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# Formation of polymer-grade ethylene by selective hydrogenation of acetylene over $Au/CeO_2$ catalyst

Yassine Azizi, Corinne Petit, Véronique Pitchon [*]

*Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse, UMR 7515 du CNRS ECPM, 25, rue de Becquerel, 67087 Strasbourg, France*

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ABSTRACT

Acetylene hydrogenation and formation of coke deposits were investigated on a gold catalyst supported on ceria. The effect of the $H_2/C_2H_2$ ratio was studied over a range of values. In all cases, the catalyst revealed a selectivity of 100% below 300 °C. Above this temperature, the only byproduct was methane formed via carbene intermediates, which polymerize above 300 °C, provoking deactivation. The deactivation was studied by TPO; accumulation of carbon at low temperature provoked deactivation only after several hours of operation, but did not affect the selectivity. The roles of the pretreatment and of the presence of CO also were examined. A mechanism for the hydrogenation reaction is proposed.

## 1. Introduction

Ethylene is by far the basic petrochemical product in greatest demand, with a worldwide production of more than 130 million tons per year. Industrially, ethylene is usually formed by the pyrolysis of hydrocarbons in the presence of steam. Acetylene is a byproduct of this process, which subsequently acts as a poison for the catalyst used for the synthesis of polyethylene from ethylene. In addition, acetylene can form acetylides, both explosive and contaminant. Therefore, its removal is essential to secure the safe production of polymer-grade ethylene; the maximum allowable acetylene concentration is 5 ppm [1,2]. The procedures for treating $C_2$ effluents depend on both the acetylene concentration and the degree of purity desired [3]. Strategically, they can be divided into two techniques, recovery of acetylene by solvent extraction and selective hydrogenation systems, the latter being a result of catalytic activation.

Several types of catalyst are suitable for the hydrogenation of acetylene, and the patent literature contains a wealth of information on the subject [4]. Among these catalysts, supported palladium predominates, largely because they have the ability to selectively hydrogenate the triple bond to ethylene [5–7]. However, certain factors affect the economic viability of an industrial process; indeed, palladium tends to form oligomers, which lead to liquid polymer mixtures ("green oil") and the formation on the catalytic surface of high concentrations of carbonaceous deposits, which shorten the catalyst lifetime. Furthermore, Pd has a lower selectivity at high degrees of conversion.

Numerous strategies have been developed to counter these negative effects. These include altering the electronic properties of palladium by adding a second metal or element, such as Ag, which has by far the greatest number of reported studies [8–11]. Cu [12], Cr [13], Co [14], Ni [15], K [16], and Si [17] also can be used. An alternative approach is to modify the interactions between the metal and the support using $SiO_2$ or $TiO_2$ [18], and yet another approach to improving selectivity is to add small concentrations of carbon monoxide to the feed. Although CO acts as a poison to the activity, it has been reported to improve the selectivity toward ethylene [19,20].

Because the aforementioned do not completely resolve the problems of selectivity at high temperatures and oligomerization, improving these catalysts remains a constant challenge for researchers. Gold has been found to be active for several hydrogenation reactions, such as acrolein [21,22], 1,3-butadiene [23], and even $\alpha$-, $\beta$-unsaturated ketones [24]. One of the striking features of hydrogenation on gold is that high selectivity is always observed. Although this property is well known [25–27], the propensity for hydrogenation has rarely been studied in alkynes. The few results available in the literature report properties that raise the possibility of a novel application for gold catalysts. Indeed, the hydrogenation of butyne [28], propyne [29], and acetylene [30,31] on gold catalysts has been reported, although these papers remain the only reported examples of the high selectivity in ethylene on gold catalysts. The work of Jia et al. carried out on $Au/Al_2O_3$ in a batch reactor, revealed that the selective production of ethylene was achieved at between 40 and 250 °C and that above this temperature, undesired ethane was obtained as a coproduct. This successive hydro-

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[*] Corresponding author.
*E-mail address:* pitchon@chimie.u-strasbg.fr (V. Pitchon).

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genation is a unique feature of gold compared with palladium on which hydrogenation to ethylene and ethane proceeds simultaneously. These authors also evaluated the affect of gold particle size on the reaction rate, with a maximum observed for sizes of 2.5 to 3 nm [30]. A few years later, Choudhary et al. studied the same reaction but with Au/$TiO_2$ in a plug-flow reactor [31]. The effect of particle size on the conversion was confirmed, although in this case, a noticeable deactivation over time on stream at 180 °C was observed and attributed to carbonaceous deposits accompanied by a moderate loss of selectivity. An attempt was made to stabilize the gold metallic phase by introducing palladium. This was not wholly successful; the stabilization of the conversion thus achieved was associated with a substantial loss of selectivity. Sárkány et al. attempted the reverse experiment—stabilizing palladium by adding gold [32]. They found results similar to those mentioned above, that is, improved selectivity but to the detriment of conversion.

These losses in activity are systematic in the reaction of acetylene hydrogenation with palladium catalysts. They result from the formation of carbonaceous deposits of various temperature-dependent structures that affect the kinetic parameters of the reaction [33]. They also block the active sites, slow diffusion of the reactants [34], and provoke geometric effects, which could explain the changes in selectivity [35].

The present study investigated the hydrogenation properties of supported gold not yet reported in the literature: ceria. We propose a mechanism for the selective hydrogenation of acetylene. We chose ceria because we are able, using a preparation method developed by our group, to perfectly control both the deposition and the dispersion of gold to obtain 2-nm particles. To do this, we studied the reaction at the laboratory scale not only by varying the different parameters affecting the reaction (e.g., pretreatment and hydrogen or acetylene concentrations), but also by considering the properties of adsorption and reduction using temperature-programmed reduction (TPR). After identifying the formation of various types of carbon formed during the course of the reaction, we studied catalyst aging and the modes of its deactivation by temperature-programmed oxidation (TPO), resulting in our proposed novel reaction mechanism for hydrogenation on this particular catalyst.

