Edited by A. Stephen K. Hashmi
and Dean F. Toste

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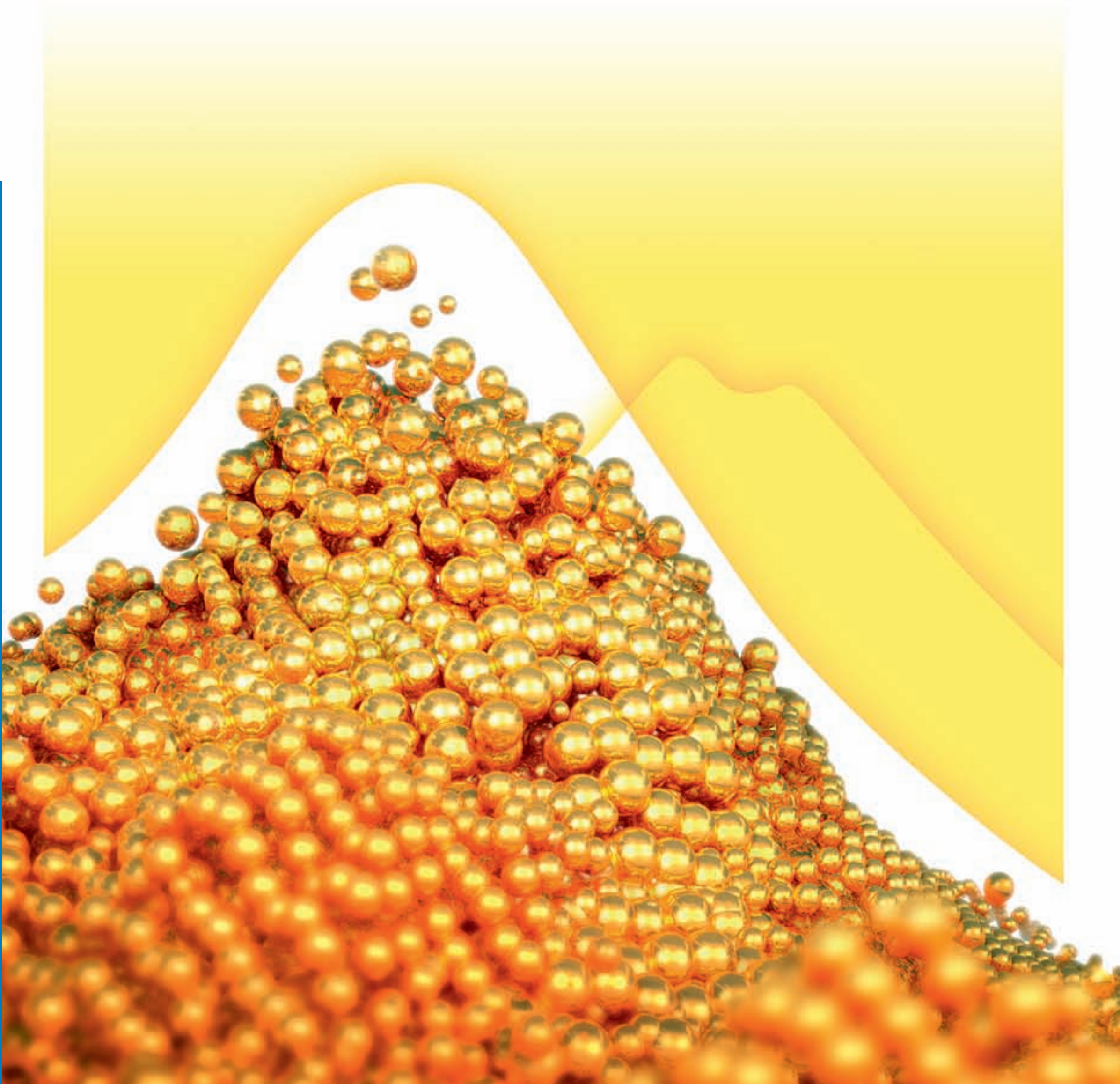
Modern Gold Catalyzed Synthesis



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1

Hydrochlorination of Acetylene Catalyzed by Gold

Marco Conte and Graham J. Hutchings

1.1

Introduction

In recent years, there has been a revolution in the chemistry of gold. Until recently, gold had been considered to be less reactive than its neighbors in the periodic table (Figure 1.1) owing to it being the most noble of metals, having the highest standard electrode potential. Indeed, until very recently, there had been the perception that gold would be unreactive in catalytic applications. As gold does not chemisorb O_2 as a bulk metal, it was considered that gold could not be effective in redox applications. As this was the perceived wisdom, then it is unsurprising that the exceptional catalytic activity of gold lay undiscovered for so long. For it is only when gold is prepared in nanoparticulate form or as soluble complexes that its high activity is observed.

