



## Role of support in the oxidation of acetylene over gold catalysts

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### ABSTRACT

The influence of the carrier ( $\text{CeO}_2$ ,  $\text{TiO}_2$  or  $\text{ZrO}_2$ ) on the reaction of acetylene oxidation over a 2% gold catalyst has been investigated in the presence or in the absence of CO. XPS reveals that gold is metallic in every case and the percentage of gold on the surface is always higher than that in the bulk confirming the wide dispersion as evaluated by TEM. There is a significant effect of the support on the activity in the absence of CO, but the presence of CO affects the reactivity differently according to the support. In a mixture of CO and  $\text{C}_2\text{H}_2$ , the oxidation of CO is systematically inhibited by  $\text{C}_2\text{H}_2$  whereas the behaviour is completely different for the oxidation of  $\text{C}_2\text{H}_2$ . CO has no effect upon Au/ $\text{CeO}_2$ , acts as an inhibitor with Au/ $\text{TiO}_2$  and as a promoter with Au/ $\text{ZrO}_2$ . Kinetic study reveals that the order towards  $\text{C}_2\text{H}_2$  remains unchanged whereas the order towards  $\text{O}_2$  clearly depends upon the support. These effects on activity and kinetics may result from various factors discussed in this paper.

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### 1. Introduction

Acetylene oxidation is a reaction widely studied as a model for the processes occurring in the combustion of hydrocarbon (HC) molecules [1–3]. The chemistry yielding products of this reaction, such as  $\text{CHCO}$ ,  $\text{CHO}$ ,  $\text{C}_2\text{H}^*$  and  $\text{CH}_2$  radicals, is of great importance to the elucidation of mechanisms implied in the flame combustion of HC. The chemistry of acetylene oxidation has been the subject of an extensive range of publications, over several decades [4,5]. New developments in this area have occurred due to studies in heterogeneous catalysis dedicated to automotive exhaust gas depollution. Indeed, during fuel combustion within an engine, a proportion of the HC remains unburned and is found in the exhaust along with other incomplete combustion products such as CO, NO and  $\text{H}_2$  or other oxygenated compounds such as formaldehyde. These unburned residues are either intact or have been partially transformed by pyrolysis processes to produce short chain HC ( $\text{C}_1$ – $\text{C}_2$ ) or aromatic compounds ( $\text{C}_6$ – $\text{C}_9$ ). Among the unburned HC are found methane, ethylene and acetylene, this latter being refractory to catalytic oxidation in the post-combustion device [6–8]. Acetylene is characterised by its very strong adsorption on the surface of noble metals which is due to its very high electron-donor character. There are few reports on the kinetics of acetylene oxidation in the literature despite a prevailing interest in the study of this reaction. Harmsen et al. [9,10], using a mixture of acetylene and carbon monoxide on Pt/Rh/ $\text{CeO}_2/\delta\text{-Al}_2\text{O}_3$ , revealed that carbon monoxide is an intermediate product of the reaction. The experiments, run under transient conditions, confirmed the involvement

of CO in the reaction as had been postulated previously by other groups employing a steady-state regime [11,12]. Of note is the importance of ceria, which through an oxygen interacting with acetylene adsorbed on the noble metal (Pt, Rh) exerts a strong influence upon this direct bi-functional reaction.

The work of Johnson and Krieger [13] on acetylene oxidation on silver nitrate revealed that the heats of combustion of acetylene and carbon monoxide are not very far apart (310 and 240 kcal/mol, respectively), and concluded that if any carbon monoxide is formed, it must be a short-lived intermediate. Also proposed was that the reactivity is a function of the partial pressure of  $\text{C}_2\text{H}_2$  and required a critical concentration of acetylene below which the reaction would not occur. This suggests that the reaction initiates at a high coverage of acetylene, a pre-requisite necessary for the formation of surface combinations of acetylene, such as diacetylene and triacetylene, species more easily oxidised than acetylene itself. For these dimers or trimers on silver nitrate, oxygen would have no direct influence on the rate, implying a zero order towards  $\text{O}_2$ .