## 2. Experimental

### 2.1. Catalyst preparation

Our preparation method was based on the direct anionic exchange (DAE) of the gold species with the hydroxyl groups of the support and reported in a previous publication [36]. An aqueous solution of $HAuCl_4$ of concentration $10^{-4}$ $mol\,L^{-1}$ (pH 3.5) was prepared to obtain a final Au loading of 2 wt%. The solution was heated to 70 °C, and $CeO_2$ (Rhodia Actalys HSA 5, 240 $m^2\,g^{-1}$) was added. The resulting slurry was filtered, then washed with ammonia to remove chlorine residues from the solution, the gold chloro-hydroxy complexes, and/or the adsorbed chlorides on the support. The catalyst was submerged for 1 h in an ammonia solution of concentration 4 $mol\,L^{-1}$. The solid was filtered and washed with water, dried overnight in an oven at 120 °C, and then calcined in air at 300 °C for 4 h.

This preparation method, originally developed for alumina, has proven very successful with a wide range of supports, including ceria [37]. The final gold concentration was 1.95%, and that of chlorine was inferior to detection limits by atomic absorption (i.e., $<$150 ppm). The average particle size was 2 nm.

### 2.2. TPR and TPO

TPR is a classical technique for characterizing the reducibility of supported catalysts. The TPR analyses were performed using an apparatus of the $\chi$-sorb range commercialized by Gira. Before reduction, the catalyst was placed in a U-shaped reactor and calcined *ex situ* in an air flow at 300 °C with a ramp rate of 4 $°C\,min^{-1}$ for 4 h. Then, after cooling to room temperature, the catalyst was reduced in a flow of 5% $H_2$ in argon. The temperature was programmed to increase at a constant rate of 15 $°C\,min^{-1}$ up to 900 °C. The gas composition was analyzed by a catharometer set at 100 mA, and the data were collected on a computer.

TPO analyses were carried out *in situ* on a catalyst sample. At the end of the hydrogenation reaction, the temperature was allowed to decrease to room temperature under a helium flow. The gas composition was then switched to 5% $O_2$ in helium, and the temperature was increased to 500 °C at a ramp rate of 10 $°C\,min^{-1}$. Oxidation was monitored by following $CO_2$ production using an online IR Rosemount analyzer.

### 2.3. Selective hydrogenation of acetylene

The reaction was performed at atmospheric pressure using a fixed-bed quartz microreactor packed with 200 mg of catalyst and a gas mixture containing acetylene and hydrogen in various proportions (with $H_2/HC = 3, 5, 7, 10, 30$ or 60) and helium so that the flow rate was adjusted to 75 $cm^3\,min^{-1}$ (GHSV $\sim$ 7500 $h^{-1}$). The level of concentration of acetylene was maintained between 0.1% and 0.3% according to the required $H_2$/HC ratio. The flow was adjusted by means of Tylan flow controllers. The temperature was monitored and controlled by a Eurotherm system. The analysis was performed by FID gas (DB-Wax column, 2 m long, 2.5 mm i.d.). The experiment was repeated twice to measure the reproducibility. Before each test, the catalyst was treated *ex situ* at 300 °C in air for 4 h. The products analyzed were $CH_4$, $C_2H_4$, and $C_2H_6$. The carbon balance and the absence of other peaks on the chromatograms demonstrated that no polymerization products were formed under these reaction conditions.

The selectivity of hydrogenation and the conversion are calculated as follows:

$$\text{Selectivity } (S) = \frac{[C_2H_4]}{[CH_4] + [C_2H_4] + [C_2H_6]} \times 100\%,$$

$$\text{Conversion } (\tau) = \frac{[CH_4] + [C_2H_4] + [C_2H_6]}{[C_2H_2]_{\text{init.}}} \times 100\%.$$

The yield in methane is equal to the product of conversion by selectivity ($\tau \times S$).

## 3. Results and discussion

### 3.1. TPR

Logically, ceria, considered an oxygen storage component in ceria-based catalysts, should readily be reduced and reoxidized. TPR was used to study the influence of gold on the reducibility of ceria. The TPR profile of pure ceria, shown in Fig. 1, comprises two reduction peaks, a low-temperature peak at about 500 °C (shoulder), which can be assigned to the reduction of surface oxygen species, and a high-temperature peak at 850 °C, which corresponds to the reduction of bulk oxygen and formation of the lower oxidation state of cerium ($Ce^{3+}$).

The TPR profiles of Au/$CeO_2$ (Fig. 1) exhibit 3 peaks. The peaks at high temperature (ca. 600 and 800 °C) are similar to those observed on pure ceria, demonstrating that the presence of a metal had no effect on reduction of the bulk. The main difference is in the low-temperature range, in which the first reduction peak of the gold-promoted ceria comprises two overlapping peaks, one peak with a maximum at 130 °C and the other with a maximum at 140 °C. We assume that the hydrogen consumption is due to two processes, one possibly related to the reduction of oxygen species on gold particles and the other related to surface ceria reduction. Taking into account the amount of gold in the sample (i.e., 1.95%), our calculations revealed that the low-temperature section of the peaks corresponds to the reduction of oxygen species in the form of $Au_2O_3$ on the gold particles. This presence of $Au_2O_3$ on ceria has been confirmed by an XPS study demonstrating that on this support and before any reaction, gold was present only as $Au^{3+}$ [38].

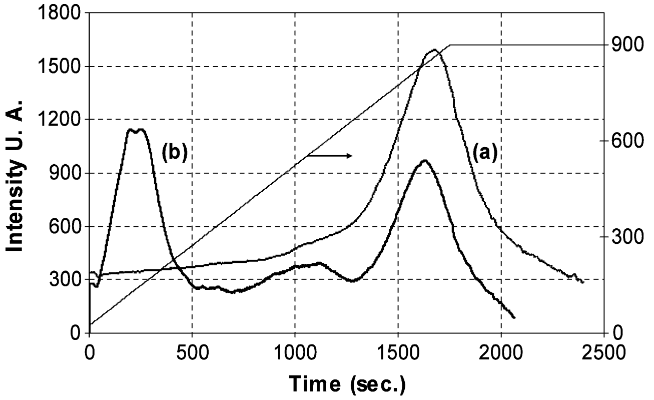

**Fig. 1.** $H_2$ TPR profile of (a) $CeO_2$ and (b) 2% $Au/CeO_2$.

### 3.2. *Effect of the $H_2/C_2H_2$ ratio on acetylene hydrogenation*

Activity and selectivity were evaluated at temperatures between 30 and 400 °C at different $H_2/C_2H_2$ ratios ($R$): 3, 5, 7, 10, 30, and 60; the results are presented in Fig. 2. The selectivity toward ethylene was 100% up to 300 °C, independent of the $C_2H_2/H_2$ ratio.