The traditional view of gold as an unreactive immutable metal has inspired great works of art and literature. In the late nineteenth century Kipling wrote about the relative roles of the coinage metals (gold, silver and copper) and iron in society:

> "*Gold is for the mistress – silver for the maid –*
>
> *Copper for the craftsman, cunning at his trade.*
>
> '*Good!' said the Baron, sitting in his hall,*
>
> '*But iron – cold iron – is ruler of them all*'."
>
> from *Cold Iron*
>
> Rudyard Kipling

At that time, gold was used mainly in coinage and in artwork, whereas iron had underpinned the industrial revolution and was at the heart of the manufacturing industry. It is no wonder that iron was the prized commercial metal. This traditional view has now been overturned and currently there is an amazingly rich chemistry of catalysis based on gold nanoparticles and complexes. It is over 25 years since the prediction was made that gold would be the best catalyst for the hydrochlorination

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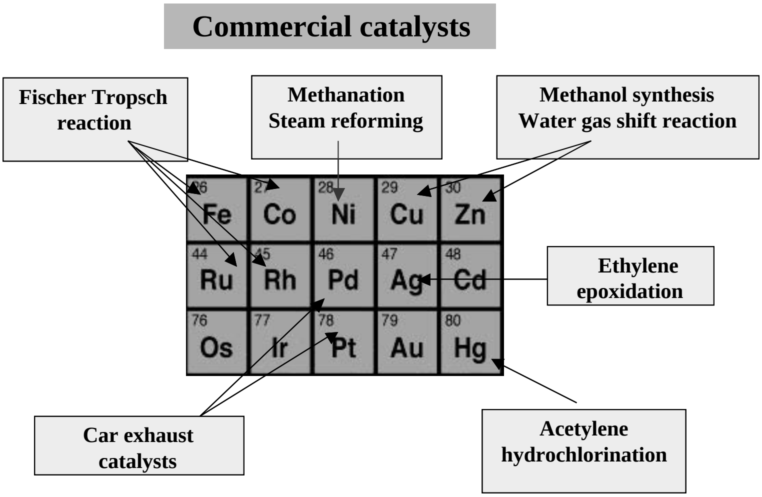


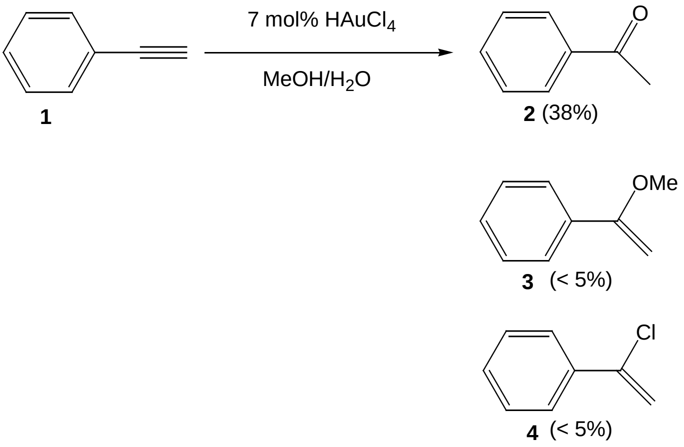
Figure 1.1 Examples of commercial catalysts using elements near gold in the periodic table.

of acetylene. Since then, there has been a phenomenal growth in gold-based reactions of acetylenes and a very rich field of homogeneous catalysis based on gold has been established. To date, gold is still the best catalyst for acetylene hydrochlorination, in addition to being the catalyst of choice for the low-temperature oxidation of carbon monoxide. In this chapter, we introduce the reactions of gold and acetylenes and set out in greater detail the discovery and chemistry of gold as a catalyst for acetylene hydrochlorination.

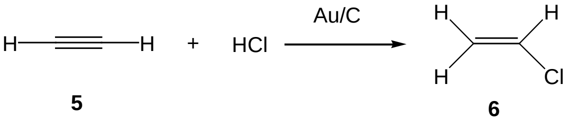
1.2
Reactions of Alkynes Using Gold Chloride as Catalyst

The discovery that cationic gold supported on carbon is a highly effective catalyst for hydrochlorination of acetylene to vinyl chloride led over the years to a surge of applications of gold salts involving alkyne-based substrates [1, 2]. These include hydrofluorination [3], hydration [4, 5], hydroxylation [6], and hydrocarboxylation [7] reactions, and also hydroamination [8] and reactions over alkynes containing proximate oxygen nucleophiles [9]. Some of these reactions will be briefly described in this section; however, it should be noted that one of the first uses of Au^{3+} salts for catalytic purposes can be traced back to Thomas and co-workers in 1976 [10] in the oxidation of phenylacetylene (**1**) in aqueous methanol in presence of $HAuCl_4$, which gave the ketone **2** as the major product, followed by the ether **3** and the chlorinated vinyl adduct **4** (Scheme 1.1).