A fundamental study of acetylene oxidation on the (1 1 1) platinum surface was undertaken by Burnett et al. [14] which revealed that the adsorption of acetylene occurs through a strong interaction between the unsaturated  $\pi$  bonding and the Pt surface. A similar type of interaction was observed between the  $\pi$ – $\sigma$  bonding of ethylene and propylene on Pt (1 1 1) [15].

To our knowledge, there are as yet no fundamental studies of acetylene oxidation on gold catalysts with the exception of our own in which gold was proposed as a potential catalyst noble metal for use in the oxidation of hydrocarbon at low temperature, the so-called “low light-off depollution” of exhaust gas [16]. However, studying the oxidation of acetylene is particularly important in this process because of its electron-donor character. Oxidation of

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acetylene in a group of gasses is difficult, despite its inhibition of the oxidation of other compounds, particularly carbon monoxide whose oxidation is fundamental for the viability of the process of low light-off oxidation. We have therefore studied the oxidation of acetylene alone, or in the presence of CO. Acetylene behaves differently towards oxygen in the presence of CO and equally in the presence of ceria, as described by Harmsen et al. [10]. According to the authors ceria is involved in the reaction mechanism, a direct bi-functional interaction between acetylene adsorbed on the noble metal and oxygen from ceria. This experiment reveals the important role played by the support in the reaction and we therefore extended the present study of reactions on gold on different supports to assess their possible effect, or influence upon this noble metal.

## 2. Experimental

### 2.1. Catalyst preparation

#### 2.1.1. Supports

The simple or mixed supports TiO<sub>2</sub>, ZrO<sub>2</sub> and CeO<sub>2</sub> were prepared by the precipitation of metallic hydroxides. The starting reagents (Strem chemicals), respectively, isopropoxide titanium (IV) (Strem chemicals), *n*-propoxide zirconia (IV) and cerium nitrate, were dissolved in ethanol and then precipitated by an ammonia solution of concentration 4 mol L<sup>-1</sup>. The solid obtained was filtered, washed several times and dried at 100 °C overnight and finally calcined at 750 °C for TiO<sub>2</sub> and ZrO<sub>2</sub> and at 450 °C for CeO<sub>2</sub>.

#### 2.1.2. Gold impregnation

The method of preparation is based upon the direct anionic exchange (DAE) of the gold species with the hydroxyl groups of the support as reported in a previous publication [17]. An aqueous solution of HAuCl<sub>4</sub> of concentration 10<sup>-4</sup> mol L<sup>-1</sup> (pH 3.5) was prepared in order that a final Au loading of 2 wt% be obtained. The solution was heated to 70 °C and the support (TiO<sub>2</sub>, ZrO<sub>2</sub> or CeO<sub>2</sub>), was added. The resulting slurry was filtered. A washing procedure with ammonia was then applied in order to remove the chlorine residues from the solution, from 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<sup>-1</sup>. The solid was then filtered and washed with water, dried overnight in an oven at 120 °C and calcined in air at 300 °C for 4 h.

### 2.2. Chemical analysis, BET and microscopy

The chemical analysis of Au and Cl was performed by inductively coupled plasma atom emission spectroscopy at the CNRS Centre of Chemical Analysis (Vernaison, France). The detection limit was 150 ppm for Cl. The analyses were carried out following the calcination of the catalyst. The Au weight loading is expressed as the weight of Au (g) per weight of calcined catalyst (g).

The surface area (by BET method) is determined by the adsorption and desorption of nitrogen at the temperature of liquid nitrogen (77 K). The specific surface area measurements were performed in an automated device (Tristar 3000) following several hours of degassing at 250 °C. The average masses used for these measurements varied between 100 and 200 mg.

