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Hydrochlorination of acetylene using a supported gold catalyst: A study of the reaction mechanism

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Abstract

A detailed study of the hydrochlorination of acetylene and higher alkynes using a supported gold catalyst is described and discussed. A series of reactions using sequential exposure of the catalysts to C_2H_2 and HCl demonstrate that exposure to HCl before reaction of C_2H_2/HCl leads to enhanced activity, whereas exposure to C_2H_2 leads to deactivation. The reaction of higher alkynes is affected by steric factors, with the following trend in activity: acetylene (ca. 40% conversion) $\gg$ hex-1-yne (10%) > phenyl acetylene (7%) > hex-2-yne (2%). Using ^{1}H NMR spectroscopy, we found that for hex-1-yne and phenyl acetylene, the anti-Markovnikov product is formed by *anti*-addition of HCl, but the Markovnikov products are equivalent for *syn*- and *anti*-addition of HCl. Thus, we investigated the reaction using deuterated substrates and confirmed that the products are formed by the *anti*-addition of HCl. The reaction mechanism is discussed in detail.

Keywords: Gold catalysis; Catalyst reactivation; Acetylene hydrochlorination

1. Introduction

Hydrochlorination of acetylene is one method by which vinyl chloride can be manufactured on a commercial scale. Industrial processes use mercuric chloride supported on carbon [1,2], but these catalysts can be short-lived due to their instability, with loss of mercuric chloride being a major catalyst deactivation mechanism, leading to environmental problems. In 1985, it was proposed that supported Au^{3+} would be a viable catalyst for alkyne hydrochlorination [3], and later this was shown to be the case [4–7]. These early studies largely predated the massive current interest in catalysis by gold [8–11] but did show that gold could be the catalyst of choice for a specific reaction, whereas previously gold had been considered of little interest as a catalyst. In these earlier studies, we studied the mechanism by which the gold catalysts were deactivated during the hydrochlorination reaction [6] and explored means by which they could be reactivated [7]. It is interesting that since those studies, there have been no further investigations on the acetylene hydrochlorination reaction using supported gold catalysts. We have revisited this reaction, and in this paper we present a study of the reaction mechanism and also explore the reactivity of higher primary and internal alkynes for the hydrochlorination reaction.

2. Experimental

2.1. Catalyst preparation and characterization

The carbon-supported gold catalyst (1 wt% Au/C) was prepared using an incipient wetness impregnation technique and aqua regia as a solvent. The carbon (Aldrich, Darco 12–20 mesh) was initially washed with dilute aqueous HCl (1 $mol\,L^{-1}$) at 70 °C for 5 h to remove Na, Fe, and Cu, which are poisons for the hydrochlorination reaction [12]. The carbon was filtered and washed with distilled water (2 $L\,g^{-1}$) and dried

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at 140 °C for 18 h. A solution of $HAuCl_4 \cdot xH_2O$ (Strem, 82 mg, assay 49.7%) in aqua regia (3.7 mL) was added dropwise to the acid-washed carbon (Aldrich, Darco 12–20 mesh, 4 g) under stirring. The product was then dried at 140 °C for 18 h and used as a catalyst.

X-ray photoelectron spectroscopy spectra were recorded on a Kratos AXIS-Ultra spectrometer, using a monochromatic AlK_α X-ray source (75–150 W) and an analyzer pass energy of 160 eV (survey scans) or 20 eV (detailed scans). Binding energies are referenced to the C(1s) binding energy of carbon, taken to be 284.7 eV.

Samples were prepared for transmission electron microscopy (TEM) analysis by dispersing the catalyst powders in high-purity ethanol and allowing a drop of the suspension to dry on a lacey-carbon film supported on a 300-mesh Cu TEM grid. Bright-field (BF) images were acquired using a JEOL 2000FX TEM operating at 200 keV with a LaB_6 filament.

2.2. *Catalyst testing*

Catalysts were tested for acetylene hydrochlorination in a fixed-bed glass microreactor operating just above atmospheric pressure. Acetylene (5 mL min^{-1}) and hydrogen chloride (5 mL min^{-1}) were fed though a mixing vessel/preheater (70 °C) via calibrated mass flow controllers to a heated glass reactor containing catalyst (200 mg), giving a total GHSV of 870 h^{-1}. Higher alkynes were used as liquids and were introduced by vaporisation in an inert gas. The pressure of the reactants, HCl and C_2H_2, was in the range of 1.1–1.2 bar. This value was chosen both for safety reasons and to test the catalyst under mild conditions. The products were analyzed in two ways. First, the exit gas mixture was passed through a Dreschel bottle containing NaOH at known concentration for a known time to determine the conversion of HCl. Alternatively, the gas stream could to be analyzed by GC. A reaction temperature of 180 °C was chosen, and blank tests using an empty reactor filled with quartz wool did not reveal any catalytic activity, even at 250 °C with the reactants under these flow conditions.

2.3. *DFT methodology*

Calculations on the interactions among $AuCl_3$, acetylene, and HCl and the pathways to the formation of chloroethene were carried out using the BH and H functional and a 6–31G(d,p) basis set [13] with the Gaussian 03 program [14]. The core electrons of Au were represented using the relativistic effective core potential developed by Stoll et al. [15]. Transition states were obtained by relaxed scans of the bond formed in the reaction; the maximum point was then used in a transition state optimization. Transition states were confirmed by a frequency calculation to show that only a single imaginary mode was present, and this mode was animated to verify that it linked reactants and products.