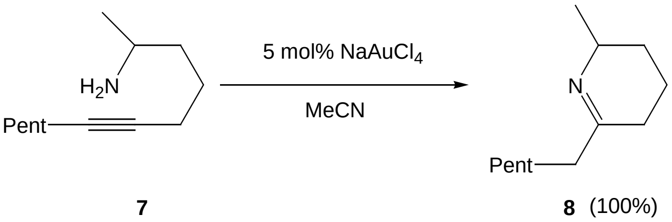
However, despite a turnover number of ~6 in this reaction, the role of gold was merely assigned as a reagent and not as a catalyst. It was almost 10 years later, in 1985 [11], that the role of cationic gold was recognized in full as it was the best catalyst for the hydrochlorination reaction of acetylene (**5**) to vinyl chloride monomer (VCM) (**6**) and can be considered as a milestone for revealing cationic gold as an effective catalyst (Scheme 1.2).



Scheme 1.1 Reaction of phenylacetylene (**1**) with tetrachloroauric acid in aqueous methanol. The ketone **2** is the major product, which is obtained by Markovnikov addition. Minor amounts of methyl vinyl ethers (**3**) and vinyl chlorides (**4**) are obtained.



Scheme 1.2 Hydrochlorination of acetylene (**5**) to vinyl chloride monomer (**6**). The reaction occurs at 180 °C and is catalyzed by an Au/C catalyst on which the active sites are Au^{3+} centers.

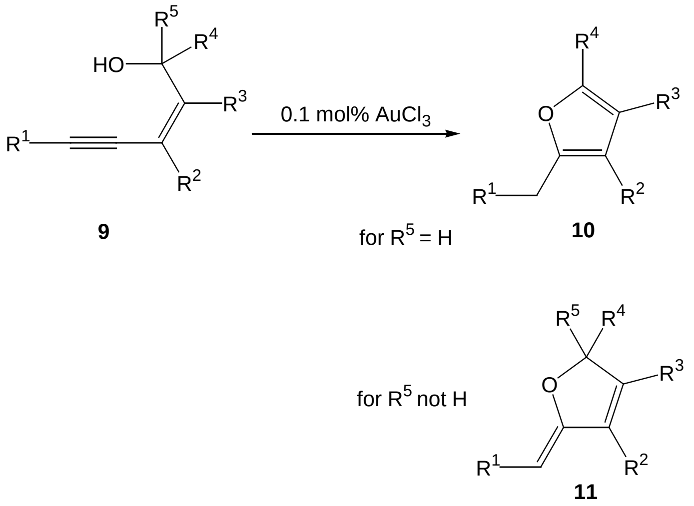


Scheme 1.3 Intramolecular addition of amine **7** to cyclic adduct **8**, using sodium tetrachloroaurate as the catalyst.

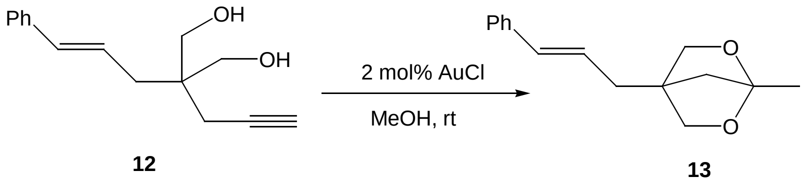
Soon afterwards, in 1987, the intramolecular addition of amines to triple bonds (**7**) to yield cyclic adducts (**8**) with $NaAuCl_4$ as catalyst was reported [12] (Scheme 1.3).

Addition of alcohols to alkynes has also been successfully achieved [13], as shown by the cyclization of (*Z*)-3-ethylallyl alcohols (**9**), which can cyclize to furans (**10** and **11**) (Scheme 1.4).

Moreover, if two alcohol functional groups are present, such as in **12**, it is even possible to obtain bicyclic ketals such as **13** by means of AuCl or $AuCl_3$ (Scheme 1.5) [14].



Scheme 1.4 Cyclization of (*Z*)-3-ethylallyl alcohols (**9**) to furans, with R^5 = hydrogen to yield **10** or R^5 = alkyl to yield **11**.



Scheme 1.5 Intramolecular reaction from the alcohol **12** to the bicyclic ketal **13**. The reaction can be catalyzed by AuCl or $AuCl_3$.

The interest in the latter reaction also relies on the circumstance that Au^{3+} is active towards carbon–carbon triple bonds, but not towards carbon–carbon double bonds. Analogies can be found also in the hydrochlorination reaction of acetylene, where Au/C-based catalysts are unreactive towards ethylene [15], making them suitable for selective chemical synthesis.

1.3
The Correlation of *E*° with the Activity of Gold for the Hydrochlorination of Acetylene

1.3.1
The Initial Correlation

In this section, we demonstrate how the activity of gold can be correlated with the standard electrode potential (*E*°) of the metal used to carry out the hydrochlorination reaction and how this correlation can predict gold to be the most effective metal for the catalytic hydrochlorination of acetylene.

