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Hydrochlorination of Acetylene Using Carbon-Supported Gold Catalysts: A Study of Catalyst Reactivation

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A study of the reactivation of carbon-supported gold catalysts (Au/C) for the acetylene hydrochlorination reaction is described. Au/C catalysts are deactivated by two competing mechanisms: (i) deposition of carbonaceous material, predominantly at low temperature (60–100°C), and (ii) reduction of Au(III), and possibly Au(I), to Au(0), which occurs mainly at higher temperatures (120–180°C). A range of gases have been found to be effective for catalyst reactivation. Air is shown to be effective only for removal of carbonaceous deposits and has no marked effect on the gold oxidation state. However, Cl_2 is shown to be effective in oxidising Au(0) and only short reactivation (1 h at 100°C) is required to restore complete catalytic activity. In addition to Cl_2, NO and N_2O have also been found to be effective and these oxidants can be used during the acetylene hydrochlorination reaction as coreactants to decrease the observed rate of catalyst deactivation. Initial experiments concerning optimisation of the Au/C catalyst are described and the overall experimental data presented suggest that a redox mechanism operates for the formation of vinyl chloride using Au/C catalysts. © 1991 Academic Press, Inc.

INTRODUCTION

Catalysts comprised of $HAuCl_4$ supported on activated carbon have been found to be particularly active for the synthesis of vinyl chloride via the acetylene hydrochlorination reaction (*1–3*). In a study of gold as a catalyst for this reaction, we have found that catalyst deactivation occurs by two processes (*4*). At low reaction temperatures (60–100°C) deactivation is mainly a result of the deposition of carbonaceous residues caused by the polymerisation of vinyl chloride on the catalyst surface. At higher reaction temperatures (120–180°C) the reduction of Au(III), and possibly Au(I), to Au(0) also becomes significant. As a detailed understanding of catalyst deactivation for this system has been obtained, it is possible that methods for catalyst reactivation can be readily identified. In this paper we present a study of catalyst reactivation using both off-line and on-line (i.e., *in situ*) methods.

EXPERIMENTAL

Gold catalysts were prepared according to the following procedure. $HAuCl_4 \cdot 2H_2O$ (subsequently denoted $HAuCl_4$) was dissolved in a small quantity of aqua regia and impregnated onto acid-washed activated carbon (Sorbonorit 3) using the incipient wetness technique. The catalysts were dried at 140°C for 5 h prior to use. Catalysts were investigated for the acetylene hydrochlorination reaction in a fixed bed microreactor using procedures previously described (2).

RESULTS AND DISCUSSION

Reactivation Using HCl

Here 2% $HAuCl_4$/C was utilised as a catalyst for acetylene hydrochlorination (180°C,

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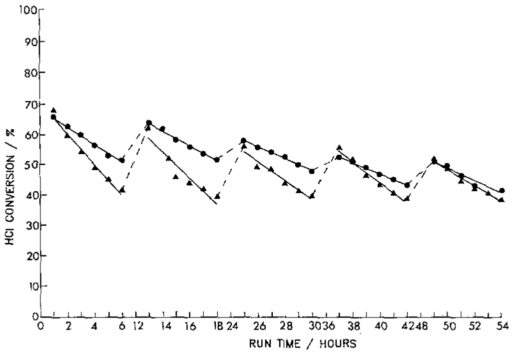

FIG. 1. Effect of HCl treatment on deactivated catalysts. ▲, $C_2H_2 : HCl = 1 : 1$, GHSV = 1140 h^{-1}; ●, $C_2H_2 : HCl = 1 : 1.5$ GHSV = 1420 h^{-1}; ----, HCl reactivation treatment at 180°C, GHSV = 580 h^{-1} for 6 h.

