

Hydrochlorination of Acetylene Using Gold Catalysts: A Study of Catalyst Deactivation

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A detailed study of the processes occurring during the deactivation of gold catalysts used for the acetylene hydrochlorination reaction is described. Catalyst deactivation is a common feature of supported metal chloride catalysts for this reaction, but in the case of HAuCl_4/C catalysts the deactivation is not due to loss of Au from the catalyst during use. The effect of a range of parameters on the deactivation rate is discussed, including method of preparation of the HAuCl_4/C catalyst, [Au] and reaction conditions (GHSV and temperature). Deactivated and fresh catalysts were characterised using ^{197}Au Mössbauer spectroscopy in combination with X-ray diffractometry, TGA, and BET surface area determinations. On the basis of this study, two deactivation processes have been identified. At low reaction temperatures, 60–100°C, deposition of carbonaceous residues is the predominant deactivation mechanism. However, at higher reaction temperatures, 120–180°C, the main deactivation process is ascribed to the reduction of Au(III), and possibly Au(I), to the less active Au(0) during the catalytic reaction. Consequently, for the experimental conditions investigated in this study, the optimum temperature for operating these catalysts is in the range 100–120°C when both these deactivation processes can be minimised. © 1991 Academic Press, Inc.

INTRODUCTION

The reaction of hydrogen chloride with acetylene in the vapour phase is a well-established industrial process for the production of vinyl chloride monomer which currently accounts for about 6% of the total world production. The catalyst utilised in the industrial process is HgCl_2 supported on activated carbon, but it is known that this catalyst exhibits a short lifetime at high production rates (1, 2). Recently (3) we have shown that the catalytic activity of metal chlorides for this reaction correlates well with the standard electrode potential. On this basis, it was predicted that gold could form the basis of a very active catalyst for-

mulation and our initial studies on this reaction have confirmed this prediction (4, 5).

In most catalytic applications gold is known to have poor catalytic activity when compared to that of other metals, due to its high standard electrode potential. The use of gold in catalysis has been reviewed (6–8) and this metal is known to be active for a range of oxidation and reduction reactions. For example, gold halides have been utilised as catalysts for the oxidation of sulphides (9) and dithioalkanes (10). A range of supported gold catalysts have been investigated for the oxidation of carbon monoxide (11), and Lee and Schwank (12) studied the mechanism of NO reduction by hydrogen on Au/SiO_2 and Au/MgO catalysts. However, in all these applications gold was not observed to exhibit any significant catalytic advantages

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over other metal catalysts. The observation that gold exhibits the highest catalytic activity for the acetylene hydrochlorination reaction represents an interesting experimental result which is worthy of further investigation. In this paper our earlier studies of this system are extended and we present a detailed study of the mechanism of deactivation of gold catalysts during the hydrochlorination of acetylene.

EXPERIMENTAL

Gold catalysts were prepared using three impregnation procedures. In procedure A, $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ (subsequently denoted HAuCl_4 in this study) was dissolved in 2 M HCl at 70°C. Active carbon extrudates (acid-washed Sorbonorit 3, ca. 10×3 mm) were then added and the mixture was stirred for 5 h, and the loaded carbon extrudates were recovered by filtration and dried (140°C, 16 h). In procedure B, HAuCl_4 was dissolved in the minimum quantity of 2 M aqueous HCl and this was adsorbed onto the carbon extrudates using the incipient wetness method and subsequently dried (140°C, 16 h). In procedure C, HAuCl_4 was dissolved in the minimum quantity of aqua regia and this was adsorbed on the carbon extrudates using the incipient wetness

method and subsequently dried (140°C, 16 h). For this experimental study, unless otherwise stated, the loading of the HAuCl_4 salt on the carbon support was 2% by mass. Other carbon-supported metal chloride catalysts can be prepared using the same procedures.

Catalysts were tested for acetylene hydrochlorination in a fixed bed laboratory microreactor at atmospheric pressure as previously described (5). Acetylene was passed through 13X molecular sieve to remove traces of acetone and water. Hydrogen chloride (Air Products, electronic grade) was similarly dried using 3A molecular sieve. The dried gases were then mixed and passed over a predried catalyst (2 g). Product gases were passed through sodium hydroxide solution for a fixed time period to remove unreacted hydrogen chloride. Titration of these samples by standard methods (5) enabled the conversion of hydrogen chloride to be determined. Product gases were also analysed by gas chromatography to determine acetylene conversion and product selectivity.

Catalysts, both unused and used, were characterised using a range of techniques, including Mössbauer spectroscopy, X-ray diffractometry (Philips PW 1050/25 X-ray

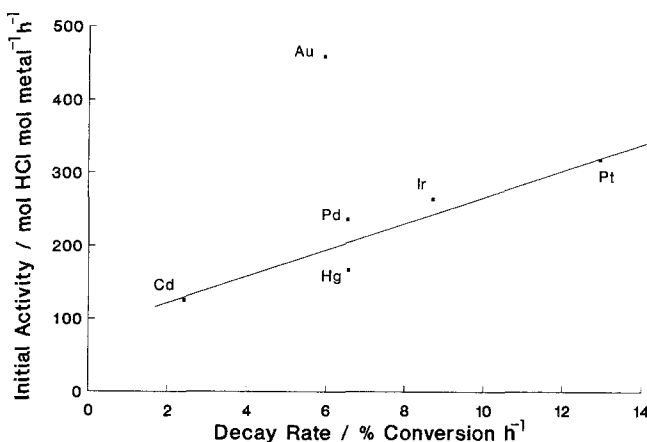


FIG. 1. Correlation of initial catalyst activity and conversion decay rate (average loss of conversion (percentage) for the initial 3 h reaction). Catalysts contain 0.0005 mol metal/100 g catalyst.