1.3.2
Conceptual Developments of the E° Correlation

Several metallic salts supported on carbon, such as $HgCl_2$, are capable of carrying out the catalytic hydrochlorination of acetylene. The reaction is exothermic ($\Delta H^\circ = -99\ \text{kJ mol}^{-1}$) but in the absence of a catalyst no reaction occurs. Detailed kinetic studies were carried out during the 1960s, identifying the addition of HCl to adsorbed C_2H_2 to produce vinyl chloride as the rate-determining step of the reaction [16–18]. This led initially to a search for metallic salts that could lead to both stable metal–acetylene and metal–hydrochloric acid complexes. A number of metallic salts may lead to metastable acetylides, such as Cu, Ag, Au, Na, K, Rb, Zn, Cd, Hg, Pd, Os, Ce, Al, Mg, Ca, Sr, and Ba and also the better known examples of Pt, Ru, Rh, and Ir. As the stability of the acetylide species can be considered as an essential parameter to control the activity, it was initially attempted to correlate the activity of the catalyst with the electron affinity of the metal. However, when this correlation was extended to a wider set of metals, as carried out by Shinoda [19] (Figure 1.2), the correlation with electron affinity was no longer valid even when the electron affinity of the metal was divided by its oxidation state as a correction factor.

In the first instance, this relationship is important because it can correlate the catalytic activity with the formation of metal–acetylene complexes, and consequently provides information on which metal would be best to carry out the reaction. Only

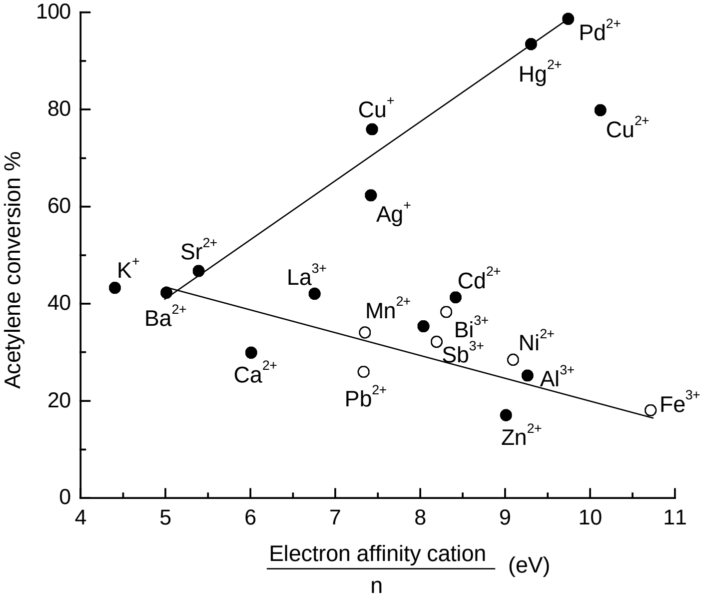


Figure 1.2 Correlation of hydrochlorination activity of different metal chlorides supported on carbon (200 °C, GHSV 150 h^{-1}), with the electron affinity of the cation divided by the metal oxidation state [19].

metals able to lead to the formation of metastable acetylides would be expected to form an active catalyst; in the plot shown in Figure 1.2, the metal species able to form the most stable acetylides are Pd^{2+}, Hg^{2+}, Cu^{2+}, and Ag^{+}, whereas the lower set includes metal cations that can form stable complexes with HCl and act as Friedel–Crafts catalysts.

However, this kind of approach has two strong limitations: (i) if the correlation exists then it consists of a set of two straight lines rather than one, hence, it cannot be used predictably, and (ii) the correlation parameter used is the electron affinity, which by definition takes into account only a single electron process, whereas the addition of HCl to acetylene involves a two-electron process (from acetylene to the metal center). Therefore, it was not considered chemically realistic to associate the formation of a metal acetylide unit to a single-electron process. It was considered that a more suitable correlation would be obtained by using the standard electrode potential rather than electron affinity. It is important to note that all the metal chlorides investigated exist in oxidation state 2+ or 3+ . Plotting the data using the $E°$ value of the metal leads to the plot shown in Figure 1.3.

In this case, a single correlation curve is obtained, which, more importantly, can be used as a predictive model. In fact, metals with higher standard electrode potentials than Pd^{2+} and Hg^{2+} should lead to enhanced activity. This hypothesis, which is at the basis of all the applications of gold as a catalyst, has been confirmed using supported Au^{3+} catalysts (Figure 1.4) [11, 20].