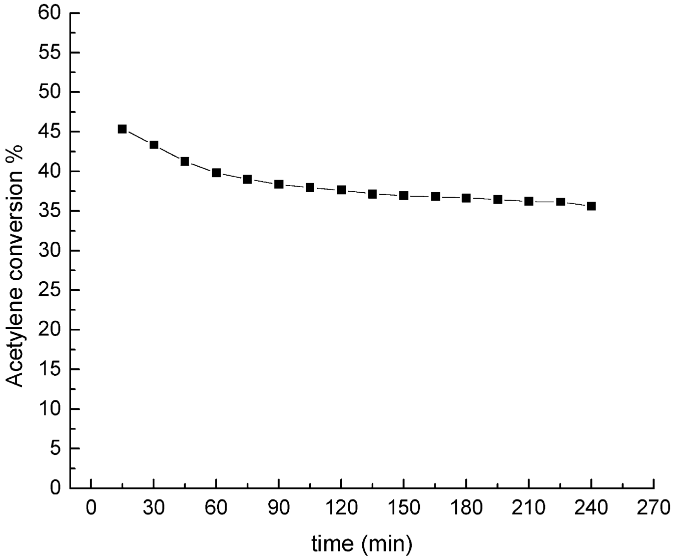


Fig. 1. Acetylene hydrochlorination using Au/C catalyst at 180 °C, HCl/C_2H_2 mol ratio = 1:1, reactant flow rates 5 mL min^{-1}.

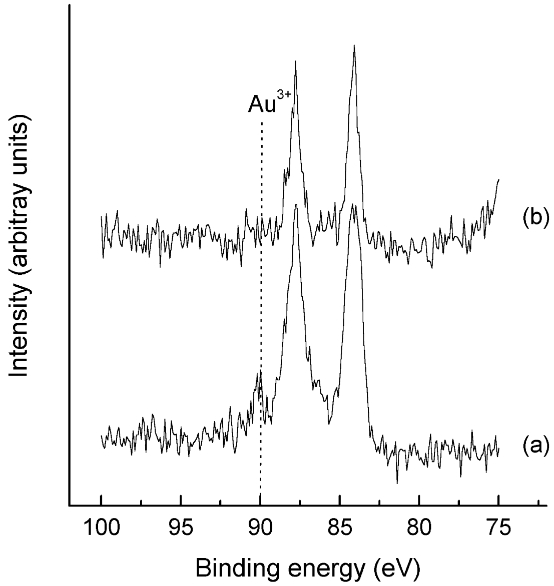


Fig. 2. Au 4f XPS spectra of Au/C catalysts, (a) before reaction it is possible to detect the presence of Au^{3+} while (b) after reaction Au^{3+} is reduced.

3. Results and discussion

3.1. *Sequential HCl/C_2H_2 during acetylene hydrochlorination*

The activity of the supported gold catalyst decreased gradually during exposure to the C_2H_2/HCl reaction mixture under the standard reaction conditions (Fig. 1). This was considered to be due to the reduction of Au^{3+} and is consistent with our previous findings [3–7]. X-ray photoelectron spectroscopy of the fresh and deactivated catalyst confirmed this earlier conclusion (Fig. 2). C_2H_2 is a well-known reducing agent, and it is important to determine whether the reduction in activity is an effect of the reaction or of acetylene only. To determine this, we carried out a series of experiments in which the catalyst was

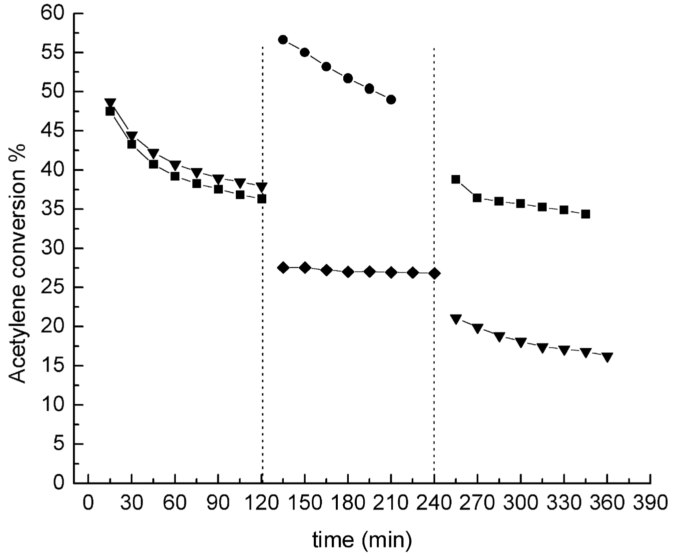


Fig. 3. Sequential flow experiments to evaluate the effect of each reactant for the hydrochlorination reaction of acetylene over Au/C catalyst. (Experiment A: ■) C_2H_2/HCl (2 h) → He/HCl (2 h) → C_2H_2/HCl (2 h); (experiment B: ●) He/HCl (2 h) → C_2H_2/HCl (2 h) → He/HCl (2 h); (experiment C: ▼) C_2H_2/HCl (2 h) → C_2H_2/He (2 h) → C_2H_2/HCl (2 h); and (experiment D: ▼) C_2H_2/He (2 h) → C_2H_2/HCl (2 h) → C_2H_2/He (2 h).