TABLE 1
Analysis of Catalysts Before and After Reaction^a

Metal	Composition (%)		Percentage of metal lost
	Fresh catalyst	Used catalyst ^b	
Au	1.05	1.04	0.95
Pt ^c	1.35	1.08	20.0
Pt ^d	0.97	0.95	2.06
Ir	0.96	0.57	40.6
Co	2.25	2.19	2.67
Hg	8.28	6.28	24.2

^a Catalysts analysed using X-ray fluorescence; experimental accuracy is 2% of the data quoted.

^b Following reaction for 6 h at GHSV = 1140 h⁻¹, 180°C, C₂H₂:HCl mol ratio = 1:1.17.

^c Prepared from PtCl₂.

^d Prepared from H₂PtCl₆.

diffrometer using Cu K_α radiation), surface area using the N₂-BET method in duplicate, skeletal densities, particle densities and pore size distribution using mercury porosimetry (Autoscan Instrument in conjunction with He pycnometry using a Quantachrome Instrument), and thermal gravimetric analysis (Dupont 9900). Metal concentration of catalysts was determined by X-ray fluorescence spectroscopy by the method of standard addition.

RESULTS AND DISCUSSION

Catalyst Deactivation Rate

In our previous studies (4, 5) we demonstrated that the catalytic activity of metal chlorides for the acetylene hydrochlorination reaction decreased markedly with increased reaction time, and that catalyst deactivation was a general feature for such catalysts. In addition, it was demonstrated (5) that, in general, a correlation existed between initial catalyst activity and the rate of deactivation. These previous studies utilised a relatively high metal chloride loading (0.005 mol metal/100 g catalyst), which showed that, at this level, mercuric chloride exhibited a much lower rate of decay than that expected from the observed correla-

tion. However, it is not possible to obtain comparative data for H₂AuCl₄ at this high loading and consequently a series of experiments were carried out using lower metal chloride loadings (0.0005 mol metal/100 g), and the results are shown in Fig. 1. From these data it is apparent that the H₂AuCl₄/carbon catalyst does not deactivate as rapidly as the other carbon-supported metal chloride catalysts, but it clearly demonstrates the highest initial catalyst activity. Analysis of catalyst metal content before and after use (Table 1) indicated that for some catalysts, e.g., PtCl₂/C, IrCl₃/C, and HgCl₂/C, the metal chloride was lost from the carbon support during the reaction, and this is probably a major cause of deactivation for these materials. However, other metal chlorides are not lost during reaction, e.g., H₂AuCl₄/C, H₂PtCl₆/C, and CoCl₂/C. In this case deactivation cannot be ascribed to loss of the metal chloride and hence must be due to alternative effects.

Dependence of Deactivation on Catalyst and Reaction Parameters

Effect of catalyst preparation method on catalyst activity. H₂AuCl₄/C catalysts were prepared using the three impregnation methods described above (A, B, and C). Analysis of the Au content (Table 2) indicated that the methods resulted in significantly different

TABLE 2
Au Loadings of Catalysts Prepared by Different Impregnation Methods

Preparation method ^a	Au loading (percentage by mass)	
	Unused	Used ^b
A	0.57 ± 0.01	0.60 ± 0.01
B	0.95 ± 0.02	—
C	1.08 ± 0.02	1.05 ± 0.02

^a For details see under Experimental; Au analysis carried out using X-ray fluorescence spectroscopy.

^b Catalysts reacted for 6 h at 180°C, GHSV = 1140 h⁻¹, C₂H₂:HCl = 1:1.1.

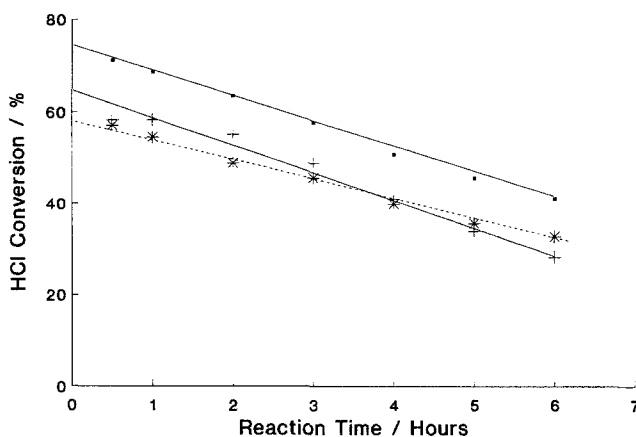


FIG. 2. Effect of preparation method on acetylene conversion at GHSV 1140 h^{-1} , 180°C , $\text{C}_2\text{H}_2 : \text{HCl} = 1 : 1.1$. *, Procedure A; +, procedure B; ■, procedure C.