The catalysts were characterised by Transmission Electron Microscopy (TEM) Topcon EM002B to determine the gold particle size distribution.

### 2.3. Xps

X-ray photoelectron spectra (XPS) were acquired on a Multi-lab 2000 spectrometer (Thermo VH Scientific), using Al K $\alpha$  radiation

(1486.6 eV). The aluminium anode was operated at an accelerating voltage of 15 kV, 15 mA, 20 Volts. Base pressure in the analysis chamber was maintained within the range of 5 × 10<sup>-9</sup> mbar.

### 2.4. Total oxidation of CO and/or acetylene

Both reactions were performed using the same apparatus. Flow regulation was achieved using Tylan flow controllers. The temperature was monitored and controlled by a Eurotherm system. The experiment was repeated several times in order to measure the reproducibility. Before each test, the catalyst was pre-treated at 300 °C in air for 2 h.

In the case of CO oxidation, the reaction was performed at atmospheric pressure using a fixed bed quartz micro-reactor packed with 50 mg of catalyst diluted in cordierite and a gas mixture of 1.5% CO and 5% O<sub>2</sub> in He with a total flow rate of 75 cm<sup>3</sup> min<sup>-1</sup> (GHSV ~ 35,000 h<sup>-1</sup>). Analysis for both CO and CO<sub>2</sub> was performed by a Rosemount Infrared analyser.

For acetylene oxidation, the reaction was performed at atmospheric pressure with 0.15 g of catalyst and a gas mixture containing 0.2% of acetylene and 5% of oxygen in helium with a flow rate adjusted to 75 cm<sup>3</sup> min<sup>-1</sup>. The analysis of C<sub>2</sub>H<sub>2</sub> was performed by FID gas (DB-Wax column, 2 m. long and of 2.5 mm inner diameter), CO<sub>2</sub> production was monitored continuously using the on-line IR Rosemount analyser as for CO oxidation. The experiment was repeated twice in order to measure the reproducibility. Before each test, the catalyst was treated *ex situ* at 300 °C in air for 4 h.

### 2.5. Kinetic study

In order to determine the kinetics of the reaction, a study of the variation of O<sub>2</sub> or C<sub>2</sub>H<sub>2</sub> pressure was undertaken. The kinetic order towards O<sub>2</sub> or C<sub>2</sub>H<sub>2</sub> was determined at low conversion in order to avoid any diffusion phenomenon. The reaction rate can be expressed as

$$r = k \times [P_{C_2H_2}]^m \times [P_{O_2}]^n \quad (\text{mol min}^{-1} \text{ g}_{\text{cata}})$$

where *m* and *n* represent the order towards acetylene and oxygen, respectively.

The partial pressure of O<sub>2</sub> was varied while maintaining the partial pressure of C<sub>2</sub>H<sub>2</sub> constant and vice versa. When possible, i.e. when the conversion remained low over a broader range of temperature, the orders were measured at different temperatures. The level of concentration of acetylene was varied between 0.05% and 0.4% and the oxygen concentration was varied according to the required O<sub>2</sub>/HC ratio. The experimental conditions for the kinetics measurements are reported in Table 1.

## 3. Results

### 3.1. Effect of support on the size and on the chemical state of gold

#### 3.1.1. Chemical analysis

The BET surface along with the final gold concentration is reported in Table 2, the chlorine concentration was always inferior

**Table 1**

Experimental conditions for the kinetics measurements of apparent orders of reaction.

	Order/O <sub>2</sub>	Order/C <sub>2</sub> H <sub>2</sub>
Mass catalyst (mg)	50 or 200 <sup>a</sup>	50 or 200 <sup>a</sup>
[O <sub>2</sub> ] (%)	0.5, 1, 2 and 3	1
[C <sub>2</sub> H <sub>2</sub> ] (%)	0.2	0.05, 0.1, 0.2 and 0.4
Flow rate (cm <sup>3</sup> /min)	75	75
Partial pressure (mbar)	5, 10, 20 and 30	0.5, 1.0, 2.0 and 4.0

<sup>a</sup> As the conversions were lower on Au/ZrO<sub>2</sub> a larger mass of catalyst was used in order to work in the same range of temperature as for Au/CeO<sub>2</sub> and Au/ZrO<sub>2</sub>.