total GHSV = 1140 h^{-1}, $C_2H_2 : HCl = 1 : 1$) and after 6 h the HCl conversion had fallen to 40% from an initial value of 68%. At this time the catalyst was treated in the reactor with HCl only at GHSV = 580 h^{-1} at 180°C for 6 h. Following this treatment the catalyst was reinvestigated for the acetylene hydrochlorination reaction (Fig. 1). It is apparent that the HCl treatment successfully restores the initial catalyst activity almost to that originally observed for the fresh catalyst. However, following a number of repeated deactivation/reactivation cycles, a gradual decrease in the initial activity following reactivation is observed with each subsequent reactivation procedure. Initially it was considered that this may be due to insufficient time being given to the reactivation procedure, so this was subsequently extended to 12 h. The results, shown in Fig. 2 for a catalyst comprising 4% $HAuCl_4/C$, demonstrate a trend identical to that of the 6 h reactivation procedure. Deactivation at this temperature has been previously shown (*4*) to be due to both deposition of carbonaceous material and reduction of Au(III) to the less active Au(0), and Mössbauer spectroscopic studies have confirmed that the Au(0) could be converted to Au(III) by treatment with oxidising agents. It was observed that after a number of deactivation/reactivation cycles the Au/C catalyst pellets changed colour from black to brown, and this has been previously shown by McDougall and Hancock (*5*) to be indicative that the gold salt has been reduced to gold metal. The sequential loss of initial activity was therefore attributed to higher Au(0) levels being present in the catalyst following each reactivation procedure and the primary role of the HCl reactivation was to affect removal of the carbonaceous material.

The observation that off-line HCl treatment can restore almost complete catalytic activity for the gold catalyst indicated that the addition of excess HCl during reaction could provide a useful on-line (i.e., *in situ*) method for catalyst reactivation. A comparison of a stoichiometric reactant mixture ($C_2H_2 : HCl = 1 : 1$) with one containing excess HCl ($C_2H_2 : HCl = 1 : 1.5$) was therefore made and the results are shown in Fig. 1 and Table 1. It is apparent that the increased HCl concentration does decrease the rate of catalyst deactivation, but off-line reactivation is still required. In addition, the same trend in loss of initial activity for subsequent reactivation procedures is observed for both $C_2H_2 : HCl$ reactant mixtures. It is interesting to note that the selectivity to vinyl chloride is unaffected by the excess HCl and remains >99.5%. The gold catalyst therefore does not readily catalyse the conver-

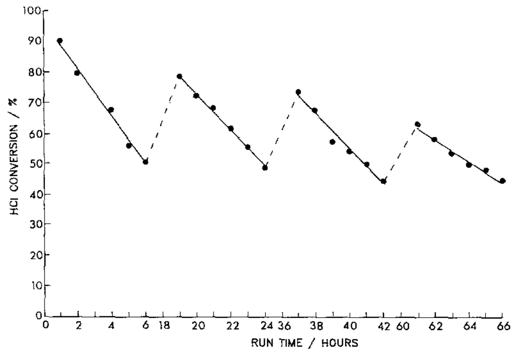

FIG. 2. Effect of HCl treatment on catalysts deactivated for 6 h at 180°C, $C_2H_2 : HCl = 1 : 1$, total GHSV = 1140 h^{-1}; ----, HCl reactivation treatment at 180°C, GHSV = 580 h^{-1}, for 12 h.

TABLE 1

Effect of Excess HCl on Catalyst Reactivation

Catalyst State	$C_2H_2:HCl = 1:1.5$		$C_2H_2:HCl = 1:1$	
	Initial HCl[a] conversion (%)	Deactivation rate[b]	Initial HCl[c] conversion (%)	Deactivation rate[b]
Fresh	66	2.0	68	4.5
After first reactivation[d]	65.5	1.0	63	5.4
After second reactivation[d]	60	1.2	55	4.3

[a] Reaction conditions: 180°C, total GHSV = 1420 h^{-1}.
[b] Percentage loss of HCl conversion per hour, averaged over initial 3 h of reaction.
[c] Reaction conditions: 180°C, total GHSV = 1140 h^{-1}.
[d] Reactivated with HCl for 6 h, 180°C, GHSV = 580 h^{-1}.

sion of vinyl chloride to 1,1-dichloroethane. In view of the observation that HCl could successfully restore catalyst activity, it was necessary to investigate the efficiency of alternative reactivation reagents.

Reactivation Using Cl_2

Here 2% $HAuCl_4/C$ was utilised as a catalyst for acetylene hydrochlorination (180°C, total GHSV = 1140 h^{-1}, $C_2H_2:HCl = 1:1.1$) and after 6 h the catalyst had become deactivated. Catalysts deactivated in this manner were separately treated with Cl_2 at 100 and 180°C (6 h, GHSV = 560 h^{-1}). The results, shown in Fig. 3, indicate that Cl_2 can successfully reactivate Au/C catalysts. However, the higher temperature treatment was not as effective as the 100°C reactivation procedure.