loadings of Au being achieved. Method A resulted in the lowest Au loading and this was due primarily to not using an incipient wetness technique and also to Au metal being plated onto the surface of the carbon pellet, which subsequently was lost from the catalyst by attrition. Method B resulted in much less pronounced plating occurring, and no plating was visually observed when the highly oxidising aqua regia media was utilised in method C. The catalytic results for acetylene hydrochlorination using the three catalysts are given in Fig. 2, and it can be seen that they exhibit similar rates of deactivation. Selectivity for vinyl chloride was $>99.5\%$ for all HAuCl_4/C catalysts investigated. Analysis before and after the reaction (Table 2) confirmed that for all preparative methods the loss of Au was not responsible for the observed deactivation. It was clear that the catalytic activity for these catalysts was in the order $\text{C} > \text{B} > \text{A}$. The lower catalytic activity observed for catalyst A is probably due to the lower Au loading. However, for catalysts B and C, which have similar Au loadings, it is apparent that the method of preparation is an important factor in determining the catalytic activity of the HAuCl_4/C catalyst.

Effect of Au loading on catalyst deactivation. The effects of Au loading on the cata-

lytic activity and deactivation rate for the acetylene hydrochlorination reaction are shown in Fig. 3. The results indicate that both activity and deactivation rate decrease with increasing Au loading, which is probably a result of the dispersion of Au on the carbon surface. From this comparative study it was concluded that a 1% Au loading as metal was an appropriate compromise between catalyst activity and rate of deactivation.

Effect of gas hourly space velocity (GHSV) on catalyst deactivation. A HAuCl_4/C catalyst containing 1% by mass Au was prepared using method C. The effect of total GHSV on the initial catalytic activity and rate of deactivation for this catalyst is shown in Fig. 4. As expected, the initial HCl conversion decreases steadily with increasing total GHSV. However, the rate of catalyst deactivation clearly shows a maximum at ca. 1000 h^{-1} . It is therefore considered that the deactivation is a result of the operation of the hydrochlorination reaction, possibly by polymerisation of the product vinyl chloride. For all conditions investigated, selectivity to vinyl chloride was $\geq 99.5\%$ and so deactivation was not caused by a change in catalyst specificity.

Effect of reaction temperature on deactivation rate. A HAuCl_4/C catalyst containing

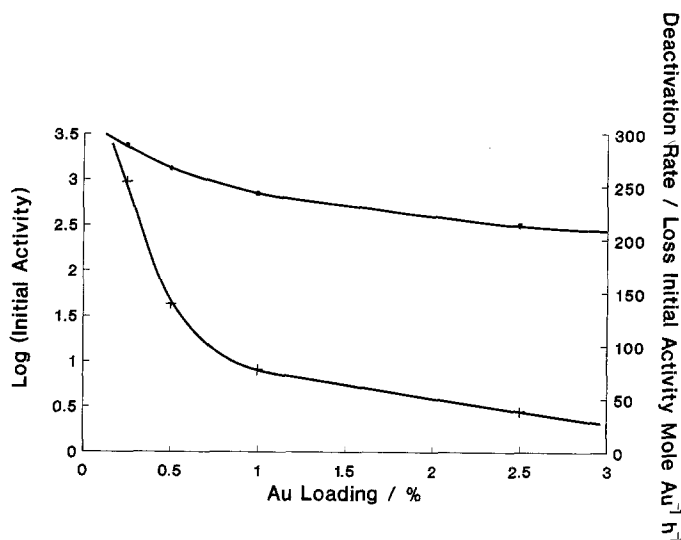


FIG. 3. Effect of Au loading on: +, rate of deactivation (loss of activity (mol HCl converted/mol Au/h) averaged over initial 3 h); and ■, initial activity (mol HCl converted/mol Au/h at 0.5 h reaction time). Reaction conditions: 180°C, GHSV 1140 h⁻¹, C₂H₂: HCl = 1:1.1.

1% mass Au was prepared using method C. The effect of reaction temperature on the rate of deactivation for this catalyst is shown in Fig. 5, and it is apparent that a minimum deactivation rate occurs at ca. 100°C. It is possible that these results indicate that two deactivation mechanisms are operating for this catalyst, one mechanism below the optimum temperature and an alternative mechanism at higher temperatures. It should be noted that it is unlikely that deactivation is due to sintering, since this is not expected at the low temperatures used in the reaction.

Effect of added chloride. Addition of KCl to a HAuCl₄/C catalyst by co-impregnation (2.11% HAuCl₄/C + 1.03% KCl) of the gold and potassium salts had no significant effect on either the initial catalytic activity or the rate of catalyst deactivation. It can therefore be concluded that the catalyst chloride concentration is not an important factor determining activity or deactivation. Addition of FeCl₃ (2.07% HAuCl₄/C + 1.36% FeCl₃) to the catalyst by co-impregnation resulted in a significant loss of initial activity. It has been noted by Popov *et al.* (13) that iron acts as a catalyst poison for the HgCl₂/C

catalysts for the acetylene hydrochlorination reaction, and it is possible that this is a general feature for these catalysts.