**Table 2**

Gold weight as percentage, surface concentration, BET surface and average particle size of the catalysts.

Catalyst	Au (%) <sup>a</sup>	Surface Au (%) <sup>b</sup>	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	Particle size (nm)
Au/CeO <sub>2</sub>	1.93	1.91	47	2–3
Au/TiO <sub>2</sub>	1.56	7.56	8	3–4
Au/ZrO <sub>2</sub>	1.32	2.1	9	Bimodal. 3 and 15

<sup>a</sup> Determined by chemical analysis.

<sup>b</sup> Calculated from XPS data.

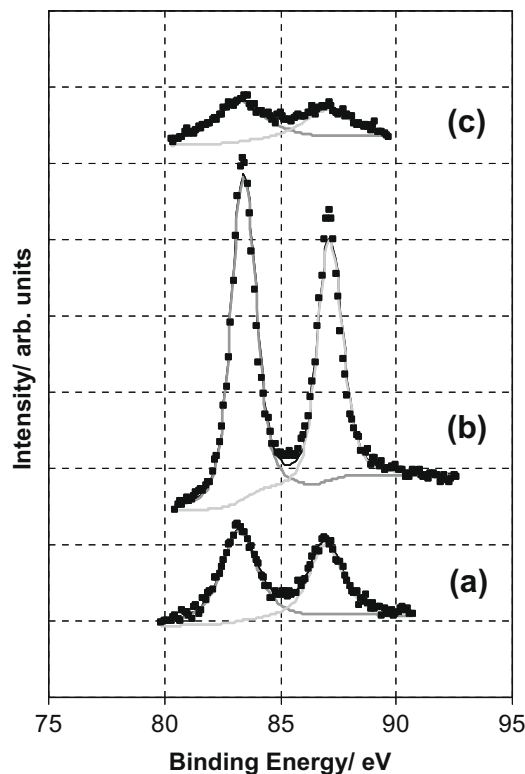
to detection limits by atomic absorption, i.e. less than 150 ppm. The method of preparation consists of an exchange of the hydroxyl group or the chloride ion of the gold precursor HAuCl<sub>4</sub> which is partially hydroxylated while put in aqueous solution. For CeO<sub>2</sub>, the amount of gold deposited is close to the theoretical value of 2%. This is explained by the fact that the exchange between the precursor and CeO<sub>2</sub> is very easy. Although the surfaces for TiO<sub>2</sub> and ZrO<sub>2</sub> were relatively small, deposition was possible though the gold content was lower than an amount of the solution equivalent to yielding 2% gold. This loss was nevertheless comparatively modest for both Au/TiO<sub>2</sub> (22% loss) and Au/ZrO<sub>2</sub> (34% loss). The difficulty to deposit the total amount of gold arises from the fact that each support has a different type of interaction with HAuCl<sub>4</sub> in solution [18]. However, the amount of gold deposited remains high in comparison with that obtained using the deposition–precipitation method [19,20]. The technique of preparation by anionic exchange, originally developed for alumina, has proved very successful with a whole range of supports including the one used in the present study [21]. This is also underlined by the average particle size obtained, as measured by electronic microscopy (Table 2). On TiO<sub>2</sub> and CeO<sub>2</sub>, the particles are small, are homogeneously dispersed and have an average size within the range of 3–4 nm and 2–3 nm, respectively. The gold particles examined on Au/ZrO<sub>2</sub> are larger, formed by the agglomeration of smaller gold crystals and with a broader size distribution. Since it was impossible to obtain a number of particles sufficient to build a truly representative histogram, only the size range (between 3 and 15 nm) is given in Table 2.