The conversion followed a volcano-shaped trend for the $C_2H_2/H_2$ ratios of 3, 5, or 7, with deactivation above 300 °C concomitant with the loss of selectivity (i.e., with maxima at 300 °C). For higher $H_2/C_2H_2$ ratios (i.e., 10, 30, or 60), the conversion remained at 100%. The decreased selectivity of $C_2H_4$ was due to the formation of $CH_4$, $C_2H_6$ was not observed. To confirm the absence of ethane formation, direct hydrogenation of $C_2H_4$ was undertaken at

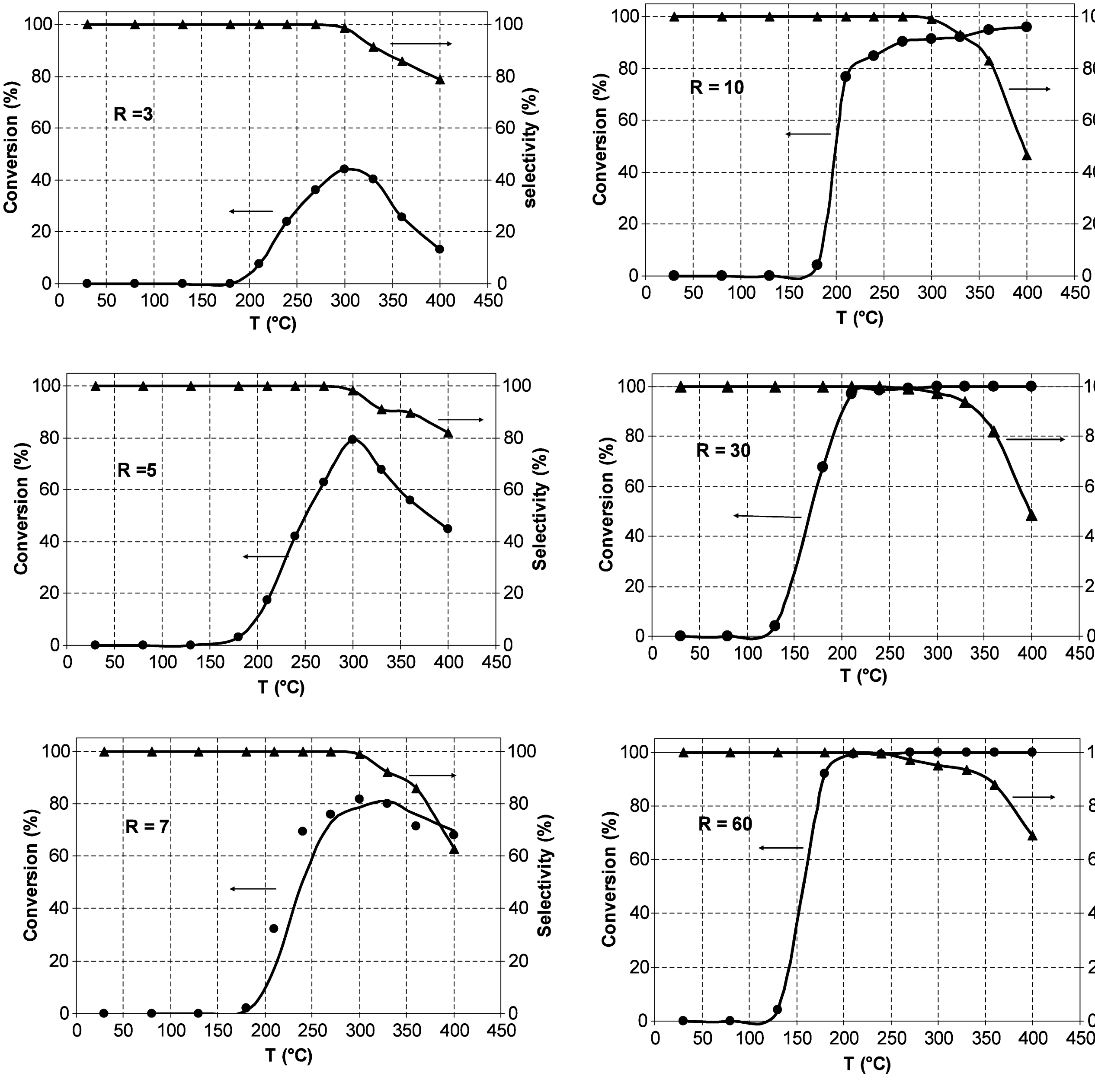

**Fig. 2.** Conversion and selectivity of $C_2H_2$ hydrogenation between 30 and 400 °C with $H_2/C_2H_2$ = 3, 5, 7, 10, 30, or 60.

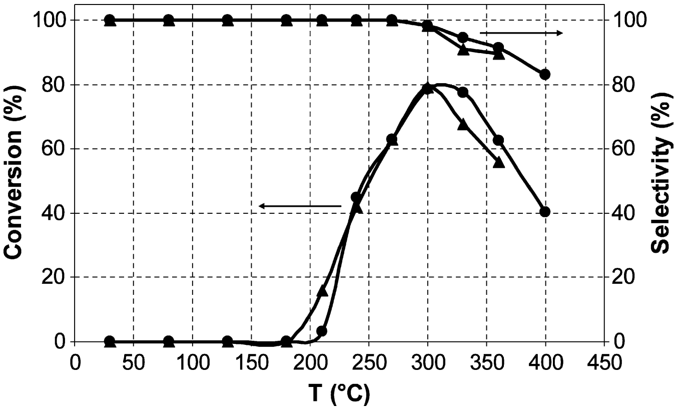

**Fig. 3.** Conversion and selectivity of $C_2H_2$ hydrogenation with $H_2/C_2H_2 = 5$ in a mixture (●) with 0.05% CO or (▲) without CO.

a $H_2/C_2H_4$ ratio of 10. A small amount of $C_2H_6$ (0.3%) was detected in the gas phase at 400 °C, a conversion value within the margin of experimental error. This result differs greatly from that of Jia et al. on $Au/Al_2O_3$ [30] and of Choudhary et al. on $Au/TiO_2$ [31]; both of these groups reported the formation of ethane at high conversion, with no methane generated.