Although gold can be considered the best catalyst in terms of initial activity, it is unfortunately affected by deactivation phenomena, the most important of which has

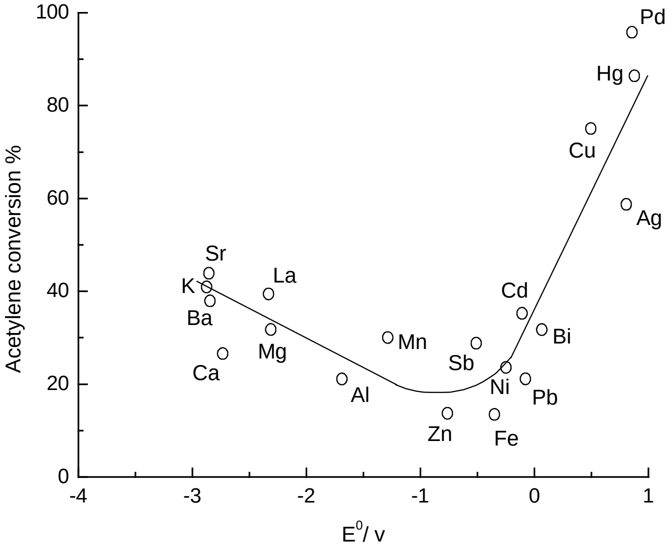


Figure 1.3 Correlation of hydrochlorination activity of different metal chlorides supported on carbon (200 °C, GHSV 150 h^{-1}), with the standard reduction potential of the metal, $M^{n+} + e^{-} \rightarrow M^{(n-1)+}$ [11]. (conversion activity values after ref 19).

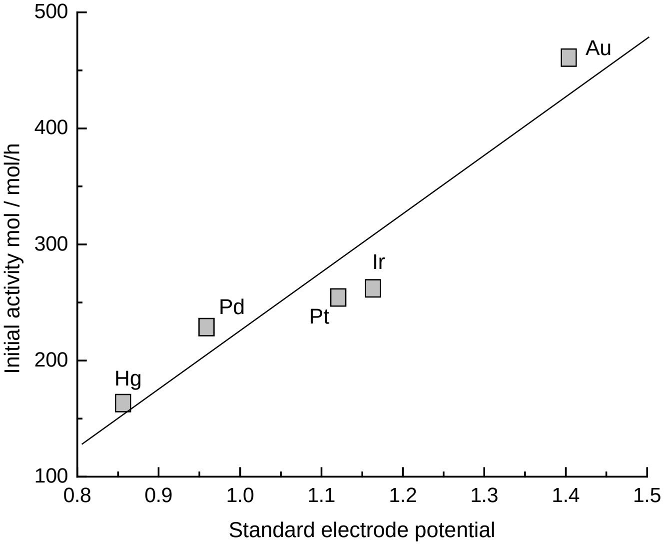


Figure 1.4 Correlation of hydrochlorination activity of metal chlorides supported on carbon (180 °C, GHSV 1140 h^{-1}) with the standard electrode potential. Catalysts contain 0.0005 mol metal/100 g catalyst. It should be noted that in this series, Pt is obtained from a Pt^{2+} precursor [20].

been identified as Au^{3+} reduction [20, 21]; this aspect will be described further in this chapter. A second deactivation pathway involves oligomer formation, and previous observations showed that the deactivation rate is minimum at 100–120 °C (Figure 1.5), but at this temperature the catalyst is not sufficiently active compared

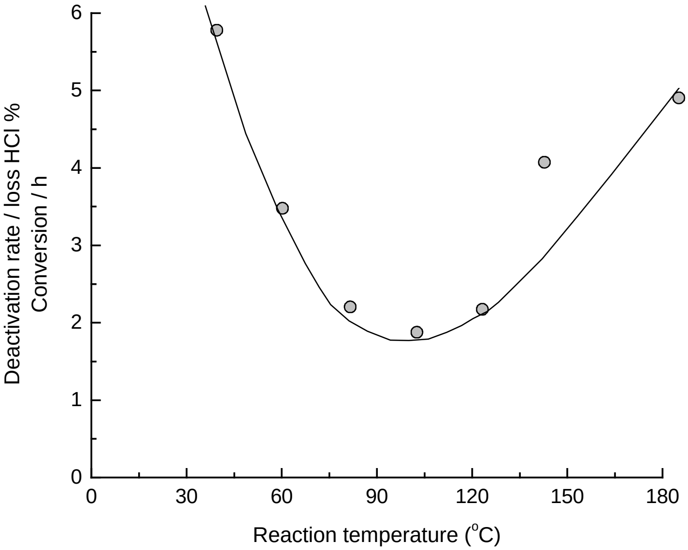


Figure 1.5 Effect of reaction temperature on rate of deactivation (loss of HCl, conversion per hour, averaged over the initial 3 h). Reaction conditions: $C_2H_2 : HCl = 1 : 1.1$ [22].

with temperatures in the region of 180 °C, which is the standard temperature to carry out the reaction over gold on carbon catalysts [22].

Nevertheless, only catalysts containing gold have the interesting properties of being reactivated on-stream by Cl_2, NO, and NO_2 [22] and off-line by aqua regia [23], making them still attractive for the catalytic hydrochlorination of acetylene. In particular, the catalytic synthesis route used in the early studies involved a relatively non-complex impregnation method and it is anticipated that by using enhanced preparation methodologies, catalysts of higher activity and durability will be produced.