The effect of adding excess HCl as a reactant was examined by increasing the HCl:C₂H₂ ratio and it was found that the deactivation rate decreased with increasing HCl:C₂H₂ ratio. This effect has been noted previously (2) with HgCl₂/C catalysts for this reaction and has been ascribed to acetylene acting as a reducing agent. In the case of the HgCl₂/C catalyst, Hg metal was formed during the catalytic reaction at low HCl:C₂H₂ ratios, and being very volatile the Hg metal was lost from the catalysts. This is the main mechanism of deactivation for HgCl₂/C catalysts. By analogy with these experimental data it is possible that deactivation in the case of the Au/C catalyst could in part be due to reduction of the active catalytic component.

Catalyst Characterisation

From the previously described studies, it is apparent that catalyst deactivation could be the result of a combination of mechanisms, i.e., deposition of carbonaceous ma-

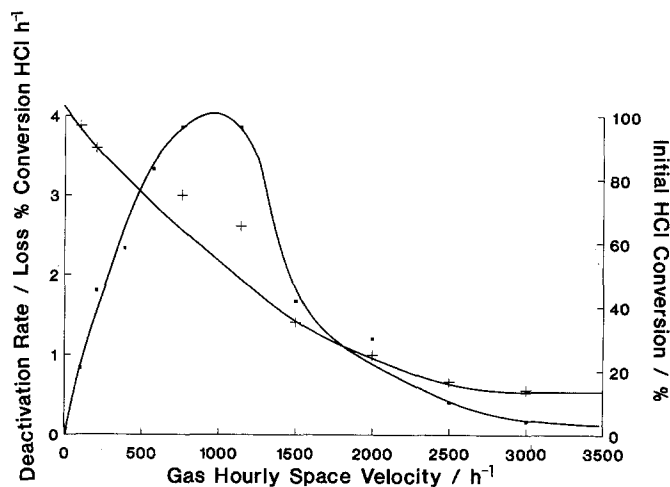


FIG. 4. Effect of total GHSV on ■, rate of deactivation (loss HCl conversion/h, averaged over initial 3 h); and +, initial HCl conversion. Reaction conditions: 180°C, C₂H₂: HCl = 1:1.1.

terial or reduction of the active gold oxidation state to gold metal. To investigate further the mechanism of deactivation the gold catalysts were characterised using a variety of techniques.

Surface area analysis. The surface areas of catalysts, both fresh and used under various reaction conditions, were determined by the BET method using nitrogen adsorption and the pore volume was determined

by mercury porosimetry; the results are shown in Table 3. The used catalysts exhibit surface areas and total pore volumes much lower than those of the fresh unused catalysts. The catalyst sample that had been deactivated at a low reaction temperature of 60°C exhibited a surface area significantly lower than that of a sample deactivated at the higher temperature of 180°C. It is shown in Fig. 5 that these two reaction tempera-

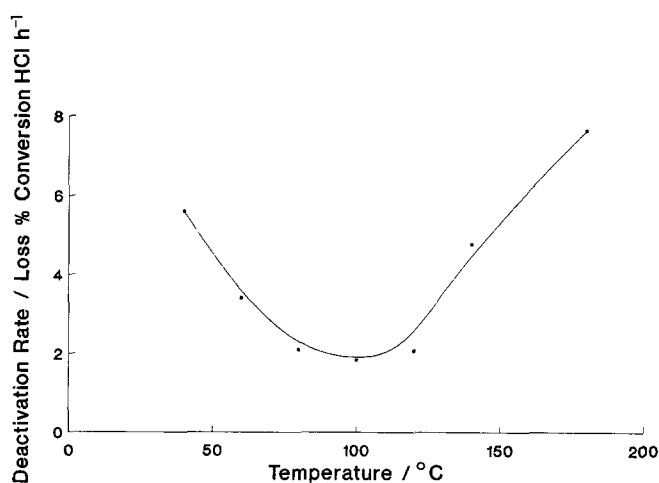


FIG. 5. Effect of reaction temperature on rate of deactivation (loss HCl conversion/h, averaged over initial 3 h). Reaction conditions: C₂H₂: HCl = 1:1.1.

TABLE 3

Surface Area and Pore Volume Data for H_{AuCl₄}/C Catalysts

Sample	Surface area (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹)
Sorbonorit 3 ^a	1240	0.97
2% H _{AuCl₄} /C		
Fresh ^b	980	0.98
Used ^c	580	0.63
Used ^d	190	—
Blank A ^e	1180	—
Blank B ^f	1210	—
Blank C ^g	940	—

^a Acid-washed carbon prior to impregnation with H_{AuCl₄}/C.

^b Catalyst prepared using method C.

^c Catalyst was reacted at 180°C, 6 h, C₂H₂:HCl ratio = 1:1.2, GHSV = 1140 h⁻¹.

^d Catalyst was reacted at 60°C, 6 h, C₂H₂:HCl ratio = 1:1.2, GHSV = 1140 h⁻¹.