The activity measurements were obtained through a kinetic study conducted by varying the partial pressure of acetylene at constant hydrogen pressure, and vice versa, to determine the apparent order of reaction, the rate of which can be expressed as

$$r = k \times [P_{C_2H_2}]^m \times [P_{H_2}]^n \ (\mathrm{mol/min^{-1}/g_{cata}})m,$$

where $m$ and $n$ represent the order toward acetylene and hydrogen, respectively. The measurements were made at low conversion to avoid external diffusion and avoid deactivation. The activation energy of 37 kJ mol$^{-1}$ ($R = 5$) is in agreement with that found in previous work on gold [30] or palladium [39]. The order toward $C_2H_2$ was negative (−1.0), whereas that toward hydrogen was 1.0. Therefore, the surface coverage by $C_2H_2$ was constant, and the reaction rate was a function of hydrogen coverage, explaining the increased conversion at constant temperature with increasing partial pressure of hydrogen.

### 3.3. Effect of CO addition in the feed

On palladium, the addition of CO leads to a loss of activity by hindering the spillover of hydrogen from the metal, effectively blocking the hydrogenation routes, both primary (to ethylene) and secondary (to ethane). Although the overall reaction rate is decreased, improved selectivity is obtained [6]. The situation is very different on a gold catalyst, however. Fig. 3 presents an experiment in which a small quantity of CO (0.05%) was introduced to a reaction mixture with a $H_2/C_2H_2$ ratio of 5. It can be seen that CO did not affect either $C_2H_2$ conversion or selectivity; in fact, the latter remained high, with methane the only product found at high temperature. This test was repeated at a higher hydrogen concentration, with a $H_2/C_2H_2$ ratio of 10 (results not shown), and again, CO demonstrated no influence on the reaction. These experiments indicate either that hydrogen or carbon monoxide adsorbs on different sites, or that the competition for the adsorption site strongly favors $H_2$.

### 3.4. Effect of pretreatment

Fig. 4 illustrates the effects of pretreatment by comparing the activity and selectivity of the hydrogenation reaction for a catalyst reduced in 60% $H_2$/He from 25 to 400 °C for 30 min and for the catalyst described in the previous section (i.e., calcined in air at 300 °C). In both cases, the catalyst was maintained at the temperature plateau for 2 h before being allowed to cool to room temperature, at which point the gas phase was switched to the reactant mixture composition with a $H_2/C_2H_2$ ratio of 7 for 30 min.

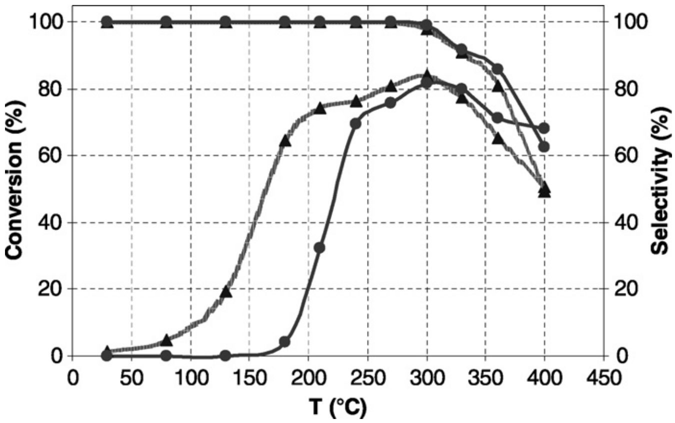

**Fig. 4.** Effect of $H_2$ pretreatment; (●) without pretreatment, (▲) with $H_2$ pretreatment at 400 °C, 4 °C/min, 1 h, ($H_2/C_2H_2$ ratio = 7).

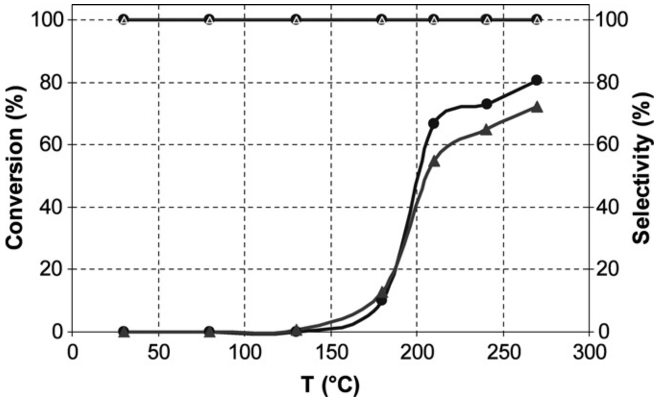

**Fig. 5.** 2 successive reactions of $C_2H_2$ hydrogenation with $H_2/C_2H_2 = 7$ between 30 and 270 °C, (●) 1st reaction, (▲) 2nd reaction.

The catalyst pretreated with hydrogen revealed higher conversion at lower temperature; for example, at 180 °C, a conversion of ca 64% was observed, compared with ca. 4% for the precalcined catalyst. No effect on selectivity was seen; the values are perfectly matched across the entire temperature range. One explanation for this finding is that vacant oxygen sites (seen on TPR) act as a hydrogen reservoir with a higher local $H_2$ pressure, which favors increased availability on the surface, resulting in higher conversion. Another popular explanation is that the presence of a large amount of hydrogen facilitates the removal of trapped hydrocarbon or impedes the formation of carbonaceous deposits that poison the reaction or slow the diffusion of the reactants towards the active sites. Given these theories, we undertook a detailed study of the carbon formation and deactivation processes.