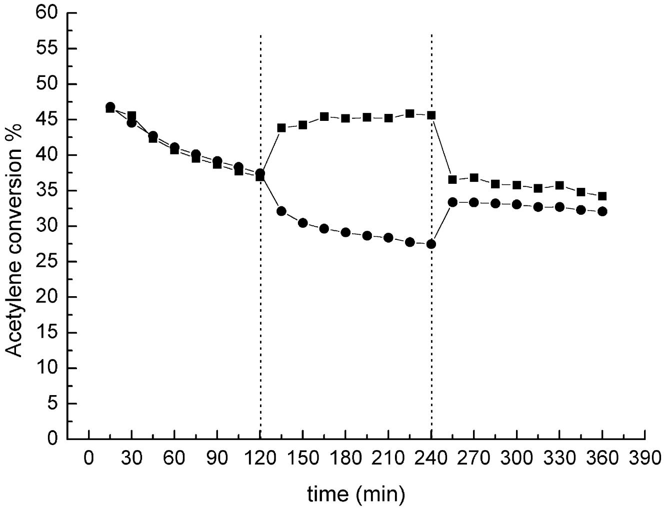


Fig. 4. Hydrochlorination reaction of acetylene with varying molar ratios of HCl. (Experiment E: ■) C_2H_2/HCl (2 h) 1:1 → C_2H_2/HCl (2 h) 1:1.5 → C_2H_2/HCl (2 h) 1:1 and (experiment F: ●) C_2H_2/HCl (2 h) 1:1 → C_2H_2/HCl (2 h) 1:0.5 → C_2H_2/HCl (2 h) 1:1.

sequentially exposed to individual components of the reactants. To achieve this, an inert gas (He) was added to the reactants to ensure that the overall flow rate could be maintained constant. Four sets of experiments were conducted, using a 1:1 molar reactant ratio (i.e., a flow of 5 $\mathrm{mL\,min^{-1}}$ for each reactant) at 180 °C, as follows:

- Experiment A:
  C_2H_2/HCl (2 h) → He/HCl (2 h) → C_2H_2/HCl (2 h),
- Experiment B:
  He/HCl (2 h) → C_2H_2/HCl (2 h) → He/HCl (2 h),
- Experiment C:
  C_2H_2/HCl (2 h) → C_2H_2/He (2 h) → C_2H_2/HCl (2 h),
- Experiment D:
  C_2H_2/He (2 h) → C_2H_2/HCl (2 h) → C_2H_2/He (2 h).

The results of these experiments are shown in Fig. 3. The role of HCl is clearly demonstrated in experiments A and B. In experiment A, where the intermediate step is He/HCl, the catalytic activity was maintained when the acetylene was reintroduced in the third phase of the experiment. In experiment B, in which the initial treatment was with He/HCl, the formation of vinyl chloride was significantly enhanced on introduction of the acetylene. In this case, the initial HCl treatment oxidized some Au^0, as we have noted in previous catalyst regeneration studies [7]. Conversely, exposure to C_2H_2 led to catalyst deactivation in the absence of HCl (experiments C and D). Even if no reaction occurred initially (experiment D), clearly the catalyst was deactivated by exposure to C_2H_2, and when the reaction was brought online again, the conversion to vinyl chloride was markedly lower compared with a standard reaction without interruption of the reactants. These experiments clearly demonstrate that both reactants are able to modify the final performance of the catalyst, but in opposing directions: HCl plays a regeneration/activation role, whereas C_2H_2 acts to decrease the catalyst activity independent of whether or not the reaction is occurring.

To further evaluate the effects of the reactants, we carried out two additional tests in which the molar ratios of HCl and C_2H_2 were varied:

- Experiment E:
  C_2H_2/HCl (2 h) 1:1 → C_2H_2/HCl (2 h) 1:1.5
  → C_2H_2/HCl (2 h) 1:1,
- Experiment F:
  C_2H_2/HCl (2 h) 1:1 → C_2H_2/HCl (2 h) 1:0.5
  → C_2H_2/HCl (2 h) 1:1.

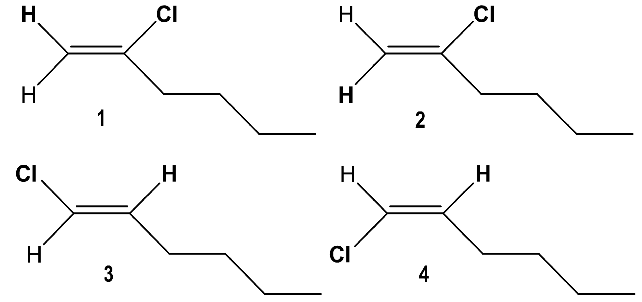
The results, shown in Fig. 4, indicate that the conversion increased and the rate of deactivation decreased when the molar ratio of the HCl was increased. Indeed, even when the standard flows of reactants were resumed, the activity of the catalysts treated with the higher molar ratio of HCl/C_2H_2 remained noticeably higher than that treated with the lower HCl/C_2H_2 ratio.

3.2. Reaction of higher alkynes

In all of our previous studies [4–7], we investigated only the hydrochlorination of acetylene. Being a symmetrical molecule, the reaction of acetylene does not provide mechanistic data, because only one product is possible. In view of this, we wished to extend the reactant molecules to substituted alkynes, to answer two questions: (a) Can higher alkynes be reacted with HCl under the same reaction conditions?, and (b) what is the selectivity of the reaction?

3.2.1. Hydrochlorination of hex-1-yne over Au/C catalyst

We studied the reaction of hex-1-yne/HCl using the Au/C catalyst and a reaction temperature of 180 °C with standard re-



Scheme 1. Possible regioselectivity and stereochemistry of the addition of HCl to hex-1-yne: **1**, Markovnikov with *syn* HCl addition; **2**, Markovnikov with *anti* HCl addition; **3**, anti-Markovnikov with *syn* HCl addition; and **4**, anti-Markovnikov with *anti* HCl addition.