^e C₂H₂:HCl = 1:1.2 passed over Sorbonorit 3, 180°C, 6 h, GHSV = 1140 h⁻¹.

^f C₂H₂:N₂ = 1:1.2 passed over 2% H_{AuCl₄}/C, 180°C, 6 h, GHSV = 1140 h⁻¹.

^g C₂H₂:N₂ = 1:1.2 passed over 2% H_{AuCl₄}/C, 60°C, 6 h, GHSV = 1140 h⁻¹.

tures incur similar deactivation rates. It is therefore considered that the mechanism of deactivation at the two temperatures could be different. However, it is also apparent that deactivation is due, at least in part, to loss of active surface area. Since this is not due to loss of Au metal (Tables 1 and 2), this effect could be due to deposition of carbonaceous material on the catalyst surface. To ensure that the decreases observed in surface area could be attributed to the reaction of C₂H₂/HCl over the H_{AuCl₄}/C catalyst, a series of blank experiments were completed. Reaction C₂H₂/HCl over the Sorbonorit carbon in the absence of the gold salt (Blank A; Table 3) indicated that no significant loss of surface area occurred. In addition, to rule out the formation of coke by the metal-catalysed polymerisation of acetylene, as has been reported by Bond (14), blank experiments were performed by pass-

ing a mixture of C₂H₂/N₂ over a 2% H_{AuCl₄}/C catalyst for 6 h at two temperatures (Blanks B and C; Table 3). No significant loss of surface area was observed, hence confirming that the loss of surface area of catalysts during use was due to the Au-catalysed acetylene hydrochlorination reaction.

Thermogravimetric analysis. Thermal analysis is a standard way to obtain information on the deposition of carbonaceous material on catalysts. In particular, the mass loss from a sample heated in oxygen can give an indication of the amount of carbonaceous material present on the catalyst. In the case of carbon-supported catalysts the analysis is more complex, since the high area active carbon can also be oxidised, a process that may be catalysed by the metal catalyst component. To overcome this problem the following procedure was adopted. Deactivated catalysts samples, which had previously been used for acetylene hydrochlorination for 6 h at temperatures ranging from 60 to 180°C, were analysed by TGA and the mass loss was recorded. These mass losses were then corrected by determining the mass loss for an unused catalyst containing the same Au content and subtracting this value from the recorded mass loss. The corrected mass loss obtained under oxidising conditions is considered to be a measure of the amount of carbonaceous deposits (coke) on the catalyst. To confirm that such a correction is valid, a series of flow experiments in which fresh Au/C and deactivated Au/C were reacted in O₂ at elevated temperatures were conducted. CO₂ analysis was carried out and it was determined that the rate of CO₂ evolution was ca. three times higher for the deactivated catalyst than for the fresh catalyst and, hence, it is concluded that the correction applied to the TGA data is realistic. A plot of the coke content versus temperature is shown in Fig. 6. These results indicate that the coke deposited decreases with increasing reaction temperature, and at low reaction temperature, <100°C, is ca. 4–6%. At higher temperatures it is apparent that

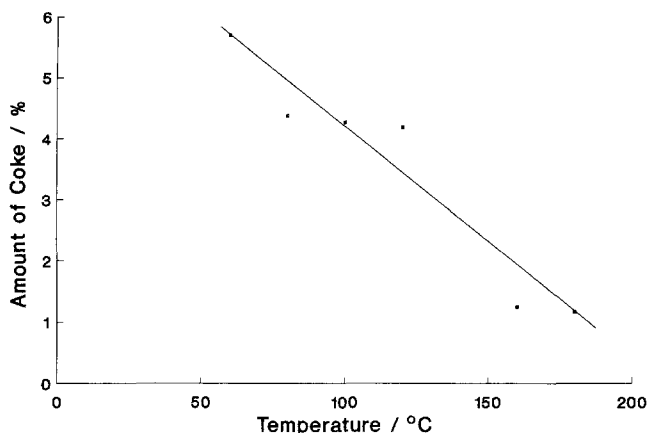


FIG. 6. Coke formation as a function of reaction temperature. 2% HAuCl_4/C catalyst reacted for 6 h, $\text{GHSV} = 1140 \text{ h}^{-1}$, $\text{C}_2\text{H}_2:\text{HCl} = 1:1.1$

only small quantities of coke are formed, possibly due to the volatility of the coke precursors at that temperature. It can therefore be concluded that the marked loss of catalyst surface area observed at a reaction temperature of 60°C (Table 3) is due to deposition of coke, and that this is the main cause for the high deactivation observed at this low reaction temperature (Fig. 5). However, at the higher reaction of 180°C less significant loss of surface area or coke deposition is observed, and hence an alternative mechanism of catalyst deactivation must be occurring.