### 3.5. Deactivation and carbon formation

As shown in Fig. 2, deactivation occurred only above 300 °C with the formation of methane. Below this temperature, 100% selectivity toward $C_2H_4$ was always observed. To investigate possible deactivation below 300 °C, we performed the reaction in 2 successive cycles with a $H_2/C_2H_2$ of 7 by raising the temperature to 210 °C and then cooling to room temperature under the reaction mixture. Fig. 5 plots our results, which suggest that any carbon formed below 210 °C did not poison the reaction. But when the catalyst was maintained at 210 °C and the same composition of re-

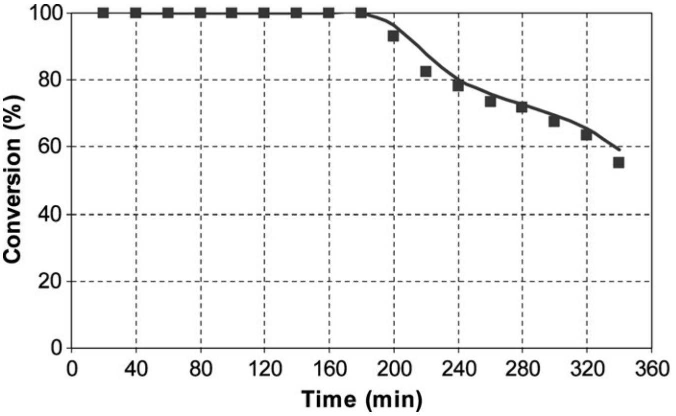

**Fig. 6.** Aging of the catalyst reactant mixture ($R$ $H_2/C_2H_2 = 7$) at 210 °C for 4 h.

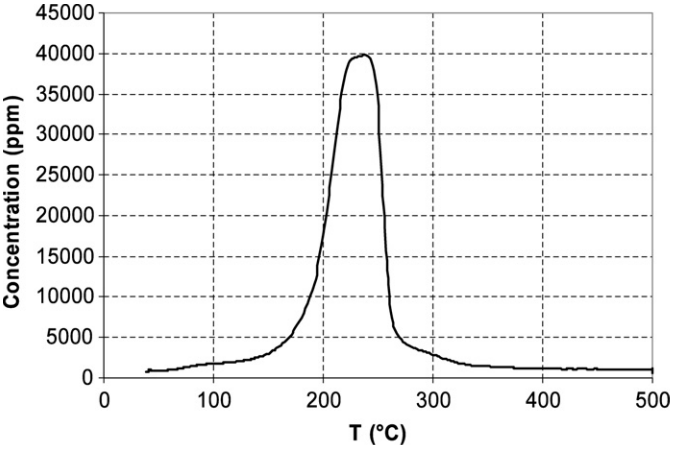

**Fig. 7.** TPO after aging under reactant mixture ($R$ $H_2/C_2H_2 = 7$) at 210 °C for 6 h.

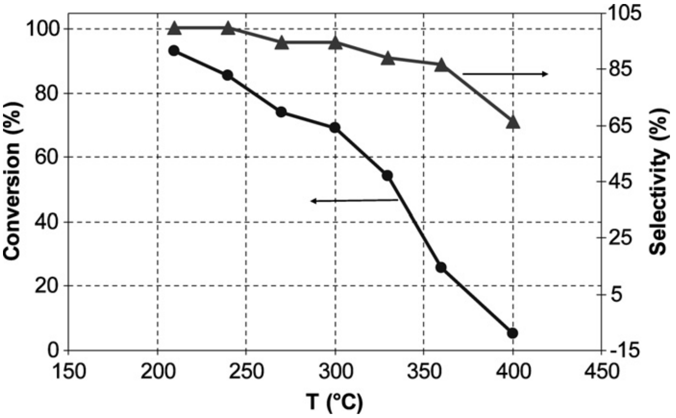

**Fig. 8.** $C_2H_2$ hydrogenation with $H_2/C_2H_2 = 5$ between 210 and 400 °C (temperature rise from 30 to 210 °C under helium).

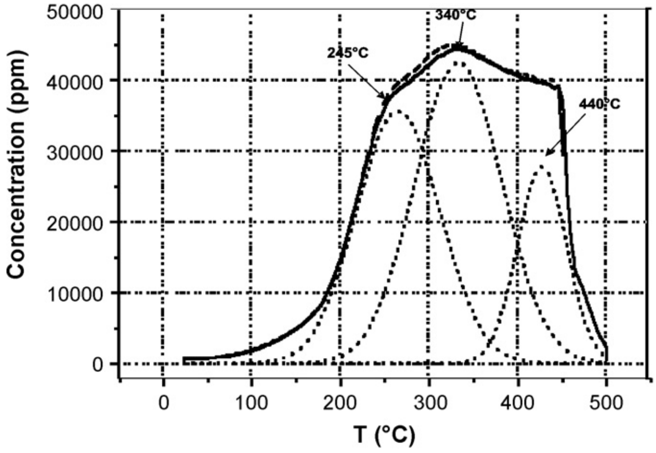

**Fig. 9.** TPO after test: (- - -) $R$ $H_2/C_2H_2 = 5$, after reaction from 210 to 400 °C, (—) $R$ $H_2/C_2H_2 = 5$, after reaction from 30 to 400 °C.

actants applied for a prolonged period (e.g., ca. 200 min), deactivation was observed, as shown in Fig. 6. This activity loss continued over time while the selectivity toward $C_2H_4$ remained constant at 100%. These findings demonstrate that the carbon formed below 300 °C has no affect on the reaction mechanism (although the accumulation of a large amount eventually will block the catalyst's pores, inducing mass transfer limitations). This phenomenon was observed with palladium-based catalysts, in which, in contrast to gold, carbon deposition provoked changes in selectivity [40].

The formation of carbon during the aging experiment was monitored by TPO. Fig. 7 presents the catalyst profile after 6 h of reaction. The oxidation profile represents the burning of the carbon residue between 30 °C and 500 °C. Although TPO cannot provide any direct information on the chemical nature of the carbonaceous deposits, it can provide information about the quantity and structure of the carbon (i.e., whether amorphous or polymeric) and its location (i.e., on the support or on the metal).

In our case, the TPO profile indicated a single peak (i.e., one coke species) centered at ca. 243 °C. This relatively low temperature of combustion suggests that the coke was located on the metal or within close proximity and implies that the metal assisted with the combustion. This coke was harmless to the reaction.