1.3.3
Further Study of the Correlation of E° with the Activity of Platinum Group Metals

The correlation of E° with activity has been recently further confirmed using other platinum group metals where the data for the chlorides were used (Figure 1.6) [24].

All the catalysts were obtained using the wetness impregnation technique and aqua regia as solvent. The precursor salts were $HAuCl_4$, $PdCl_2$, H_2PtCl_6, $RhCl_3 \cdot 3H_2O$, $IrCl_3 \cdot 3H_2O$, and $RuCl_3 \cdot 3H_2O$. This trend confirms the previous findings for this reaction, that is, the higher the standard electrode potential, the higher is the activity [11, 25], with the trend: that the Au/C catalyst gave the highest conversion of acetylene, with the following order of initial activity: Au > Ru ≈ Ir > Pd > Pt ≈ Rh. However, there is a notable exception in the above series, as Pt, clearly does not fit the

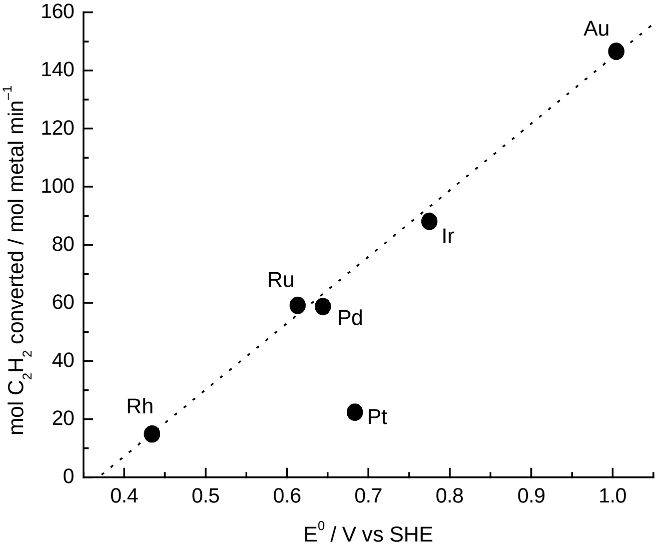


Figure 1.6 Correlation between initial acetylene conversion and the standard electrode potential of platinum group metals. Potentials were obtained from the reduction of the following chloride salts: $RhCl_6^{3-}$, $RuCl_5^{2-}$, $PdCl_2$, $PtCl_6^{2-}$, $IrCl_6^{3-}$, and $AuCl_4^-$. The reaction was carried out at 180 °C, GHSV 870 h^{-1} [24].

data set. In contrast to the original set [11, 20], where Pt^{2+} was used, in this case Pt^{4+} data were used, whereas all the other metals had initial oxidation state 1 + or 2 +, and the reduction of M^{n+} to M^0 was considered. In contrast, in this set [24], Pt has an initial oxidation state of 4 +, we used the reduction Pt^{4+} to Pt^{2+} because the reaction is a two-electron process, and reduction to the metal is unlikely.

Moreover, it is also worth noting that the initial activity displayed by platinum is much lower than that expected from the correlation. This can be explained taking into account that this catalyst deactivates very quickly, and can display dehydrochlorination properties [25]. Moreover, Pt^{4+} usually does not form stable complexes with unsaturated species, and it is often considered inert towards alkyne complex formation [26]. However, iodo–Pt^{4+} complexes, in acidic aqueous or methanolic solutions, catalyze acetylene hydroiodination to vinyl iodide [27], and mechanically activated K_2PtCl_6 can catalyze the hydrochlorination reaction of acetylene [28], but this latter case cannot take into account possible effects induced by the carbon support.

1.3.4
The E° Correlation Applied to Homogeneous and Nonhomogeneous Gold Nanoalloys

Au nanoalloys, such as Au–Pd alloys, can be very efficient catalysts for the direct synthesis of hydrogen peroxide [29] and the oxidation of alcohols to aldehydes [30]. This is not the case for the hydrochlorination reaction. Despite a wide range of alloys containing Pd, Pt, Ru, Rh, and Ir, in different ratios, none except Au–Rh systems (with a 90 : 10 atomic ratio) are capable of increasing the activity of gold for the hydrochlorination reaction during the time on-stream. Apparently, at first sight this a disappointing result with respect to catalyst design. However, it is rather a further demonstration of the validity of the E° correlation and the formation of homogeneous alloy systems. In order to clarify this important aspect of the hydrochlorination reaction, the example of the bimetallic Au–Pd system will be illustrated.

Au and Pd are able to form an alloy at all Au : Pd ratios. This means that, if the total metal loading per catalyst is kept constant, the addition of a second metal to gold leads to dilution of gold by the second metal, in this case Pd, provided that a homogeneous alloy is present. This implies that the addition of a second metal leads to a decrease in the standard electrode potential which is a linear function of the atomic fraction x of the second metal added. This can be explained by calculating E° for a general homogeneous alloy of composition $Pd_xAu_{(1-x)}$.