Nature of carbonaceous deposits. Surface area, pore volume, and TGA measurements indicated that carbonaceous deposits were formed on the catalyst during the acetylene hydrochlorination reaction. Extraction with tetrahydrofuran of catalysts deactivated at 60 and 180°C followed by subsequent infra red analysis of the extractate indicated that the composition of the carbonaceous deposits was different at the two temperatures; analysis of the chloride content of fresh and deactivated samples is shown in Table 4. The sample deactivated at 60°C , which contained ca. 5% coke, showed a marked increase in chloride content. This indicates that the carbonaceous deposits are probably formed by polymeri-

sation of vinyl chloride, the product of acetylene hydrochlorination. However, further studies are required to enable a detailed characterisation of the coke to be achieved.

X-ray diffraction studies. Previous studies (15) have shown that at temperatures greater than 400°C gold on carbon in the form of $\text{Au}(\text{CN})_2$ can be completely converted to $\text{Au}(0)$ in the metallic state. In the present work this procedure was carried out, and the peak intensities in the X-ray diffraction pattern of the $\text{Au}(0)$ from $\text{Au}(\text{CN})_2^-$ were taken to be 100% $\text{Au}(0)$. Quantitative analysis for metallic gold in the catalyst samples was then achieved by comparison of the peak intensities due to $\text{Au}(0)$ with those of the reference sample for the

TABLE 4
Chloride Analysis of Catalyst Samples

Sample	Cl (percentage by mass)
Fresh catalyst, 2% HAuCl_4/C , prepared by method C	2.1
Calculated content ^a	1.1
Used catalyst at 60°C	6.2
Used catalyst at 120°C	2.1
Used catalyst at 180°C	1.5

^a Based on the chlorine content of 2% mass HAuCl_4/C supported on carbon.

same loading level of gold. Analysis of fresh and deactivated catalyst samples indicated that a significant proportion of the gold present in deactivated catalysts was present as Au(0), (Table 5). It is apparent that the proportion of Au(0) increases with increasing reaction temperature, and hence this may be a cause of catalyst deactivation at the elevated temperatures.

Mössbauer spectroscopy. Mössbauer spectroscopy using the 77-keV resonance of ^{197}Au (16–18) is particularly useful in revealing the oxidation states of gold present in a catalyst without requiring crystallinity. When several different gold species are present, it can also be utilised to determine the amounts of gold in the different forms once the recoilless fractions, or Mössbauer–Lamb f -factors, of the individual species have been determined.

All Mössbauer spectra were measured at liquid helium temperature with sources made by neutron irradiation of metallic, isotopically enriched ^{196}Pt . Figure 7 shows the spectra of a freshly prepared 2% HAuCl_4/C catalyst made by method C, of the same catalyst after deactivation at 180°C for 6 h, and of a catalyst that was first deactivated and then reactivated by boiling in aqua regia. Additionally, a spectrum of crystalline $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ is shown for comparison. All spectra were least squares fitted with appropriate superpositions of Lorentzian lines.

In the spectrum of the fresh catalyst one

TABLE 5

Amount of Gold Metal Present on Catalysts as Determined by X-Ray Diffraction Analysis

Sample	Percentage Au(0)
Fresh catalyst ^a	9
Used catalyst ^b at 60°C	30
Used catalyst ^b at 120°C	40

^a 2% HAuCl_4/C prepared by method C.

^b Catalysts reacted at temperature stated for 6 h, GHSV = 1140 h^{-1} , $\text{C}_2\text{H}_2:\text{HCl} = 1:1.1$.

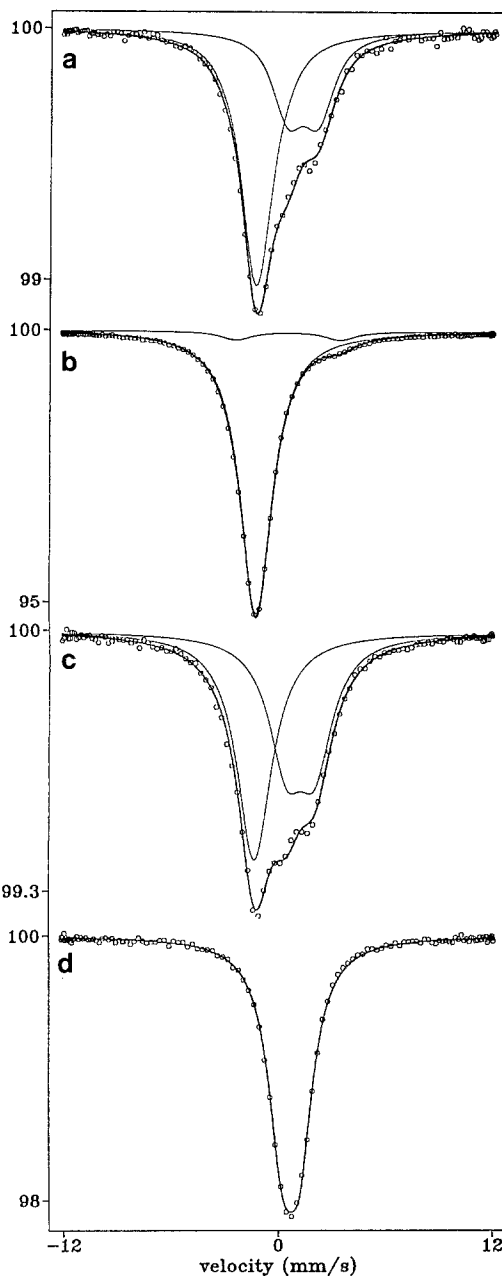


FIG. 7. ^{197}Au Mössbauer spectra of (a) 2% HAuCl_4/C adsorbed on activated carbon from an aqua regia solution, (b) the same catalyst after deactivation at 180°C for 6 h (GHSV = 1140 h^{-1} , $\text{C}_2\text{H}_2:\text{HCl} = 1:1.1$), (c) a sample of the same type after reactivation by boiling in aqua regia, and (d) crystalline $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$.