The effect of reactivation time is shown in Fig. 4. In contrast to HCl reactivation, Cl_2 treatment is not as dependent on reactivation time and complete catalytic activity can be re-established even after a 1-h treatment at 100°C. In addition, it is interesting to note that Cl_2 reactivation did not result in an enhanced deactivation rate (Fig. 4) as was apparent for HCl reactivation. Significantly, pretreatment of the fresh Au/C cata-

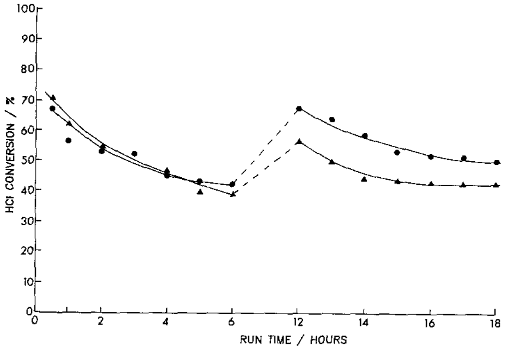

FIG. 3. Effect of Cl_2 treatment on catalysts deactivated at 180°C for 6 h, $C_2H_2:HCl = 1:1.1$, total GHSV = 1140 h^{-1}. ●, Cl_2, 100°C, 6 h, GHSV = 560 h^{-1}; ▲, Cl_2, 180°C, 6 h, GHSV = 560 h^{-1}; ----, reactivation.

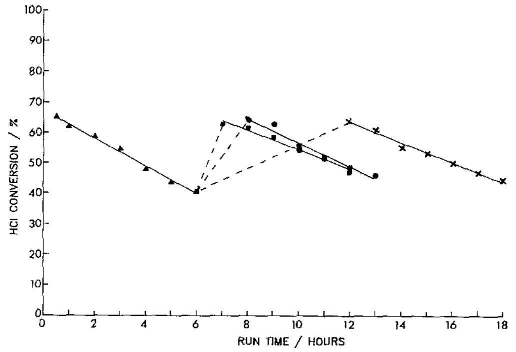

FIG. 4. Effect of time of Cl_2 reactivation procedure (100°C, GHSV = 560 h^{-1}). Catalyst deactivated for 6 h at 180°C, $C_2H_2:HCl = 1:1.1$, GHSV = 1140 h^{-1}. ■, 1 h; ●, 2 h; ×, 6 h.

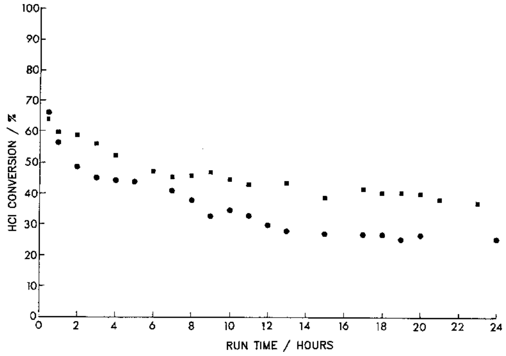

FIG. 5. Effect of catalyst pretreatment with Cl_2. ●, Catalyst not pretreated; ■, catalyst pretreated with Cl_2, 6 h, 100°C, GHSV = 560 h^{-1}. Catalysts reacted at 180°C, C_2H_2:HCl = 1:1.1, GHSV = 1140 h^{-1}.

lyst with Cl_2 prior to reaction decreased the rate of deactivation observed (Fig. 5); this indicates that the control of the oxidation state of the Au is of crucial importance for the acetylene hydrochlorination reaction.

Reactivation Using Air

As noted by us previously (*4*), deactivation for Au/C catalyst is due to two factors, namely, deposition of carbonaceous residues (coke) and reduction of gold salts to the metal. Coke laydown is a common cause of catalyst deactivation, particularly for microporous materials, and is usually removed using an air oxidation process (*6*). Air reactivation procedures were therefore investigated for the Au/C catalysts deactivated using the standard reaction conditions (180°C, 6 h, GHSV = 1150 h^{-1}, C_2H_2:HCl = 1:1.1), and the results are shown in Fig. 6. Again, it is shown that this oxidation treatment is successful in restoring catalytic activity. For air reactivation elevated temperatures (180°C) are most effective. In addition, time is also an important factor and extended reactivation treatments are required. A comparison of the efficiency of the Cl_2 and air reactivation treatments is given in Table 2, and it is clear that low temperature reactivation with Cl_2 for 2 h is particularly effective.

