (a) the hydrochlorination of ethyne to produce vinyl chloride; (b) the hydrogenation of α, β unsaturated aldehydes to produce the unsaturated alcohol. For the first of these examples, a correlation between the catalyst activity and the standard electrode potential was used as the basis for predicting that gold would be the best catalyst for this reaction. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Hydrochlorination; Selective hydrogenation; Gold; Standard electrode potential; Chemical processing

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1. Introduction

During the last 20 years, there has been a renaissance concerning the topic of catalysis by gold [1–3]. Initially, most of this interest has been focused on the exciting discovery that supported gold catalysts, in particular Au/TiO_2 and Au/Fe_2O_3, could oxidise CO to CO_2 at ambient temperature [4–6]. This has prompted a considerable body of research on this reaction [2,3]. However, at much the same time, gold was predicted to be the most active catalyst for the synthesis of vinyl chloride from ethyne hydrochlorination [7] and this was subsequently confirmed [8–11]. Recently, the use of supported Au catalysts in other reactions producing chemical intermediates has shown that oxidation reactions and synthesis gas reactions can all be expected to be catalysed by supported gold catalysts. In this respect, we have shown that Au/ZnO catalysts can be highly effective for the selective hydrogenation of α, β unsaturated aldehydes to produce the unsaturated alcohol [12,13]. In this article, the experimental observations concerning two reactions, namely: (a) the hydrochlorination of ethyne; (b) the hydrogenation of crotonaldehyde, will be briefly reviewed.

2. Hydrochlorination of ethyne: prediction of enhanced activity of gold catalysts

The heterogeneously catalysed addition of HCl to ethyne is a synthetic route for the production of vinyl chloride. Mercuric chloride, supported on activated carbon, is often used as a catalyst commercially [14] but, unfortunately, this catalyst rapidly deactivates. The high rate of deactivation, together with the toxicity associated with mercury compounds, has prompted many studies concerning the search for alternative catalysts. In this respect, one of the most extensive studies of metal chloride catalysts was carried out by Shinoda [15]. In this study, 20 metal chlorides supported on carbon were investigated for ethyne hydrochlorination (Fig. 1), and it was proposed that a correlation existed

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* Tel.: +44-29-2087-4805; fax: +44-29-2087-4075.
E-mail address: hutch@cardiff.ac.uk (G.J. Hutchings).

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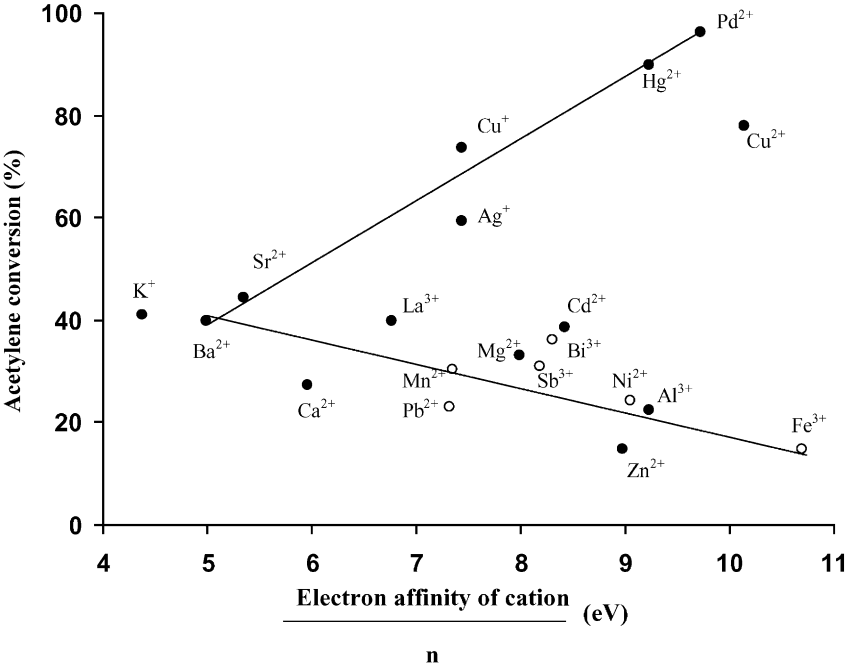

Fig. 1. Correlation of hydrochlorination activity of metal chlorides supported on carbon (200 °C, 150 h^{-1}) with electron affinity of the cation divided by the metal valence (from Ref. [15]). Solid symbols denote cations that can form a metastable acetylide.