It is necessary to consider first the following equilibria:

$$x\mathrm{Pd} + (1-x)\mathrm{Au} \rightleftharpoons \mathrm{Pd}_x\mathrm{Au}_{(1-x)} \tag{1.1}$$

$$\mathrm{Pd}^{2+} + 2\mathrm{e}^- \rightleftharpoons \mathrm{Pd} \tag{1.2}$$

$$\mathrm{Au}^{3+} + 3\mathrm{e}^- \rightleftharpoons \mathrm{Au} \tag{1.3}$$

The value of E° for any alloy composition $Pd_xAu_{(1-x)}$ is required:

$$x\mathrm{Pd}^{2+} + (1-x)\mathrm{Au}^{3+} + (3-x)\mathrm{e}^- \rightleftharpoons \mathrm{Pd}_x\mathrm{Au}_{(1-x)} \tag{1.4}$$

The last equation can be obtained as a combination of the equilibria (1.1), (1.2) and (1.3):

$$(4) = (1) + x(2) + (1-x)(3)$$

where 1–4 represent equilibria (1.1–1.4), and therefore

$$\Delta G_4^\circ = \Delta G_1^\circ + x\Delta G_2^\circ + (1-x)\Delta G_3^\circ \tag{1.5}$$

$$-(3-x)FE_4^\circ = \Delta G_1^\circ - 2xFE_2^\circ - 3(1-x)FE_3^\circ \tag{1.6}$$

By using the E° potentials for equilibria (1.2) and (1.3) reported below:

$$\mathrm{Pd}^{2+}_{(aq)} + 2e^- \rightleftharpoons \mathrm{Pd}_{(s)} \quad E_2^\circ = 0.951\,\mathrm{V} \tag{1.7}$$

$$\mathrm{Au}^{3+}_{(aq)} + 3e^- \rightleftharpoons \mathrm{Au}_{(s)} \quad E_3^\circ = 1.498\,\mathrm{V} \tag{1.8}$$

$$E_4^\circ = \frac{-\Delta G_1^\circ}{(3-x)F} + \frac{2xE_2^\circ}{3-x} + \frac{3(1-x)E_3^\circ}{3-x} \tag{1.9}$$

$$E_4^\circ = \frac{-\Delta G_1^\circ}{(3-x)F} + \frac{1.902x}{3-x} + \frac{4.494(1-x)}{3-x} \tag{1.10}$$

$$E_4^\circ = \frac{-\Delta G_1^\circ}{(3-x)F} - \frac{2.592x}{3-x} + \frac{4.494}{3-x} \tag{1.11}$$

In order to calculate finally the value of $E^\circ{}_4$, estimates of ΔG° for the different alloy compositions are required. In the case of $\mathrm{Pd}_x\mathrm{Au}_{(1-x)}$, literature values are available [31], and using the form of the equation reported above it is possible to construct the plot shown in Figure 1.7. It is clear that E° decreases almost linearly from the value for Au to that for Pd with change in composition of the homogeneous nanoalloy.

In view of this effect, we consider that gold will invariably always be the best metal for the hydrochlorination reaction. However, alloys such as Au–Rh with an atomic fraction ratio of 90:10 can actually be better catalysts than those containing only gold (Figure 1.8) [24].

Whereas the Au–Pd catalyst leads to the formation of homogeneous alloys, Au and Rh are basically immiscible in each other. Binary-phase diagrams suggest that Rh has very limited solubility in Au (<1%), and vice versa. However, as the Au–Rh/C catalysts showed VCM selectivities similar to those of undoped Au/C catalysts with no marked deactivation, it is realistic to suggest that the increased activity for the Au–Rh catalysts could be due to a slightly enhanced dispersion of gold and the inability to form homogeneous alloy particles containing substantial quantities of Au and Rh [32–34]. This also gives an insight into how Au-based catalysts with enhanced performances can be prepared, that is, the focus should be on methods of catalyst preparation that can lead to enhanced gold dispersion and improved stabilization of its higher oxidation state.

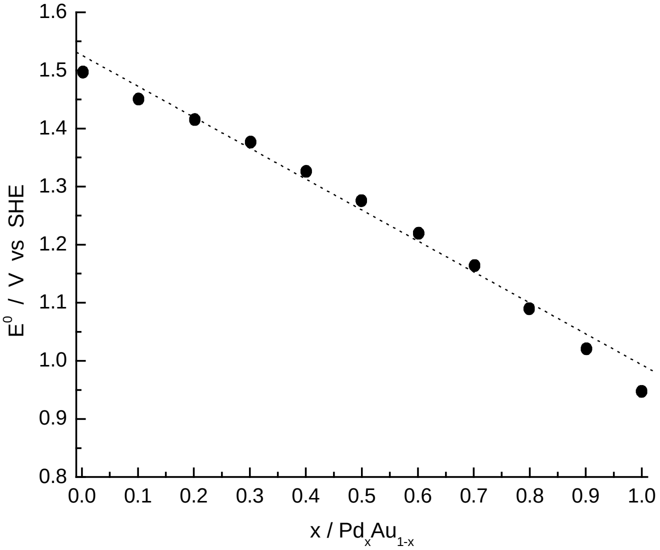


Figure 1.7 Standard electrode potential versus palladium mole fraction in a Pd–Au alloy, according to reactions (1.9–1.11) [24].