The determination of the surface area following reactivation confirms that the original surface area of the fresh catalyst is almost recovered using the air reactivation treatment (Table 3). However, analysis of catalysts using X-ray diffraction methods demonstrated that the air reactivation treatment did not, as would be expected and in contrast to Cl_2 reactivation, oxidise Au(0) to Au(I) and Au(III) (Table 4).

On-line and in Situ Reactivation with NO and N_2O

An Au/C catalyst was reacted at 180°C with C_2H_2/HCl (1:1.1 molar ratio) with N_2 as diluent at a total GHSV of 3000 h^{-1}. Under these conditions a steady decline in catalyst activity was observed. Substitution of the N_2 diluent with N_2/NO (0.42% NO in N_2) in the reactant gases facilitated a steady restoration in catalytic activity, as shown in Fig. 7. During the N_2/NO cofeeding no change was observed in catalyst selectivity. Replacement of the N_2/NO with N_2 caused catalyst deactivation to occur at a rate similar to that observed prior to the NO/N_2 cofeeding. This "on-line" reactivation procedure could be successfully repeated a number of times without loss of catalytic performance.

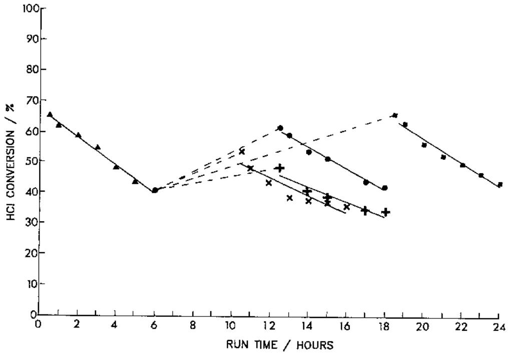

FIG. 6. Effect of time of air reactivation procedure (GHSV = 560 h^{-1}); ▲ catalyst deactivated for 6 h at 180°C, C_2H_2:HCl = 1:1.1, GHSV = 1140 h^{-1}. ●, 180°C, 12 h; ■, 180°C, 6 h; × 180°C, 4 h; +, 160°C, 6 h.

TABLE 2

Comparison of Cl_2 and Air Reactivation Treatments

Catalyst State	Reactivation oxidant	Reactivation conditions[a]		Initial activity (mol HCl conv/mol Au/h)[b]	Catalyst deactivation rate[c]
		T (°C)	Time (h)		
Fresh	—	—	—	655	4.5
Reactivated	Air	180	12	657	5.4
Reactivated	Air	180	6	612	5.7
Reactivated	Air	180	4	533	5.6
Reactivated	Air	160	6	482	5.3
Reactivated	Cl_2	100	6	671	4.6
Reactivated	Cl_2	100	2	645	4.2

[a] GHSV = 560 h^{-1}.

[b] Reaction at 180°C, $C_2H_2:HCl = 1:1.1$, GHSV = 1140 h^{-1}.

[c] Percentage loss of HCl conversion per hour, averaged over initial 3 h reaction period.

The success of the on-line reactivation procedure prompted the investigation of continuous cofeeding of NO to enable "*in situ*" reactivation to be investigated. An Au/C catalyst was reacted with C_2H_2/HCl/NO (1 : 1.25 : 0.8, total GHSV = 1560 h^{-1}) at 180°C, and the results are shown in Fig. 8. Catalyst selectivity remained unchanged at >99.5% vinyl chloride, even though a significant excess of NO was utilised in this experiment. The rate of deactivation in the presence of cofeed NO was significantly less than that observed in its absence, but a slight decline in activity was still apparent. Similar experiments were conducted with N_2O in place of NO; again no change in catalyst selectivity was observed, but a higher rate of deactivation was apparent for N_2O than for NO. However, this study indicates that for the Au/C catalyst, deactivation due to the reduction of Au(III) to lower oxidation states, in addition to the laydown of carbonaceous deposits, can be successfully abated by the inclusion of suitable oxidising agents in the reaction gases. Although excess HCl can be beneficial (Table 1), other more powerful oxidants, e.g., NO and N_2O, can be more effective. In addition, it is significant to note that the presence of excess HCl or other oxidising agents does not affect

TABLE 3

Surface Area Data for Air Reactivation

Catalyst state	Surface area ($m^2 g^{-1}$)
Fresh catalyst[a]	980
Used catalyst[b]	580
Reactivated catalyst[c]	1070

[a] 2% $HAuCl_4$ by mass adsorbed onto activated carbon (2 g) from aqua regia.