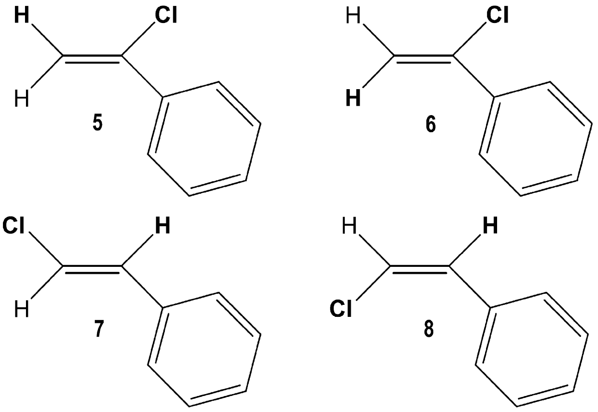
actant flow rates (HCl flow rate: 5 mL min^{-1} and hex-1-yne introduced via a saturator with an He flow of 10 mL min^{-1}, HCl:alkyne molar ratio = 0.74 cf. 1.0 for acetylene). The products were analyzed by gas chromatography to determine conversion. This was determined to be steady at 10% for hex-1-yne (compared with ca. 40% conversion for acetylene under the same conditions), indicating that the steric hindrance of the larger substrate significantly affected reactivity. We used ^{1}H NMR spectroscopy to determine the nature of the product by collecting the reaction products in a chloroform trap at the outlet of the reactor for a time on line of 3 h (see Supplementary material). Taking into account all of the possible isomers (i.e., the Markovnikov and anti-Markovnikov and the *syn*- or *anti*-addition of HCl to the triple bond), the number of possible products that can be obtained was four; these are shown in Scheme 1 and Table S1.

The reaction was found to display very high selectivity toward the Markovnikov products **1** and **2** (which are, unfortunately, NMR-equivalent). Only traces (3.7% of the amount relative to the Markovnikov product) of the anti-Markovnikov product **4** were detected (see Supplementary material, Fig. S1 and Scheme S1), whereas product **3** was absent.

Concerning the trace levels of the anti-Markovnikov products found, the difference in terms of chemical shift between the HCl addition products with *syn*- and *anti*-stereochemistry was not significant for unambiguous characterization. However, at 6.03 ppm, a doublet of triplets was observed, with a coupling constant J_{AB} equal to 6.7 Hz (see Supplementary material, Fig. S2 and Table S1). This numerical value is consistent with that of the HCl addition product with *anti*-stereochemistry, expected to have a value of 6–12 Hz [16], whereas the HCl addition product with *syn*-stereochemistry is expected to have a value of 12–18 Hz.

3.2.2. Hydrochlorination of phenyl-acetylene over Au/C catalyst

To collect further information on the reactivity toward different substrates, hydrochlorination of phenyl acetylene was studied using the same reaction conditions as those used for hex-1-yne (180 °C, a flow of HCl of 5 mL min^{-1}, with phenyl acetylene introduced via a saturator with an He flow of 10 mL min^{-1}, and a HCl:alkyne molar ratio = 1.75 cf. 1.0 for acetylene). Online gas chromatography found a 7% conversion of phenyl acetylene under these conditions. This difference in reactivity compared with that of hex-1-yne can be explained by the fact that in phenyl-acetylene, the triple bond is conjugated with the aromatic ring. The selectivity of the product was determined by ^{1}H NMR spectroscopy (Scheme 2; also see Supplementary material, Scheme S2), and the major product was determined to be the Markovnikov NMR equivalent products **5** and **6** (see Supplementary material, Fig. S3). Traces of the product for the *anti*-addition of HCl (1.2% of relative amount) **8** (see Supplementary material, Fig. S4) were found, whereas the product for the *syn*-addition **7** was absent.



Scheme 2. Possible regioselectivity and stereochemistry of the addition of HCl to phenyl-acetylene: **5**, Markovnikov with *syn* HCl addition; **6**, Markovnikov with *anti* HCl addition; **7**, anti-Markovnikov with *syn* HCl addition; and **8**, anti-Markovnikov with *anti* HCl addition.

3.2.3. Hydrochlorination of hex-2-yne over Au/C catalyst and effects of terminal alkynes

In a catalytic test using hex-2-yne as a substrate using the same experimental conditions used for hex-1-yne (HCl:hex-2-yne molar ratio = 0.77 cf. 1.0 for acetylene), very little conversion (<2%) was detected. In addition, in this case it was not possible to carry out assignments for the stereochemistry of the final products obtained. This is because the proton coupling constants of the two Markovnikov isomers for the *syn*- or *anti*-addition of HCl were both in the same range [13] for an unambiguous determination of minor amounts of one isomer in the presence of the other. However, the very low reactivity of hex-2-yne in comparison with terminal alkynes demonstrates the effects of steric hindrance on reactivity. Based on the reaction data, the trend in activity was as follows: acetylene (ca. 40% conversion) $\gg$ hex-1-yne (10%) > phenyl acetylene (7%) > hex-2-yne (2%). Note, however, that there were differences in the amounts of the alkyne fed to the reactor for the longer-carbon chain alkynes, because these were fed to the reactor using a saturator. Thus, the substrate:HCl ratio was different for the longer-carbon chain alkynes compared with acetylene. However, the ratios for the two hexynes that we have studied were similar within experimental error (hex-1-yne, 0.74; hex-2-yne, 0.77), and thus the difference in their reactivity was significant. We found that the rate of reaction was dependent on the alkyne:HCl molar ratio (Fig. 4), with increasing conversion and decreasing rate of deactivation when the HCl molar ratio was increased. This effect must be taken into account when considering the effect of the substrate structure on reactivity. But as phenyl acetylene is studied with a high HCl:alkyne molar ratio (1.175), the experiments will tend to overestimate its reactivity relative to that of acetylene. Similarly, we have slightly underestimated the reactivity of the hexynes relative to that of acetylene. For acetylene, at an acetylene:HCl molar ratio of 1:0.5, the reactivity decreased by ca. 25%, and thus we can estimate that the effect of the molar ratio on the reactivity of hexenes as ca. 10–15%. Taking these factors into account, we consider that the relative order of reactivity that we have described based on the reaction data is validated.