between the catalytic activity and the electron affinity of the metal cation, divided by the metal valence. The correlation consists of two straight lines and, for this reason, cannot be used predictively. However, electron affinity is necessarily, a one-electron process, whereas the hydrochlorination of ethyne is more likely to be a two-electron process, involving 2π electrons of ethyne. Many of the metal cations investigated in the original study of Shinoda [15] (Fig. 1) are divalent and, consequently, the standard electrode potential was proposed as a more suitable correlation parameter. Fig. 2 shows the catalytic data for Fig. 1 re-plotted

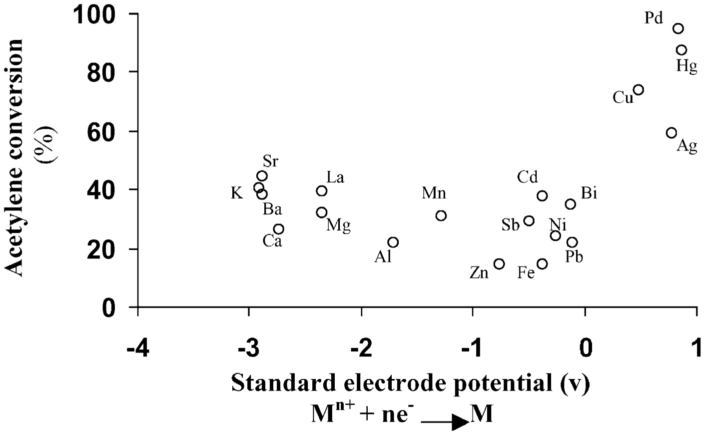

Fig. 2. Correlation of hydrochlorination activity of metal chlorides supported on carbon with the standard electrode potential (from Ref. [7]).

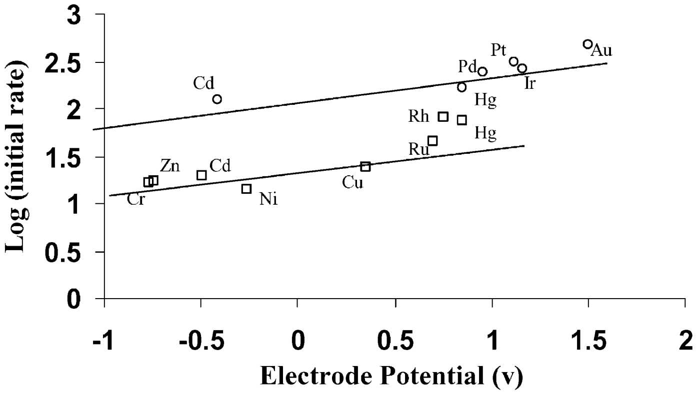

Fig. 3. Correlation of initial activity for the hydrochlorination of ethyne with the standard electrode potential of the metal cation. (○) Catalysts contain 0.0005 mol metal/100 g catalyst; (□) catalysts contain 0.005 mol metal/100 g catalyst.

against the standard electrode potential. The data fall on a smooth curve and, hence, can be satisfactorily represented by a single function. The importance of this observation is that this correlation can be used predictively, since any metal cation with an electrode potential higher than that of Hg^{2+} or Pd^{2+}, the two catalysts with the highest activity (Figs. 1 and 2), would be expected to give enhanced activity. On the basis of this correlation, gold was predicted to be the most active catalyst for ethyne hydrochlorination [7] and this was subsequently confirmed [8–11], and data from these studies are shown in Fig. 3. Indeed, under appropriate conditions, supported catalysts are considerably more active than mercuric chloride and the best catalysts are obtained using an incipient wetness method in which $HAuCl_4$ was dissolved in aqua region [10,11].

One unfortunate observation for all the supported metal chloride catalysts is that they all deactivate with time on stream when used in a standard fixed bed reactor. However, supported Au catalysts deactivate much less rapidly than other supported metal catalysts and, if high loadings of gold are used (≥1 wt.%), then deactivation is minimised. Interestingly, the deactivation with Au catalysts for ethyne hydrochlorination was found to be temperature dependent, and high rates of deactivation were observed at both high and low temperatures (Fig. 4). The low temperature deactivation was observed to be caused by coke deposition [10], probably the result of surface polymerisation reactions