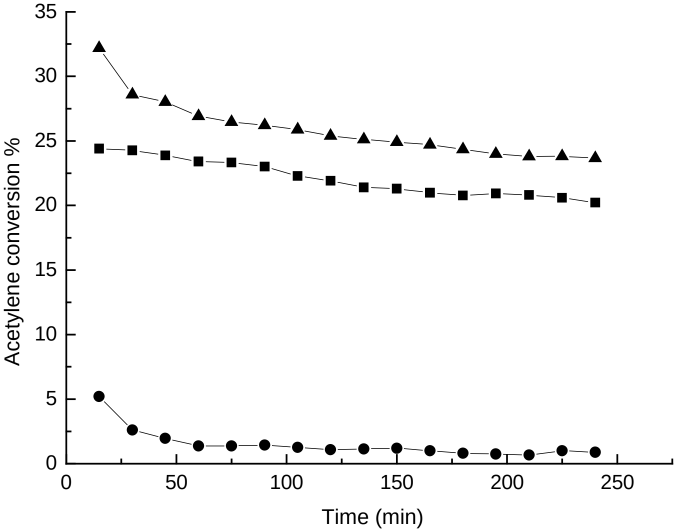


Figure 1.8 Acetylene conversion for (▲) Au–Rh catalyst (90:10 molar ratio), (■) Au, and (●) Rh only using carbon as support. Reaction conditions: 180 °C, GHSV 870 h^{-1} [24].

1.4
Central Role of Au^{3+} and Regeneration of Au/C Catalysts

As described previously, two main routes are responsible for the deactivation of Au/C catalysts: (i) the possible formation of oligomers on the catalyst surface with consequent site blocking and (ii) the reduction of Au^{3+} to Au^0. Whereas the oligomer formation can be minimized by the choice of a suitable reaction temperature, the Au^{3+} reduction is unavoidable. Moreover, it is possible to identify a direct correlation between the activity of Au/C catalysts and the amount of Au^{3+}. This correlation can be obtained by treating Au^{3+} catalysts off-line with aqua regia. In fact, unlike other supports, carbon presents the interesting property that no significant amount of gold is leached from the carbon even if it is treated with boiling aqua regia for a short time (20 min) [23]. Moreover, such treatment can restore the initial gold activity (Figure 1.9). X-ray photoelectron spectroscopic (XPS) characterization of an Au/C catalyst before and after use, and before and after aqua regia treatment, indicated (Figure 1.10) that the activity is related to the presence of Au^{3+}. This experimental result was further confirmed by the use of Mössbauer spectroscopy (Figure 1.11) [20].

In addition to off-line treatment, it is also possible to proceed to time on-stream treatment, by introducing into the reaction mixtures reagents such as HCl, Cl_2, NO, and NO_2, with the most marked effect being displayed by NO [22], which allows full recovery of catalytic activity and slower decay of activity after the catalyst was regenerated. Moreover, when HCl and Cl_2 are compared, Cl_2 leads to a lower deactivation rate for the regenerated catalysts, but also to a slower deactivation if it is used to pretreat the catalysts (Figure 1.12). This indicates that control of the gold oxidation state is of essential importance for the acetylene hydrochlorination reaction.

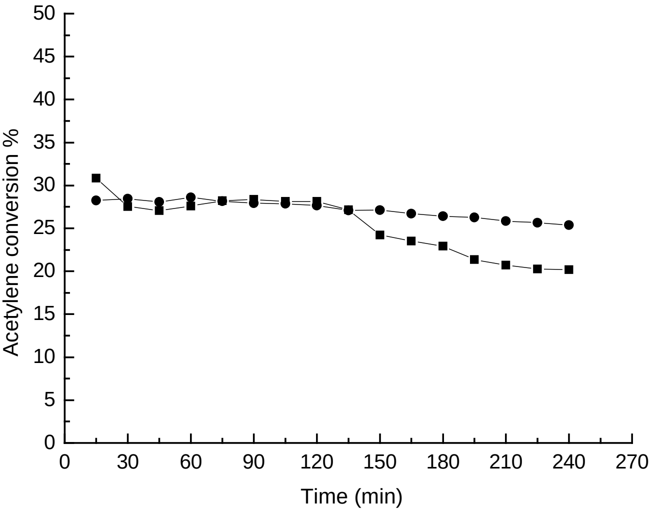


Figure 1.9 Activity trend for the hydrochlorination reaction over Au/C, (■) fresh catalyst and (●) regenerated catalyst using a short treatment with aqua regia. Reaction conditions: 180 °C, GHSV 870 h^{-1} [23].