3.3. Hydrochlorination using deuterated reactants

Using ^{1}H NMR spectroscopy, we found that for hex-1-yne and phenyl acetylene, the anti-Markovnikov was formed by *anti*-addition of HCl. But because the Markovnikov products are equivalent for *syn*- and *anti*-addition of HCl, we investigated the reaction using deuterated substrates.

3.3.1. Hydrochlorination of hex-1-yne with DCl

The hydrochlorination reaction was carried out with hex-1-yne and DCl. The DCl was used in a diethylether solution ($1\ \mathrm{mol\,L^{-1}}$) and fed to the reactor via a saturator. The effect of the presence of the diethylether was tested separately; no reaction occurred with this molecule, nor did it affect the reaction. The reaction products were collected in deuterated chloroform and ^{1}H NMR revealed the presence of only one deuterated Markovnikov product (see Supplementary material, Fig. S5) with *anti*-stereochemistry, and it was concluded that this product was formed via *anti*-addition of DCl to hex-1-yne. However, traces of H_2O were found in the He carrier gas, and thus traces of HCl could be present as well. In view of this finding, we reacted deuterated hex-1-yne.

3.3.2. Hydrochlorination using D-hex-1-yne and HCl

To collect more detailed mechanistic information, a catalytic test using deuterated D-hex-1-yne was carried using the same experimental conditions described for the other tests involving hex-1-yne. In contrast with the experiment in which DCl was used, the deuterated product was that formed by *syn*-addition of the HCl (see Supplementary material, Fig. S6). This discrepancy could be related to an isotope effect involving DCl cleavage, an effect that did not operate in the presence of deuterated D-hex-1-yne. Hydrochlorination of phenyl-acetylene using DCl was also investigated, but no reaction was observed.

3.4. Investigation of the catalysts using transmission electron microscopy

In Section 3.1 we reported that the catalyst deactivation that we observed can be ascribed to a loss of Au^{3+} during use. This is consistent with our previous findings [6,7]. However, it is feasible that some deactivation could have been caused by sintering of the metallic gold nanoparticles, because this is the predominant form of the metal present on the catalyst during the reaction. In view of this, we studied the catalyst before and after use for acetylene hydrochlorination using transmission electron microscopy (Fig. 5). We found that a small amount of sintering occurred on use and that the mean gold nanoparticles size increased from 4.8 to 5.9 nm, which we do not consider particularly significant with respect to the overall catalyst deactivation.

3.5. DFT studies

We carried out a series of theoretical studies aimed at improving our understanding of the reaction mechanism of alkyne hydrochlorination using supported gold catalysts. The $AuCl_3$ structure geometry optimization gave a T-shaped complex with a largest Cl–Au–Cl angle of 169 degrees. The lowest unoccupied molecular orbital (LUMO) of this structure exhibited a large lobe in the plane of the complex between the two *trans* Cl ligands (Fig. 6). This is consistent with the well-known electrophilic nature of Au(III) and suggests complexation of a nucleophilic reactant in a square planar geometry.

The overall calculated reaction energy profile is shown in Fig. 7. The energy scale shown takes the sum of the calculated energies for the individual components of the reaction, $AuCl_3$, C_2H_2, and HCl as the arbitrary zero (labeled level **1** in Fig. 7). The initial comparison of the complexation of HCl and acetylene showed that both have a favorable interaction with the Au center in the position expected from the shape of the $AuCl_3$ LUMO. Initial coordination of HCl resulted in a calculated energy of $-105\ \mathrm{kJ\,mol^{-1}}$ with respect to the reference state (level **2**), whereas placing C_2H_2 into the vacant co-ordination site of $AuCl_3$ gave structure **3** with a relative energy of $-168\ \mathrm{kJ\,mol^{-1}}$. This indicates that the alkyne is a better ligand than HCl. Further calculations based on the coordinated HCl structure reacting with acetylene did not identify any low-energy route to chlorinated products; indeed, introduction of acetylene in an axial position over the Au center in complex **2** gave only a very weak interaction.

In the absence of HCl, the structure of the coordinated acetylene, **3**, showed an angle of 59 degrees between the C–C bond and the $AuCl_3$ plane. This twisted arrangement gives a better overlap of the C_2H_2 HOMO π-orbital with the LUMO state shown in Fig. 6. Using constrained optimizations, we calculated the energy of the complex as a function of this twist angle and found the low-lying intermediate **5** (energy $-213\ \mathrm{kJ\,mol^{-1}}$) via transition state **4**. The calculated barrier between the π-complex, **3**, and metallocycle, **5**, was $69\ \mathrm{kJ\,mol^{-1}}$. However, attempting to find transition states involving addition of HCl to the C–C bond in **5** resulted in barriers considerably higher than those reported in Fig. 6. This may indicate that the coordination of acetylene in the absence of HCl results in site blocking via the formation of this stable metallocycle structure.

Returning to the π-complex, **3**, HCl was introduced with the Cl atom close to an axial site at the Au center. But on relaxation, the HCl molecule moved away to the position shown in structure **6**, and a Bader analysis of the charge density confirmed that the main interaction between HCl and the complex was via a HCl–HC hydrogen bond. To search for a transition state for HCl addition, the Cl atom was stepped toward the nearest