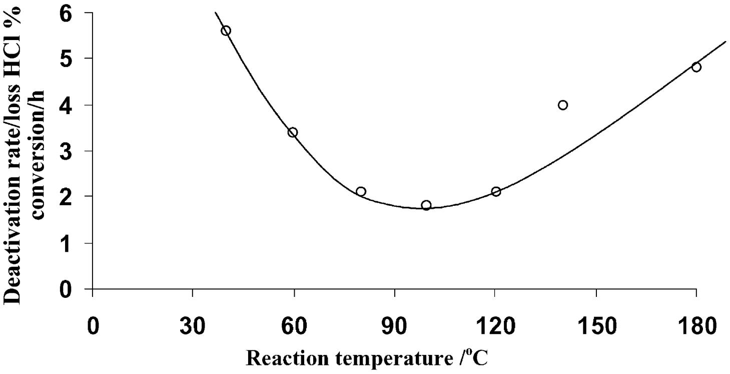

Fig. 4. Deactivation rate of Au/carbon catalysts as a function of temperature. Catalysts contain 0.0005 mol Au/100 g catalyst, C_2H_2:HCl = 1:1.2.

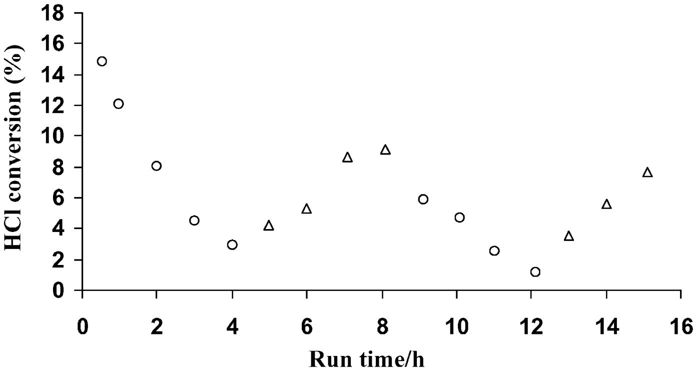

Fig. 5. Effect of in situ NO reactivation of 2 wt.% Au/carbon catalysts. (○) Standard reaction conditions, 180 °C, 3000 h^{-1}, $C_2H_2/HCl/N_2$; (Δ) 0.42 vol.% NO co-fed with reaction gases at 180 °C, 3000 h^{-1}.

of vinyl chloride and ethyne. The high temperature deactivation was probed using ^{197}Au Mössbauer spectroscopy [10] and it was found that this deactivation was due to the reduction of Au(1 1 1) to Au(0).

Although deactivation was observed to be a problem with Au catalysts, in common with other supported metal chloride catalysts, it was found that Au catalysts could be reactivated by treatment off-line with HCl or Cl_2 [11]. However, perhaps the most important observation was that NO could significantly enhance and restore the catalyst activity when co-fed with the reactants (Fig. 5). Indeed, co-feeding NO with the reactants from the start of the reaction showed that deactivation could be virtually eliminated (Fig. 6). Most importantly, no effect on vinyl chloride selectivity was observed during the NO co-feeding experiment [11]. This represents an important example of on-line reactivation of a heterogeneous catalyst.

During use, the commercial carbon-supported mercuric chloride deactivates primarily as the result of loss of mercury from the reactor [14]. This is not the case for gold catalysts since, under the reaction conditions used, no gold is lost from the catalyst. In this case deactivation, as a result of the reduction of Au(1 1 1), is readily overcome by co-feeding NO. Hence, supported gold catalysts should be the catalysts of choice for this reaction.

3. Hydrogenation of crotonaldehyde: an example of Au catalyst promotion by thiophene

In recent years, there has been considerable interest in the design of catalysts for the selective hydrogenation of α, β unsaturated aldehydes to produce the unsaturated alcohol, since this is an important

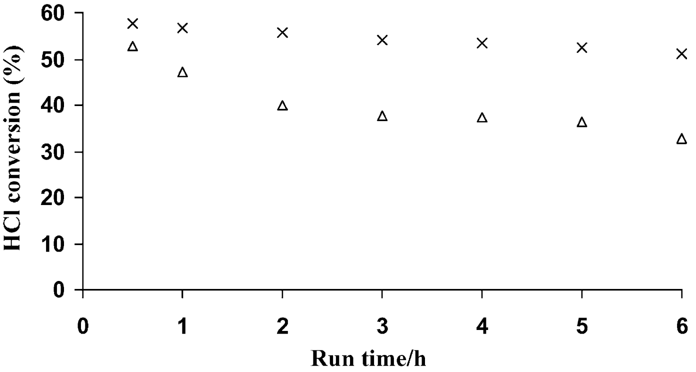

Fig. 6. Effect of in situ reactivation of 2 wt.% Au/carbon catalyst at 180 °C. (Δ) $C_2H_2/HCl/N_2$; (×) 0.42 vol.% NO co-fed with reactants.

intermediate in fine chemical manufacture [16–19]. Interestingly, it was shown [20,21] that thiophene addition to Cu/Al_2O_3 catalyst promoted the catalytic activity for the synthesis of crotyl alcohol from crotonaldehyde hydrogenation.