In another experiment, we increased the temperature under pure helium before the gas phase was switched to the reactant mixture with a $H_2/C_2H_2$ ratio of 5 at 210 °C. The results are displayed in Fig. 8. We chose this temperature specifically to allow the reaction to begin on a surface free of contaminating carbon species. In this case, the conversion reached a higher value than was achieved when the temperature was increased under acetylene; for example, at 210 °C, under helium, a conversion of ca. 95% was obtained when switching to the reacting mixture, compared with a conversion of only ca. 17% when the temperature was raised under the same mixture with acetylene (Fig. 2; for $R = 5$). However, as the temperature was increased, the conversion decreased rapidly to ca. 5% at 400 °C, a value even lower than the ca. 41% obtained when the temperature was raised from 30 to 400 °C under an acetylene-containing mixture. This experiment demonstrates the formation of a carbon species that strongly inhibits the reaction above 300 °C. It is noteworthy that the selectivity was not affected in this experiment; the values observed after switching to the gas mixture at 210 °C were similar to those obtained when starting the experiment with $C_2H_2$ and $H_2$ at room temperature. In both cases, only $C_2H_4$ and $CH_4$ were produced, with the latter requiring formation of this “harmful” carbon species.

Fig. 9 presents results from the TPO experiments for a catalyst reacted under two different sets of conditions: submitted to a gas mixture from 30 to 400 °C (as shown in Fig. 2) and from 210 to 400 °C (as shown in Fig. 8). In both cases, the $H_2/C_2H_2$ ratio was 5. The most striking feature is that the characteristics of the coke (e.g., temperature of combustion and TPO profile) are independent of the reaction conditions; the curves overlap perfectly. The profile comprises 3 maxima at ca. 245, 340, and 440 °C, respectively, which presumably correspond to 3 coke species. A study of the chemical nature of these carbonaceous deposits is beyond the scope of this work; however, some interpretations of the structure of this carbon material are available in the literature [32,41,42]. The TPO peak at the lowest temperature is attributed to unstructured carbon or trapped hydrocarbons, the presence of which

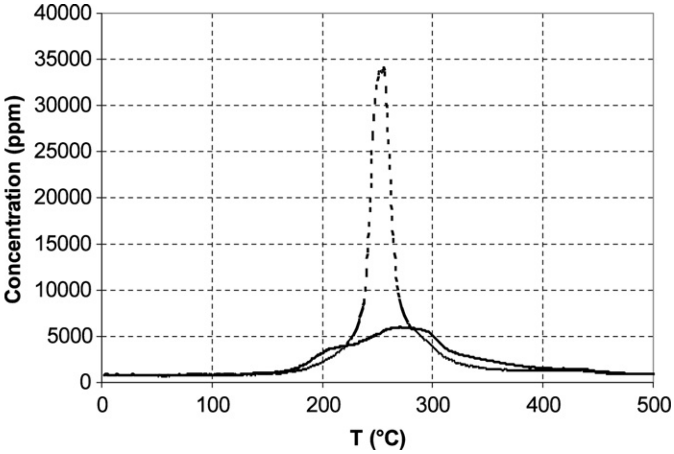

**Fig. 10.** TPO after test with $R$ $H_2/C_2H_2 = 60$: (- - -) after reaction from 30 to 210 °C, (—) after reaction from 30 to 400 °C.

does not affect the reaction even though they may be in contact with the metal particles, because their combustion is most readily affected. The peak located around 340 °C can be associated with the combustion of amorphous coke, a precursor of graphitic carbon that has a structure of oligomeric hydrocarbon, $C_xH_y$. The third TPO peak is due to an acidic carbon, the polymerization of which is facilitated by ionic sites. In general, this is a graphitic carbon held firmly on the support. Its accumulation provokes considerable steric hindrance, which reduces the availability of hydrogen and/or acetylene.

### 3.6. *Influence of hydrogen partial pressure*

We also investigated the formation of carbonaceous deposits as a function of hydrogen pressure. To do this, the deposition of the coke was measured by TPO on a reacted catalyst that had been exposed to a mixture of $H_2/C_2H_2 = 60$, either from 30 to 210 °C or from 30 to 400 °C. The results, shown in Fig. 10, merit some comments. The first comment concerns the nature and the quantity of carbon formed between 30 and 210 °C. This carbon was burned off in a single peak, as described by the maximum at ca. 249 °C. Comparing this finding with that reported in Fig. 6 for $H_2/C_2H_2 = 7$ shows that in both cases the carbon burned off at almost the same temperature, implying that it was of the same chemical nature. Moreover, this peak existed for a catalyst submitted to a mixture with $H_2/C_2H_2 = 5$ (Fig. 9). It is noteworthy that in all 3 cases, peak integration revealed an identical amount of carbon (peak at ca. 245 °C), indicating that the nature and amount of carbon formed at low temperature are independent of the hydrogen concentration.

A second comment concerns the amount of carbonaceous deposits formed between 30 and 400 °C. The deposits were ca. 10-fold smaller at $H_2/C_2H_2 = 60$ (Fig. 10) than at $H_2/C_2H_2 = 5$ (Fig. 9). This comparatively low carbon formation at high temperature is directly related to the hydrogen concentration. The finding that it was weaker at high hydrogen pressure indicates that this carbon type reacted with hydrogen to form methane, the only product observed above 300 °C. This is also demonstrated by the experiment reported in Fig. 11, which plots the $CH_4$ yield against the $H_2/C_2H_2$ ratio and shows that indeed the yield increased with hydrogen concentration and with temperature.

Several groups have report that on palladium, coke formation decreases with increasing hydrogen pressure [43,44] except at low partial pressure of hydrogen, in which case the rate of coke formation increases with increasing surface coverage of hydrogen [35]. On gold, however, the effect of hydrogen partial pressure is clearly a function of temperature. In summary, carbon formation is independent of hydrogen at low temperature (i.e., below 300 °C), and above this temperature, its formation is strongly decreased in the presence of a high hydrogen coverage, which reacts with the carbon to form methane.