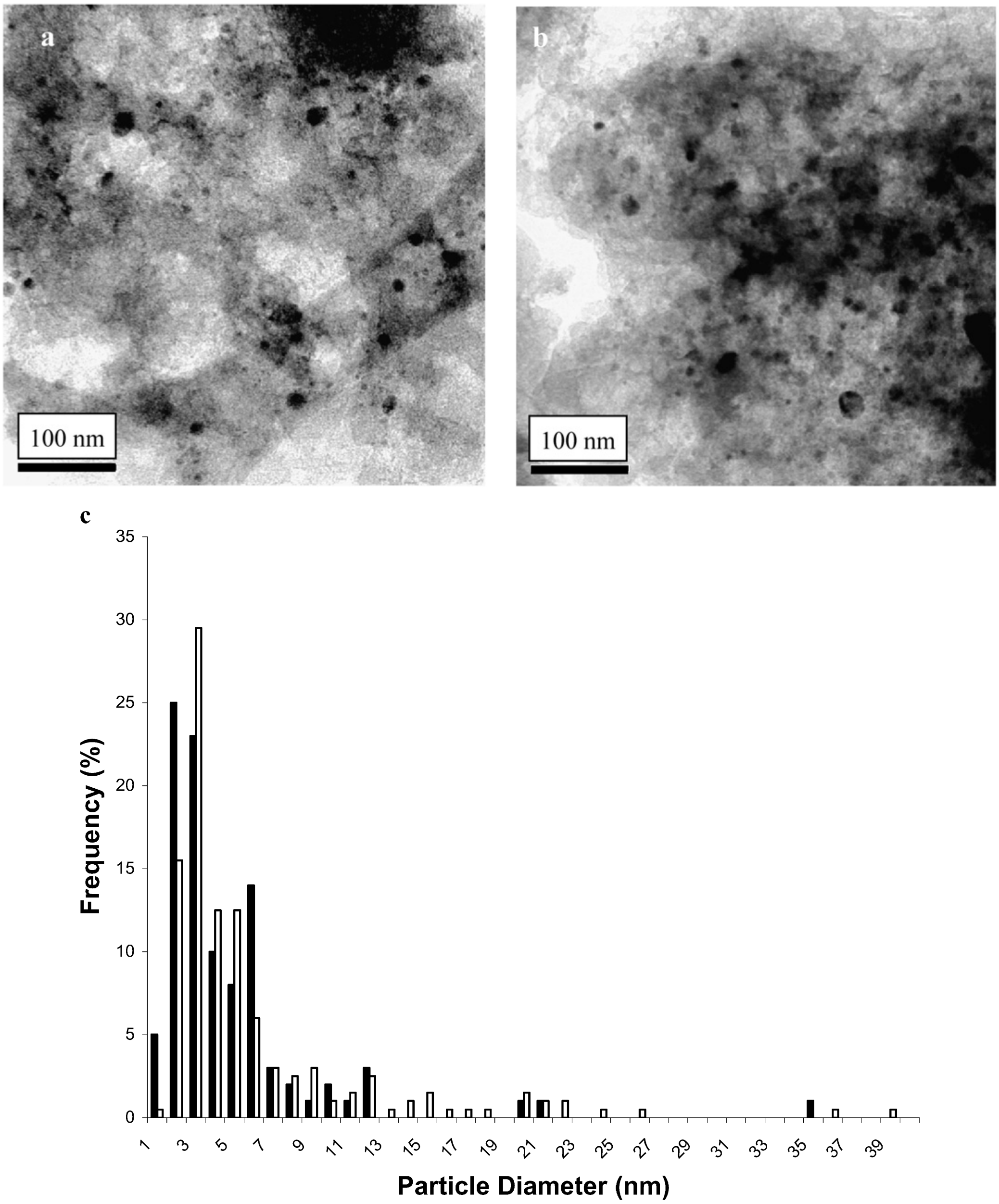


Fig. 5. Representative TEM micrographs of the Au/C catalyst before (a) and after (b) reaction; mean particle sizes were 4.8 and 5.9 nm, respectively. Also shown are the Au particle size distributions (c) of these catalysts, filled columns pre-reaction and open columns post-reaction, showing a slight increase in the particle size after the reaction.

C atom in a series of constrained optimizations. This resulted in Cl addition via the transition state shown as structure **7**. At this point in the reaction, the HCl bond cleaved to add Cl to the alkyne, with the H(Cl) atom cleaving to one of the Cl ligands on Au. In addition, the second carbon atom exhibited a σ-bond to the Au center that is *anti* to the forming Cl–C bond. The final stereochemistry was set by this transition state because transfer of the H atom to replace the Au center was facile and resulted in a complex with the product alkene in a π-complex akin to **3**.

3.6. Comments on the reaction mechanism

Based on the preceding experimental evidence and discussion, we can comment on the reaction mechanism by which alkyne hydrochlorination occurs using the gold catalyst. One possibility is based on an analogy with the mechanism of hydrogenation using Wilkinson's catalyst [17] with Rh and Ir analogues complexes, in which the initial step is oxidative addition of H_2 followed by coordination of an alkene, transfer of the hydrogen to form an alkyl group initially and an alkane subsequently, thereby regenerating the catalytic complex. Such a mechanism based on $AuCl_3$ involving the formation of an octahedral intermediate is shown in Scheme 3.

This mechanism involves oxidative addition of HCl followed by coordination of acetylene and then reductive elimination. A point of debate is whether Au^{3+} can act in this way. It is more likely that such a mechanism could operate with Au^{+}, which could be present in the operating catalyst. But the mech-