Relatively little attention has been given to the development of Au-based hydrogenation catalysts and, in particular, the subject of the promotion of Au catalysts has been almost ignored. Until recently, there have been relatively few studies of Au as a hydrogenation catalyst and some studies concerning CO and CO_2 hydrogenation [22–24] and alkadiene hydrogenation have been reported [25]. Very recently, we have shown [12] that Au/ZnO catalysts, when appropriately prepared, can be highly selective for the formation of unsaturated alcohols and, furthermore, pre-treatment of the Au catalysts with thiophene can improve the selectivity to crotyl alcohol in the hydrogenation of crotonaldehyde, whilst maintaining catalytic activity (Table 1 and Fig. 7). The best catalysts were observed to be prepared by co-precipitation and the highest selectivities for crotyl alcohol were observed with Au/ZnO and Au/ZrO_2 catalysts. In a subsequent series of experiments [13] we have shown that selectivities to crotyl alcohol ≥80% can be achieved using 5 wt.% Au/ZnO when they are reduced at temperatures significantly higher than 250 °C (Table 2). ZnO in the absence of Au is not active under these conditions. Interestingly, in this case, thiophene pre-treatment does not significantly enhance

Table 1
Crotonaldehyde hydrogenation over 5 wt.% Au catalysts [12][a]

Catalyst	Time (min)	Conversion (%)	Selectivity (%)[b]					
			B–AL	B=OL	B–OL	2EH	2E2H	Others
Au/ZnO	10	41.4	43.8	29.7	10.7	4.6	2.1	9.1
	30	8.7	37.8	47.8	–	–	0.9	13.5
	60	8.9	35.1	51.7	–	–	–	13.2
	180	7.8	34.1	54.1	15.8	1.5	1.1	10.7
S–Au/ZnO	10	27.9	44.5	20.0	–	–	1.6	16.6
	30	9.3	32.3	56.6	–	–	–	11.1
	60	11.1	29.6	60.6	13.7	2.7	–	8.8
	180	10.9	26.8	65.4	5.1	–	–	7.8
Au/ZrO_2	10	30.4	45.1	32.5	5.9	–	–	5.9
	30	18.2	38.8	50.9	7.1	7.8	–	5.2
	60	12.0	49.1	38.2	13.3	8	–	6.9
	150	9.2	54.5	32.1	7.2	–	–	6.3
$S–Au/ZrO_2$	10	21.3	42.3	34.4	5.9	–	–	2.3
	30	14.2	37.9	44.6	4.8	–	–	2.3
	60	12.2	40.8	50.8	–	–	–	2.5
	150	7.3	44.5	47.8	–	–	–	2.9
Au/SiO_2	10	11.2	96.2	–	–	–	–	3.8
	30	23.2	97.7	–	–	–	–	2.3
	60	21.9	97.9	–	–	–	–	2.1
	180	21.6	97.8	–	–	–	–	2.2
$S–Au/SiO_2$	10	8.6	98.2	–	–	–	–	1.8
	30	11.9	98.6	–	–	–	–	1.4
	60	13.3	98.5	–	–	–	–	1.5
	180	14.6	98.4	–	–	–	–	1.6

[a] Reactions were carried out in a continuous flow fixed bed microreactor, 1 bar, crotonaldehyde WHSV $= 0.7\,h^{-1}$, H_2:crotonaldehyde = 14:1, catalyst (0.2 g), 250 °C. Catalyst reduced at 250 °C in situ in a flow of hydrogen.

[b] B–AL: butanal, B=OL: but-2-en-1-ol, B–OL: butan-1-ol, 2EH: 2-ethyl hexanal, 2E2H: 2-ethyl-2-hexenal, other: butane and C_3 molecules.