[b] Following reaction, 6 h, $C_2H_2:HCl = 1:1.1$, GHSV = 1140 h^{-1}, 180°C.

[c] Reactivated with air, 6 h, GHSV = 560 h^{-1}, 180°C.

TABLE 4

Determination of Au(0) in Catalysts

Sample	Percentage of Au(0)
Fresh catalyst[a]	9
Used catalyst[a]	40
Air reactivated catalyst[b]	26
Cl_2 reactivated catalyst[c]	0

[a] 2% $HAuCl_4$ by mass adsorbed onto activated carbon (2 g) from aqua regia.

[b] Air, 6 h, 180°C, GHSV = 560 h^{-1}.

[c] Cl_2, 6 h, 180°C, GHSV = 560 h^{-1}.

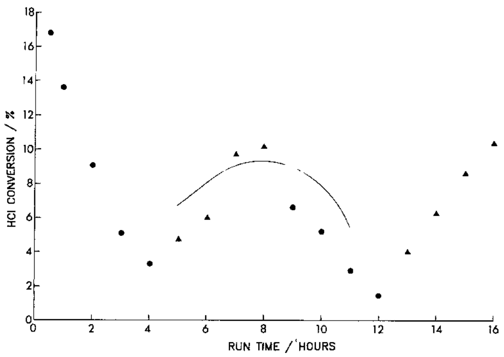

FIG. 7. Effect of on-line reactivation using NO. ●, 2% $HAuCl_4$/C catalyst reacted with C_2H_2/HCl/N_2, GHSV = 3000 h^{-1}, 180°C; ▲, N_2 diluent replaced with 0.42% NO in N_2.

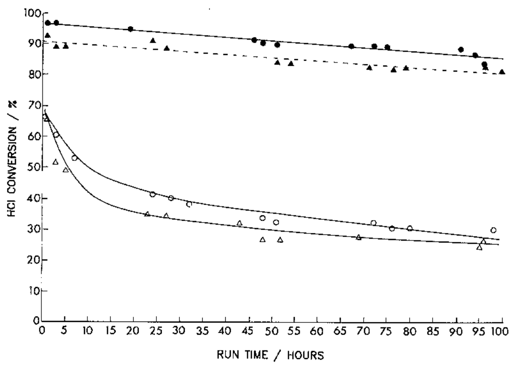

FIG. 9. Effect of extended reaction time on the deactivation rate of Au/C catalyst, C_2H_2 : HCl = 1 : 1.1. ○, 120°C, GHSV = 1140 h^{-1}; △, 180°C, GHSV = 1140 h^{-1}; ▲, 100°C, GHSV = 205 h^{-1}; ●, 120°C, GHSV = 205 h^{-1}.

catalyst selectivity, and under all conditions Au/C catalysts gave >99.5% selectivity to vinyl chloride.

Initial Catalyst Optimisation Studies

Effect of extended reaction times. In the experimental work described in both this and our previous studies (*1–4*) the catalyst evaluations that have been carried out have been for short reaction times, typically 6 h. As catalysts have been observed to deactivate with increased reaction times, it is of interest to observe whether the catalytic activity would reach a steady value at extended reaction times; 2% $HAuCl_4$/C catalysts were therefore reacted under a range of conditions for 96 h at a total GHSV = 1140 h^{-1}, which has been utilised as a standard value in the experimental studies, and the results are shown in Fig. 9. The catalytic activity at both 180 and 120°C declined to a steady conversion level after ca. 20 and 45 h, respectively. Analysis of the deactivated catalysts indicated that Au(0) was the predominant gold oxidation state present, and the activity observed is consistent with that which we have previously observed for Au(0). We have also previously shown (*4*) that the production of Au(0) in the catalysts is enhanced at elevated temperatures, and this is consistent with the observation of the more rapid achievement of the steady conversion level at 180°C compared to that at 120°C. At a lower reactant flow rate (GHSV = 205 h^{-1}), which is close to that operated in the commercial acetylene hydrochlorination process, the rapid initial decline is not observed, but instead a steady slow deactivation occurs, and in the timescale of this experiment a steady conversion level was not attained. It should be noted that in all these extended experiments the selectivity to vinyl chloride remained >99.5%.