finds both metallic gold, which is expected to yield a single line with an isomer shift of -1.23 mm/s , and a quadrupole doublet that

can be attributed to adsorbed AuCl_4^- . The latter has an isomer shift (IS) of $+1.25 \pm 0.04$ mm/s and a quadrupole splitting (QS) of 1.65 ± 0.05 mm/s, which are close to the parameters found for the crystalline $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ (Fig. 7, IS = $+0.71 \pm 0.01$ mm/s, QS = 0.98 ± 0.02 mm/s) and for other crystalline compounds containing AuCl_4^- species (16).

The AuCl_4^- represents $(37 \pm 1)\%$ of the area under the Mössbauer spectrum, while the remainder arises from the metallic gold. The fraction of gold bound in AuCl_4^- is thus markedly higher than that found previously by Cashion *et al.* (19) in a sample prepared by impregnation of an aqueous solution of HAuCl_4 (i.e., equivalent to method B utilised in this study). Gold complexes adsorbed on carbon are, however, known to have substantially smaller recoilless fractions, f , than metallic gold (20). It is therefore necessary to determine the recoilless fraction of the adsorbed gold species before the mass ratio of Au(0) and Au(III) can be given.

A method by which the f -factor of adsorbed species can be determined even without an exact knowledge of the amount of gold present on the carbon has been described recently (20). It consists of first measuring a spectrum of the sample containing the adsorbed species. Then the chemically bound gold is reduced to the metal by heating the specimen to about 600°C in an airtight vessel, carefully avoiding any loss of material. After the reduction, the Mössbauer spectrum will contain only the line of metallic gold. From the intensity of this line, or its increase if some of the gold was already metallic before the reduction, the ratio of the f -factors of the bound and metallic gold can be calculated. In order to avoid uncertainties introduced by the nonresonant background in the X-ray spectrum, which may change from measurement to measurement, or even during individual measurements because of the ageing of the source, a standard absorber to which all intensities could be referred was measured together

with the samples in both cases. The reference absorber was an alloy of 1 at.% gold in vanadium metal, which is convenient because its Mössbauer line has an isomer shift of $+5.63$ mm/s and therefore does not overlap with the spectra of the catalysts.

The result of these experiments is that the ratio of the recoilless fractions of AuCl_4^- on carbon and metallic gold is $f(\text{AuCl}_4^-)/f(\text{Au}) = 0.11 \pm 0.01$, a value that is only slightly higher than that found for $\text{Au}(\text{CN})_2^-$ adsorbed on carbon (20). The metallic component is thus largely enhanced in the Mössbauer spectra. Only 16% by mass of the gold on the fresh catalyst is metallic, while 84% is present as AuCl_4^- . The amount of Au(0) found by Mössbauer spectroscopy is nearly twice that found by X-ray diffraction for a catalyst prepared by the same method (9% Au(0), Table 5), perhaps because Mössbauer spectroscopy detects even extremely small Au(0) clusters that do not contribute to the diffraction pattern.

The Mössbauer spectrum of the spent catalyst (Fig. 7) shows that deactivation at 180°C converts most of the Au(III) to metallic gold. In addition to the Mössbauer line of the latter at -1.22 mm/s, there is a weak but well-defined absorption line at $+3.49 \pm 0.05$ mm/s with an intensity of 2.7% of the total area under the spectrum. Such a large isomer shift combined with a vanishing electric quadrupole splitting is unexpected for either Au(III) or Au(I) (16–18). Even though an unidentified component with similar Mössbauer parameters has been reported for carbons loaded with $\text{Au}(\text{CN})_2^-$ (20), in the present case a more plausible explanation is that the visible shoulder represents one component of a quadrupole doublet whose second line is hidden under the strong metallic peak at negative velocities. Although the position of this second line is not very well defined, a fit (Fig. 7) yields Mössbauer parameters (IS = $+0.53 \pm 0.03$ mm/s, QS = 5.77 ± 0.06 mm/s) indicative of a Au(I) species (16–18). This gold could thus represent an intermediate product of the reduction of Au(III) to Au(0) as the cata-