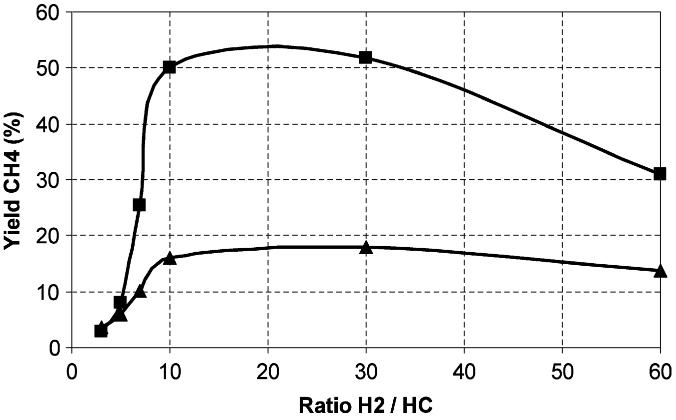

**Fig. 11.** $CH_4$ yield vs $H_2$/HC ratio, (▲) at 360 °C, (■) at 400 °C.

### 3.7. *Mechanism of $C_2H_2$ hydrogenation*

Based on our results, we can propose a mechanism for the hydrogenation of acetylene on $Au/CeO_2$. This mechanism, schematized in Fig. 12, involves several features that explain the high selectivity toward ethylene and the formation of methane, not ethane, as the sole product at high temperature, along with the formation of carbon species that may or may not be harmful to the reaction. The high selectivity can be explained by the difference in the strength of adsorption of acetylene onto the gold surface compared with ethylene. Indeed, direct hydrogenation of ethylene did not occur on the catalyst, indicating that the adsorption of ethylene was almost impossible and thus its desorption was rapid. One possible explanation for the difference in adsorption between C≡C and C=C bonds has been provided by a DFT study, which found adsorption and activation of only C≡C on Au nanoparticles [45]. Below 300 °C, ethylene desorbs from the surface, but above 300 °C, it dissociates by carbon–carbon breaking to form what is thought to be a surface carbene. This species would explain the unique feature of gold on which methane is formed and the absence of further hydrogenation to ethane. The reaction of the carbene with hydrogen is a function of the partial pressure of hydrogen, because a high concentration of hydrogen favors the formation of methane. In another reaction pathway, the recombination of this carbene either forms methane by further hydrogenation (with methane the only product observed at high temperature in the gas phase) or, due to the high temperature, it is dehydrogenated and polymerizes to form a harmful type of carbon that poisons the reaction.

The kinetics data suggest that the surface is covered by $C_2H_2$. The increased rate with increasing hydrogen pressure indicates that the hydrogen adsorption is irreversible. The role of hydrogen in the formation of carbon deposits is very different from that on palladium, where it is assumed that spillover of hydrogen is required to hydrogenate the adsorbed hydrocarbon, with this spillover promoted by coke deposits. The improved selectivity in the presence of CO results from the effects of CO in hindering this spillover and impeding further hydrogenation to ethane [6]. In the case of gold, the situation is very different. CO has no influence either on the selectivity or on the activity, because it should be adsorbed onto sites different from hydrogen or not adsorbed at all in the presence of acetylene. This latter situation has been observed during the oxidation of $C_2H_2$ in the presence of CO [46]. There are two different types of carbon, that formed at high temperature, which acts as a precursor of deactivation, as discussed earlier, and that formed at low temperature (i.e., below 300 °C), which is

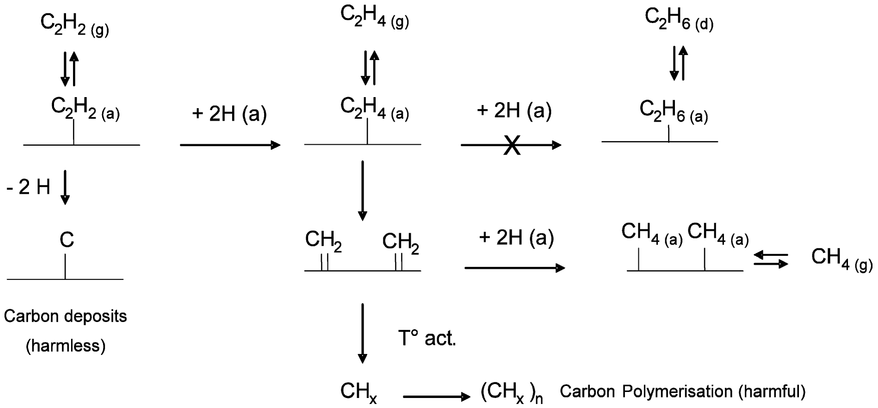

**Fig. 12.** Proposed reaction pathways for the hydrogenation of acetylene on Au/$CeO_2$.

harmless to the reaction and whose formation is independent of the hydrogen pressure. Eventually, however, its accumulation does block the pores and impedes the continuity of the reaction.

## 4. Conclusion

Using Au/$CeO_2$ as catalyst in acetylene hydrogenation, a selectivity of 100% toward ethylene was obtained even at a high level of conversion up to 300 °C. The conversion was a function of the hydrogen partial pressure. Below this temperature, a carbonaceous deposit was formed that had no affect on selectivity. Its formation was independent of the hydrogen coverage. Above 300 °C, deactivation concomitant to a decrease in selectivity was obtained. Formation of methane is the gas phase was observed, with no ethane produced. This formation of methane can be linked directly to the formation of a surface carbene species due to the splitting of an ethylene carbon–carbon bond, which reacts with hydrogen at high temperature to form methane. The methane yield is a function of the hydrogen concentration.