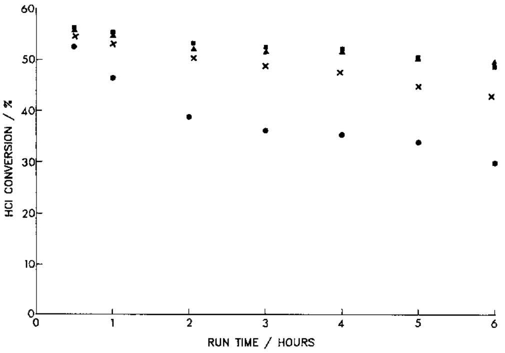

FIG. 8. Effect on *in situ* reactivation using oxidising gases with Au/C catalyst. ■, Reaction of C_2H_2/HCl/NO; ▲, repeat following reactivation "off-line" using NO, 180°C, 6 h, GHSV = 640 h^{-1}; ●, reaction of C_2H_2/HCl/N_2 following off-line reactivation using NO; × reaction of C_2H_2/HCl/N_2O.

TABLE 5

Acetylene Hydrochlorination on Supported $HAuCl_4$ Catalyst[a]

Catalyst support	Surface area ($m^2\ g^{-1}$)	Initial activity[b]	Deactivation rate[c]
Activated carbon			
Sorbonorit 3[d,h]	1200	705	6.9
Norit C[e,h]	1200	706	5.3
G210[f,h]	1160	546	4.1
Norit RO3515[g,h]	1000	544	4.7
AURC[d,h]	1160	683	6.7
γ-Alumina[i]	200	215	1.1
MgO[j]	170	326	4.4

[a] Catalysts prepared by impregnation of the support with $HAuCl_4$ in aqua regia. Reaction conditions: 180°C, 6 h, $C_2H_2 : HCl = 1 : 1.1$, GHSV = 1140 h^{-1}.

[b] Moles HCl converted per mole Au per hour determined at 0.5 h.

[c] Percentage loss in conversion per hour, averaged over initial 3 h.

[d] Derived from coal.

[e] Derived from wood.

[f] Derived from coconut shells.

[g] Derived from peat.

[h] Washed 2 *M* HCl, 70°C, 5 h.

[i] Strem Chemicals, pelleted and sieved prior to use.

[j] Prepared by calcining $Mg(OH)_2$, 550°C, 48 h, pelleted and sieved prior to use.

Investigation of catalyst supports. Previous studies (*7*) have shown that carbon is the preferred catalyst support for use in the acetylene hydrochlorination reaction. Activated carbons can be produced from a number of different precursors, e.g., wood, coal, coconut shell, sugar, and peach stones (*8*), and the chemical and physical properties of the resultant carbons can be significantly different. In the present studies a coal-derived active carbon, Sorbonorit 3, has been utilised. To evaluate the suitability of this support a number of alternative activated carbons and oxides were investigated and the results are given in Table 5. It is apparent that the activated carbon supports are considerably more effective than γ-Al_2O_3 or MgO, and that the carbons with the highest surface areas give both the highest initial activity and the highest deactivation rates. It is interesting to note that catalysts prepared using MgO are more active than those prepared using γ-Al_2O_3, although the surface area of the latter material is higher. This is ascribed to the observation that MgO stabilises Au(III) more effectively than other oxides (*9*), which would result in the observation of a higher initial activity.

Studies on the reaction mechanism. A preliminary kinetic evaluation was performed under conditions of low conversion and low deactivation rate (GHSV = 3000 h^{-1}, 180°C) using N_2 as a diluent for the reactants. The rate of acetylene hydrochlorination was followed as a function of the partial pressure of HCl at a constant acetylene partial pressure that was in considerable excess over that of the HCl ($P_{C_2H_2}$ ca. $15P_{HCl}$). The rate was observed to be directly proportioned to P_{HCl}. Similar experiments in which the effect on rate of varying $P_{C_2H_2}$ at constant and excess P_{HCl} also gave a linear dependence, indicating that reaction rate was proportional to $P_{C_2H_2}$. Hence the overall rate expression for the acetylene hydrochlorination reaction over an Au/C catalyst can be expressed as

$$\frac{-d[\mathrm{HCl}]}{dt} = \frac{-d[\mathrm{C_2H_2}]}{dt} = k \cdot P_{\mathrm{HCl}} \cdot P_{\mathrm{C_2H_2}}.$$