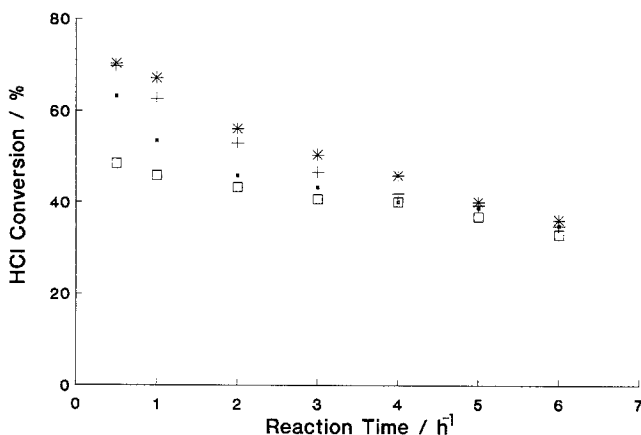


FIG. 8. HCl conversion as a function of reaction time for gold catalysts: *, HAuCl_4/C (Au(0) and Au(III)); +, $\text{KAu}(\text{CN})_2/\text{C}$ (Au(I)); ■, AuCN/C (Au(I)); □, Au/C (Au(0)); 180°C, $\text{GHSV} = 1140 \text{ h}^{-1}$, $\text{C}_2\text{H}_2:\text{HCl} = 1:1.1$.

lyst becomes deactivated, or an intermediate product essential in the catalytic process. As for its nature, one can only speculate, and more experiments will be needed to clarify the role of this component in the catalytic process. It is striking, however, that the Mössbauer parameters of the suggested quadrupole doublet are similar to those of $L\text{-Au-Cl}$ complexes, where L is an olefin or an acetylene derivative. The dimethylacetylene complex, for instance, has Mössbauer parameters ($IS = +0.79 \text{ mm/s}$, $QS = 6.38 \text{ mm/s}$) (21–22) that are quite close to those of the present Au(I) doublet.

The relative spectral area of the Au(I) doublet in the spent catalyst is $5.5 \pm 0.5\%$. The f -factor of this component has not yet been determined. If it is similar to that of the adsorbed AuCl_4^- , about 30% of the gold in the spent catalyst is present as Au(I), the remainder being Au(0).

The Mössbauer spectrum of the reactivated catalyst shows that the reduction of Au(III) to Au(I) and Au(0) during deactivation is reversible. In fact, compared to the fresh specimen, the reactivated catalyst contains an even higher fraction, namely ($90 \pm 1\%$), of the gold as AuCl_4^- , which has

practically the same Mössbauer parameters ($IS = 1.26 \pm 0.04 \text{ mm/s}$, $QS = 1.61 \pm 0.04 \text{ mm/s}$) as those in the fresh sample. While 10% of the gold is still Au(0), no trace of the Au(I) species can be seen in the spectrum after reactivation.

Mössbauer spectroscopy thus confirms the notion that the catalytic activity is based on the presence of AuCl_4^- species on the carbon, and that deterioration of the catalyst during use at high temperatures is connected with the reduction of the Au(III) to metallic gold. An intermediate species, presumably Au(I), has been observed on the spent catalyst, but its nature and its possible role in the catalytic process requires future clarification.

Investigation of Au(0) and Au(I) catalysts. A range of supported gold catalysts were prepared and compared for their reactivity with respect to the acetylene hydrochlorination reaction. A sample containing Au(0) was prepared by impregnating $\text{Au}(\text{CN})_2^-$ onto the activated carbon followed by thermal decomposition at 400°C. Catalysts containing Au(I) were prepared by impregnating $\text{KAu}(\text{CN})_2$ onto the active carbon. The AuCN/C catalyst was prepared by boiling the $\text{KAu}(\text{CN})_2$ catalyst in 4% HCl

for 6 h (23). For comparison, a catalyst containing both Au(0) and Au(III) was prepared by adsorption of HAuCl_4 onto active carbon using the standard preparation procedure. These catalysts were tested for acetylene hydrochlorination at 180°C and the results, shown in Fig. 8, indicate that all catalysts deactivate with reaction time and reach a similar conversion level after ca. 5 h reaction. This study confirms that catalysts containing only Au(0) are much less active initially than those containing gold in higher oxidation states. In addition, the Au(0) catalyst exhibited the slowest deactivation rate of all the gold catalysts tested, whereas the catalysts containing higher oxidation states initially deactivated at higher rates. Analysis of the deactivated catalysts by X-ray diffraction confirmed that after 5 h reaction at 180°C , the catalysts were comprised mainly of Au(0). The reduction of AuCN to Au is a well-known reaction (24). It is therefore concluded that at the high reaction temperature of 180°C a major cause of catalyst deactivation is the reduction of Au(III) and Au(I) to Au(0).

CONCLUSIONS

Carbon-supported gold catalysts for the acetylene hydrochlorination reaction have been shown to be deactivated by two processes. Deposition of carbonaceous material on the catalyst is the predominant deactivation process occurring at temperatures $<100^\circ\text{C}$. At these low temperatures the coke precursors, considered to result from the polymerisation of vinyl chloride, are not readily desorbed from the catalyst surface. A second deactivation pathway is ascribed to the reduction of Au(I) and Au(III) to Au(0) during the catalytic reaction. This deactivation pathway is predominant at temperatures $>120^\circ\text{C}$. As demonstrated in Fig. 5, these two deactivation processes result in an optimum temperature in the range of $100\text{--}120^\circ\text{C}$ being observed for the catalyst lifetime under the conditions utilised in this study.

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