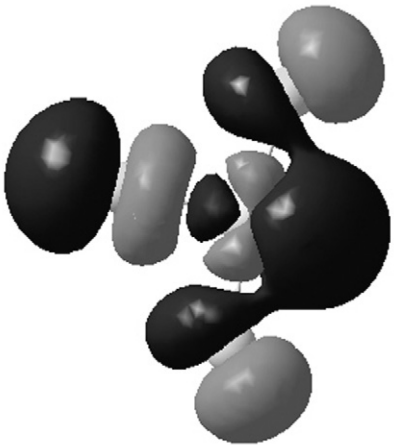
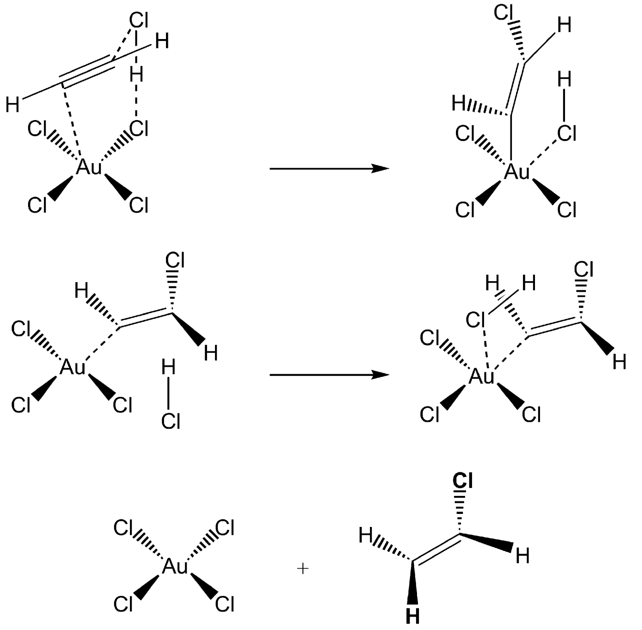


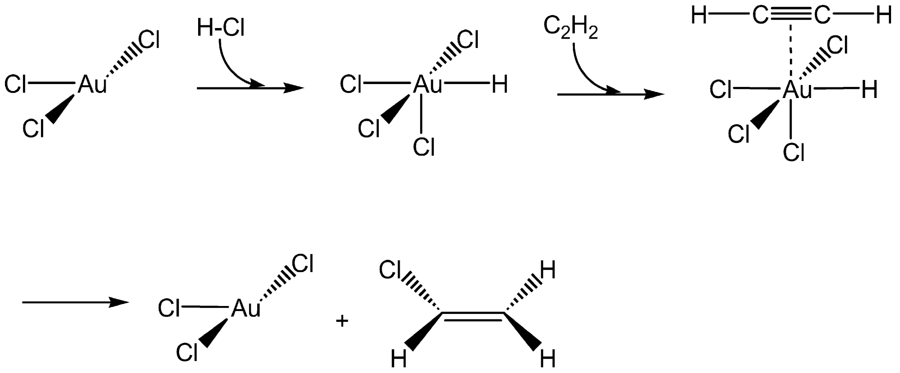
Fig. 6. The calculated LUMO state for $AuCl_3$ at the BH and H/6–31(d,p) level.

anism denoted in Scheme 3 could be a viable reaction pathway for terminal alkynes, whereas it is unlikely that internal alkynes could undergo reaction via the oxidative addition mechanism shown in Scheme 3. Because internal alkynes are not reactive with the supported gold catalyst, this may demonstrate that the mechanism shown in Scheme 3 can be possible. But the theoretical studies indicate that formation of an intermediate in which both the alkyne and HCl are adsorbed together results in only a weak interaction, which may mitigate against this mechanistic proposal.

Consequently, we need to consider other potential reaction pathways. The reactivity of gold, especially Au^{3+}, toward alkynes is usually explained in one of two ways: (i) a nucleophilic–electrophilic interaction between the Au^{3+} center and the triple bond via π-coordination [18] observed for gold or (ii) use of the acidity of the acid protons of the terminal alkyne (I)–alkynyl complexes [19] to give a σ-coordination. In addition, sometimes both π- and σ-coordinations can be observed [20] using two gold centers. It should be noted that π and σ coordination of alkynes [10,21] have been observed for homogeneous catalysis reactions, and previous studies have shown a possible pathway that could explain the observed reactivity for primary alkynes and the absence toward secondary alkynes that could be operating for the systems studied in this work. This could indirectly support a mechanism involving a C_2H_2/Au/HCl complex. The key piece of mechanistic information is that which HCl adds in accordance with the Markovnikov rule and in an *anti*-configuration to the alkyne. This *anti*-addition also has been observed in the hydrochlorination of acetylene using mechanically activated K_2PtCl_6 [21], for which it is proposed that the reaction could occur via a complex formed by adsorption of acetylene at a defect site on the surface of the mechanically activated K_2PtCl_6 and HCl adsorbed via hydrogen bonding with the surface Cl. It is feasible that a similar mechanism could operate with supported gold catalysts via the mechanism shown in Scheme 4, with gold tetrachloroaurate as the active species. The hypothesis is that the C_2H_2/Au/HCl complex is consistent with the high selectivity; the regeneration effect of HCl, and the deleterious effect of C_2H_2 and can explain polymerization, which is one of the mechanisms by which catalyst deactivation occurs. However, this mechanism requires the presence of both reactants to give an initial six-member ring in which the alkyne coordinates axially to the Au center. In our DFT studies, we found only weak coordination of either alkyne or HCl in this position and thus would expect the resulting penta-coordinated complex to be unstable. It noteworthy, that if C_2H_2 is present



Scheme 4. Proposed model for the hydrochlorination of acetylene over Au/C catalyst, assuming C_2H_2/Au/HCl complex formation.



Scheme 3. Proposed model for the hydrochlorination of acetylene over Au/C catalyst, assuming an oxidative addition pathway.