A number of previous mechanistic studies of the acetylene hydrochlorination reaction using the $HgCl_2/C$ catalyst have been made (*10–16*) and the following scheme of elementary reactions has been suggested,

$$\mathrm{C_2H_2(g)} \rightleftharpoons \mathrm{C_2H_2(a)} \tag{1}$$

$$\mathrm{HCl(g)} \rightleftharpoons \mathrm{H^+(a) + Cl^-(a)} \tag{2}$$

$$\mathrm{C_2H_2(a) + H^+(a)} \rightleftharpoons \mathrm{CH_2{=}CH^+(a)} \tag{3}$$

$$\mathrm{CH_2{=}CH^+(a) + Cl^-(a)} \rightleftharpoons \mathrm{CH_2{=}CHCl(a)} \tag{4}$$

$$\mathrm{CH_2{=}CHCl(a)} \rightleftharpoons \mathrm{CH_2{=}CHCl(g)}, \tag{5}$$

where (a) signifies an adsorbed species.

It should be noted that supported gold catalysts do not produce significant levels of 1,1-dichloroethane, even when excess HCl is utilised. This observation cannot be accounted for in the previous scheme since a subsequent addition of H^+(a) and Cl^-(a) to $CH_2{=}CHCl(a)$ would be expected to be favoured at high HCl concentration. It is apparent that an alternative mechanism could therefore be operating for the Au/C as compared to the $HgCl_2/C$ catalyst.

A catalyst prepared from $HAuCl_4$ was reacted with C_2H_2 (GHSV = 100 h^{-1}, 180°C) in the absence of HCl. The product was analysed using gc/ms and was found to contain vinyl chloride and unreacted acetylene, with no 1,1-dichloroethane being observed. Analysis of the catalyst following this procedure indicated that an increased concentration of Au(0) was present. Hence, $HAuCl_4$/C can be stoichiometrically reacted with C_2H_2 to produce vinyl chloride with concomitant reduction of the gold salt. To further probe this possibility, a series of model homogeneous experiments were performed using ultraviolet/visible spectroscopy. A solution of $HAuCl_4$ in aqua regia was treated with acetylene (GHSV = 560 h^{-1}) at ambient temperature for varying reaction times and the reaction product was investigated using ultraviolet/visible spectroscopy. As the reaction proceeded it was observed that the concentration of $AuCl_4^-$ in solution decreased. After reaction for 0.7 h, $AuCl_4^-$ was no longer present. Significantly, Au(0) was observed to be deposited on the reaction vessel during this reaction procedure, also confirming that reaction of C_2H_2 with $HAuCl_4$ had occurred. A second series of experiments in which C_2H_2 and HCl were cofed into a solution of $HAuCl_4$ in aqua regia was conducted. Again the concentration of $AuCl_4^-$ decreased. However, no Au(0) was observed to be formed and it was considered that this was due to stabilisation of Au in a higher oxidation state (e.g., as Au(I) in $AuCl_2^-$) when HCl is present in the homogeneous model studies.

The data presented in this and previous studies have enabled a number of mechanistically significant conclusions to be made, namely (i) the rate of acetylene hydrochlorination correlates with the standard electrode potential; (ii) Au(0), Au(I), and Au(III) can all be active for the reaction, but Au(III) from $HAuCl_4$ and Au(I) from $KAu(CN)_2$ are most effective; (iii) there is a stoichiometric formation of vinyl chloride, but not 1,1-dichloroethane, from the reaction of carbon-supported $HAuCl_4$ and C_2H_2; (iv) the overall rate of reaction is linearly dependent on both P_{HCl} and $P_{C_2H_2}$; (v) Au/C catalysts are deactivated by the reduction of Au(III) and Au(I) to Au(0) and a number of oxidising agents (Cl_2, NO, N_2O) can successfully reactivate the catalysts; (vii) addition of NO in high concentration does not affect catalyst selectivity, indicating that a radical mechanism can be discounted with Au/C catalysts. All the above evidence points to a redox mechanism involving gold. From a knowledge of the common oxidation states of gold (*17*) and the known ability of HCl (and other reagents) to induce oxidative addition reactions in which oxidation states change in multiples of two (*18*), it seems likely that the redox process involves an Au(I)–Au(III) cycle.

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