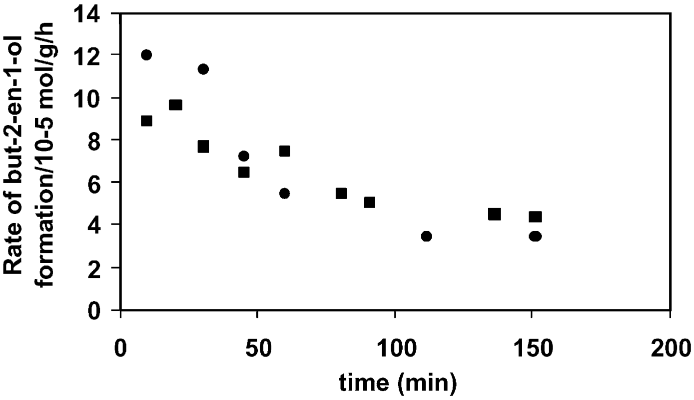

Fig. 7. Effect of thiophene addition on the rate of crotyl alcohol formation ($10^{-5} \times \text{mol}\,\text{h}^{-1}$) over 5 wt.% Au/ZnO. (●) Unmodified; (■) thiophene modified.

Table 2
Effect of reduction temperature on the performance of 5 wt.% Au/ZnO for crotonaldehydehydrogenation at 250 °C[a]

Reduction temperature[b] (°C)	Time (min)	Conversion (%)	Product selectivity (%)[c]					
			B–AL	B=OL	B–OL	2EH	2E2H	Others
250	20	13.1	32.5	50.2	–	2.8	1.4	13.1
	30	8.7	37.8	47.8	–	–	0.9	13.5
	60	8.9	35.1	51.7	–	–	–	13.2
	120	7.6	35.9	51.0	–	–	1.1	12.0
	180	7.8	34.1	54.1	–	–	1.1	10.7
300	20	13	28.6	60.1	–	–	–	11.3
	30	12.3	27.7	57.1	–	4.5	–	10.7
	60	10.8	27.9	56.0	–	5.1	–	11.0
	130	13.5	25.0	63.9	–	2.4	–	8.7
	180	11.8	25.2	62.9	–	2.4	–	9.5
350	20	6.7	26.1	63.8	–	–	–	10.1
	30	3.4	29.5	57.7	–	–	–	12.8
	70	4.5	28.4	61.2	–	–	–	10.4
	120	4.4	28.6	60.8	–	–	–	10.6
	195	3.7	30.6	57.5	–	–	–	11.9
400	20	6.1	18.9	76.5	–	–	–	4.6
	30	7.7	16.4	80.2	–	–	–	3.4
	60	6.3	17.4	79.2	–	–	–	3.4
	120	4.7	17.6	79.6	–	–	–	2.8
	185	5.3	16.1	80.7	–	–	–	3.2

[a] Reactions were carried out in a continuous flow fixed bed microreactor, 1 bar, crotonaldehyde WHSV = $0.7\,\text{h}^{-1}$, H_2:crotonaldehyde = 14:1, catalyst (0.2 g), 250 °C. Catalyst reduced at 250 °C in situ in a flow of hydrogen.

[b] Catalysts calcined at 400 °C, 4 h; treated with H_2 from ambient temperature to the specified reduction temperature prior to cooling to the reaction temperature of 250 °C.

[c] B–AL: butanal, B=OL: but-2-en-1-ol, B–OL: butan-1-ol, 2EH: 2-ethyl hexanal, 2E2H: 2-ethyl-2-hexenal, others: butane and C_3 molecules.

the catalyst performance and, in a detailed study [13] using transmission electron microscopy, we conclude that the high selectivity can be associated with large Au particles ($\geq$10 nm). This is in distinct contrast to previous studies involving supported Au catalysts for which high activity for total oxidation is associated with smaller Au particles, typically in the range 2–5 nm [1–6]. As noted earlier, a number of recent studies have indicated that supported Au catalysts are now being considered for the synthesis of chemical intermediates, for example Au/TiO_2 for the oxidation of propene to propene oxide [26], and Au/α-Fe_2O_3 for the low temperature water gas shift reaction [27–29]. It is possible that reactions requiring the selective synthesis of intermediates may require Au particle size distributions that are considerably different from those known to be optimal for CO oxidation. This clearly indicates an area worthy of further investigation.

4. Concluding remarks

Recent research confirms that supported Au catalysts can be used for the synthesis of chemical intermediates. Indeed, in some cases, as demonstrated for the hydrochlorination of ethyne, supported Au catalysts can give the highest activity and, hence, are the catalysts of choice. For other reactions, interesting selectivity affects can be anticipated when Au catalysts are used, as demonstrated for the hydrogenation of crotonaldehyde, when crotyl alcohol can be synthesised with a selectivity $\geq$80%. In addition, a research area that requires further attention concerns the search for promoters for Au catalysts. Our initial study has shown that sulphur can act as a promoter for Au catalysts for selective hydrogenation of α, β unsaturated aldehydes.

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