## References

[1] B. Didillon, P. Sarrazin, J.P. Boitiaux, in: AIChE Spring Meeting, Session 43, March 1995, Houston, TX.
[2] K. Sasaki, J. Kimble, M. Scharre, R. Callejas, Effects of selectivity on acetylene removal unit, in: AIChE (EPC), Session 33, March 1997, Houston, TX.
[3] E.L. Mohundro, Overview on C2 and C3 selective hydrogenation in ethylene plants, http://kolmetz.com/Article-061.htm, access on February 2008.
[4] See for example: S.A. Blankenship, et al., Process for selective hydrogenation of acetylene in an ethylene purification process, US Patent # 6,509,292, 2003;
J.H. Brophy, et al., Selective hydrogenation of acetylene, US Patent # 4,705,906, 1987;
T.T.P. Cheung, et al., Selective acetylene hydrogenation, US Patent # 5,510,550, 1996;
T.T.P. Cheung, et al., Selective hydrogenation catalyst and processes, US Patent # 6,465,391, 2002;
K. Flick, et al., Supported palladium catalyst for selective catalytic hydrogenation of acetylene in hydrocarbonaceous streams, US Patent # 5,856,262, 1999.
[5] G.C. Bond, P.B. Wells, Adv. Catal. 15 (1964) 92–226.
[6] A. Sárkány, A.H. Weiss, L. Guczi, J. Catal. 98 (1986) 550.
[7] A. Borodzinski, A. Golebiowski, Langmuir 13 (1997) 883–887.
[8] Q. Zhanga, J. Li, X. Liu, Q. Zhu, Appl. Catal. A 197 (2000) 221–228.
[9] P. Praserthdam, B. Ngamsom, N. Bogdanchikova, S. Phatanasri, M. Pramotthana, Appl. Catal. A 230 (2002) 41–51.
[10] G. Meitzer, J.H. Sinfelt, Catal. Lett. 30 (1995) 1.
[11] A.A. Lamberov, S.R. Egorova, I.R. Il'yasov, Kh. Gil'manov, S.V. Trifonov, V.M. Shatilov, A.Sh. Ziyatdinov, Kinet. Catal. 48 (1) (2007) 136–142.
[12] S. Leviness, V. Nair, A.H. Weiss, Z. Schay, L. Guczi, J. Mol. Catal. 25 (1984) 131.
[13] A. Borgna, B. Moraweck, J. Massardier, A. Renoupez, J. Catal. 128 (1991) 99.
[14] A. Sarkany, Z. Zsoldos, Gy. Stefler, J.W. Hightower, L. Guczi, J. Catal. 157 (1995) 179.
[15] P. Miegge, J.L. Rousset, B. Tardy, J. Massardier, J.C. Bertolini, J. Catal. 149 (1994) 404.
[16] Y.H. Park, G.L. Price, Ind. Eng. Chem. Res. 31 (1992) 469.
[17] E.W. Shin, J.H. Kang, W.J. Kim, J.D. Park, S.H. Moon, Appl. Catal. A 223 (2002) 161–172.
[18] J.H. Kang, E.W. Shin, W.J. Kim, J.D. Park, S.H. Moon, J. Catal. 208 (2002) 310–320.
[19] M.L. Derrien, Stud. Surf. Sci. Catal. 27 (1986) 613.
[20] G.C. Battiston, L. Dalloro, G.R. Tauszik, Appl. Catal. 2 (1982) 1.
[21] C. Mohr, H. Hofmeister, P. Claus, J. Catal. 213 (2003) 86.
[22] P. Claus, A. Bruckner, C. Mohr, H. Hofmeister, J. Am. Chem. Soc. 122 (2001) 11430.
[23] M. Okumura, T. Akita, M. Haruta, Catal. Today 74 (2002) 265–269.
[24] C. Milone, R. Ingoglia, A. Pistone, G. Neri, F. Frusteri, S. Galvagno, J. Catal. 222 (2004) 348.
[25] P.A. Sermon, G.C. Bond, P.B. Wells, J. Chem. Soc. Faraday Trans. 1 (1979) 75, 385–394.
[26] G.C. Bond, P.A. Sermon, Gold Bull. 6 (4) (1973) 102–105.
[27] G.C. Bond, D.T. Thompson, Catal. Rev. Sci. Eng. 41 (1999) 319–388.
[28] G.C. Bond, P.A. Sermon, G. Webb, D.A. Buchanan, P.B. Wells, J. Chem. Soc. Chem. Commun. (1973) 444.
[29] J.A. Lopez-Sanchez, D. Lennon, Appl. Catal. A 291 (2005) 230–237.
[30] J. Jia, K. Haraki, J.N. Kondo, K. Domen, K. Tamaru, J. Phys. Chem. B 104 (2000) 11153.
[31] T.V. Choudhary, C. Sivadinarayana, A.K. Datye, D. Kumar, D.W. Goodman, Catal. Lett. 86 (2003) 1.
[32] A. Sárkány, A. Horvath, A. Beck, Appl. Catal. A 229 (2002) 117–125.
[33] A. Borodzinski, A. Cybulski, Appl. Catal. A 198 (2000) 51–66.
[34] Y. Jin, A.K. Datye, E. Rightor, R. Gulotty, W. Waterman, M. Smith, M. Holbrook, J. Maj, J. Blackson, J. Catal. 203 (2001) 292–306.
[35] M. Larsson, J. Jansson, S. Asplund, J. Catal. 178 (1998) 49–57.
[36] S. Ivanova, C. Petit, V. Pitchon, Appl. Catal. A 267 (2004) 191–201.
[37] S. Ivanova, V. Pitchon, C. Petit, J. Mol. Catal. A Chem. 256 (2006) 278–283.
[38] S. Ivanova, Ph.D. dissertation, Université de Strasbourg, France, 2004.
[39] H. Molero, B.F. Barlett, W.T. Tysoe, J. Catal. 181 (1999) 49–56.
[40] S. Asplund, J. Catal. 158 (1996) 267–278.
[41] P. Maetz, R. Touroude, Appl. Catal. A 149 (1997) 189.
[42] C. Guimon, A. Auroux, E. Romero, A. Monzon, Appl. Catal. A 251 (2003) 199–214.
[43] G.C. Battiston, L. Dalloro, G.R. Tauszik, Appl. Catal. 2 (1982) 1.
[44] Z.E. Gandman, M.E. Aerov, V.A. Men'shchikov, V.S. Getmantsev, Int. Chem. Eng. 15 (1975) 183.
[45] Y. Segura, N. Lopez, J. Perez-Ramirez, J. Catal. 247 (2007) 383–386.
[46] S. Ivanova, C. Petit, V. Pitchon, Catal. Today 113 (2006) 182.