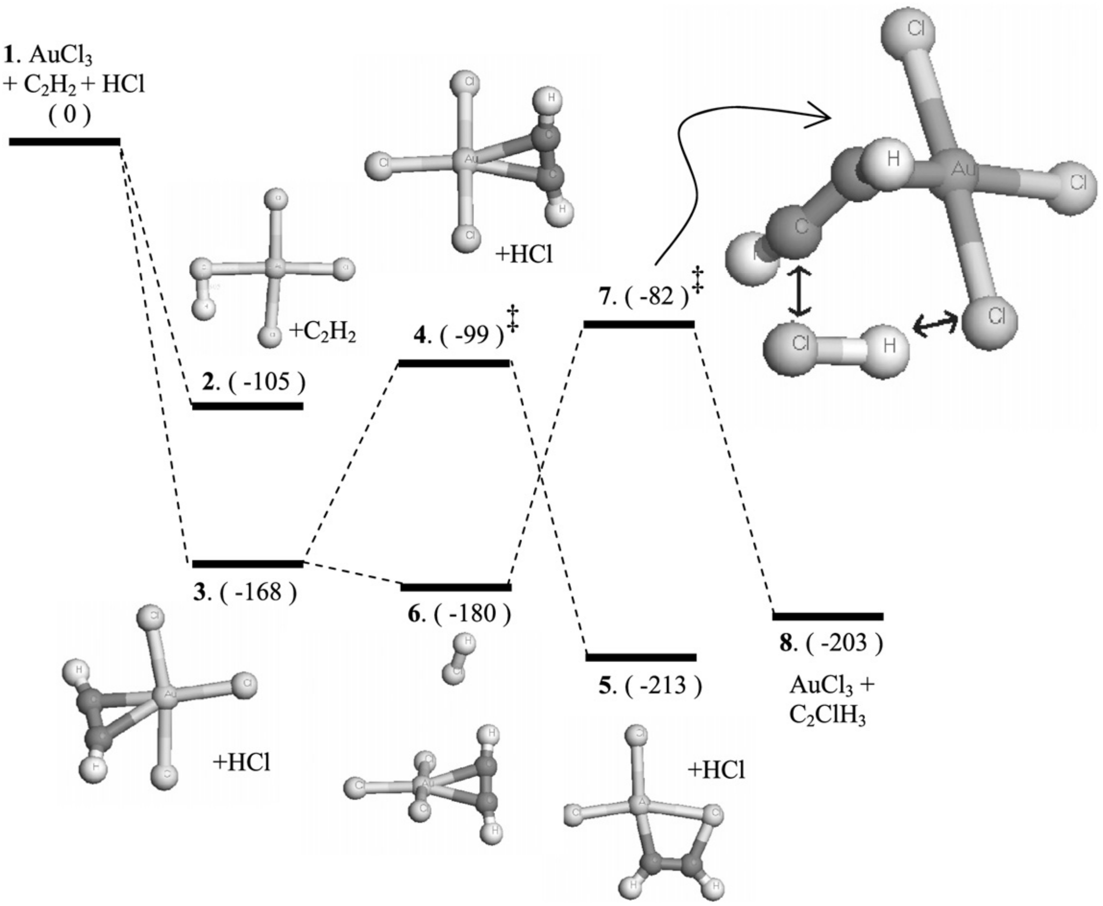


Fig. 7. Reaction energy profile for hydrochlorination of acetylene, all energies in kJ mol^{-1}, transition states marked ‡.

instead of HCl on the regeneration step, then it is possible to obtain a conjugate polymer with an even number of carbon atoms. This also could be true in the case of our DFT-generated transition state (**7**, Fig. 7), which does not require axial coordination of the alkyne.

Although the cationic active gold species was represented in both of these reaction mechanisms as a single site, and the computational studies that we have carried out used this as a basis, we consider the active center to be associated with the surface of a gold nanoparticle. In particular, it might be of interest to consider that the reaction occurred in an analogous manner to a homogeneous catalyst, and that the cationic gold species was not associated with the surface of the heterogeneous catalyst. Such effects are well known in palladium catalysts, such as for the Heck reaction [22,23], where attempts to heterogenize the catalyst have not succeeded and the catalysis continues to result from Pd^{2+} leaching from the catalyst surface. But this analogy does not work well in the present case, because there was no fluid phase in which the leached cationic gold species could be stabilized. Of course, the reaction could proceed in the gas phase, but there are two pieces of evidence that argue against this possibility. First, gold compounds are not particularly volatile under the reaction conditions used; indeed, gold chlorides decompose at elevated temperatures and they do not sublimate; Au(I) chloride decomposes at 289 °C, and gold (III) chloride decomposes at >160 °C. Thus, any gas-phase gold chloride species formed would not be stable, and we consider such species to be stabilized on the surface of the catalyst and expect them to be formed as intermediates. Second, if the reaction occurred in the gas phase, then in the flow reactor, gold would be continually redispersed down the catalyst bed and then out of the reactor. This would severely affect the catalyst lifetime, as is observed when the markedly more volatile $HgCl_2$ is used as a catalyst [1,2]. We did not observe any loss of gold in this study or in our previous extensive studies [4–7], and thus we do not believe that this reaction occurs via a gas-phase species.

4. Conclusion

In the hydrochlorination of acetylene and higher alkynes using deuterated reactants with supported gold catalysts, the addition of HCl was shown to occur in the *anti*-stereochemistry configuration and in accordance with Markovnikov rule for the formation of the main product. However, with higher alkynes, trace amounts of minor products formed via anti-Markovnikov addition. The reactivity of higher primary alkynes decreased with their steric bulk, and internal alkynes were unreactive. DFT calculations indicate that the simultaneous coordination of alkyne and HCl to the Au(III) center of $AuCl_3$ is unlikely. The calculated transition state for HCl addition to the π-complex of C_2H_2 with $AuCl_3$ demonstrates that the stereochemistry of Cl addition is controlled by a hydrogen bond between HCl and a Cl ligand of Au. The *anti*-addition of HCl observed experimentally is then a consequence of a sequential addition of Cl and H to the alkyne. This scheme is similar to that proposed for hydrochlorination using mechanically activated K_2PtCl_6 but takes note of the preference for square planar geometries in Au(III) complexes.

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Supplementary material

The online version of this article contains additional supplementary material.

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