### 3.1.2. Chemical state: XPS

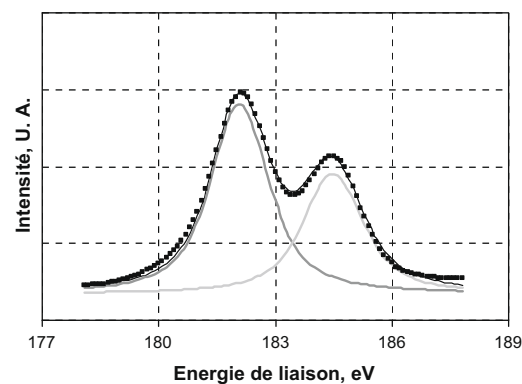
The de-convolution of XPS spectra following the *ex situ* calcination allowed the detection, assuming their presence, of multiple oxidation states, Au<sup>0</sup> and Au<sup>3+</sup> [22]. In the present study, the detection of a sole doublet indicated the presence of gold in a metallic state, exclusively [23,24]. For the three catalysts, as described in Fig. 1, the values of binding energy ( $\pm 0.15$  eV) are Au/TiO<sub>2</sub>: [Au 4f<sub>7/2</sub> 83.4 eV, Au 4f<sub>5/2</sub> 87.1 eV]; Au/ZrO<sub>2</sub> [Au 4f<sub>7/2</sub> 83.3 eV, Au 4f<sub>5/2</sub> 87.0 eV] and Au/CeO<sub>2</sub>, [Au 4f<sub>7/2</sub> 83.3 eV, Au 4f<sub>5/2</sub> 87.0 eV].

In order to calculate the surface ratio, the spectra were also de-convoluted in the region corresponding to the binding energy of the elements comprising the support. Fig. 2a presents the spectrum corresponding to level 3d of zirconium which is characterised by a doublet located at  $181.9 \pm 0.15$  and  $184.2 \pm 0.15$  eV which according to the literature corresponds to Zr<sup>4+</sup> [25]. In Fig. 2b, the spectrum of the 2p energy level of Ti is shown with a doublet at  $458.3 \pm 0.15$  and  $464 \pm 0.15$  eV characterising Ti<sup>4+</sup> [26]. The interpretation of the cerium spectrum is more complex but has been extensively described in the literature. As shown in Fig. 2c, the main peaks are at the binding energies which conform to the values reported in the literature [27,28]. Evaluating these values led to the conclusion that there was a non-negligible amount of Ce<sup>3+</sup>, representing 13.2%, while the remainder was Ce<sup>4+</sup>.

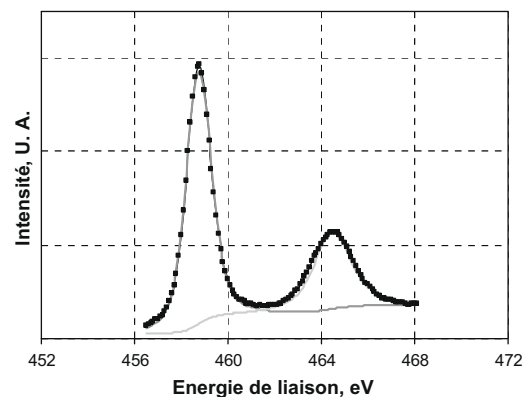
Following this de-convolution, a quantitative evaluation of the percentage of gold on the surface could be made and compared with the bulk values as obtained by chemical analysis, which are



**Fig. 1.** X-ray photoelectron spectra of the energy level 4f of gold: (a) Au/ZrO<sub>2</sub>, (b) Au/TiO<sub>2</sub> and (c) Au/CeO<sub>2</sub>.



**Fig. 2a.** X-ray photoelectron spectrum of the energy level 3d of zirconium in Au/ZrO<sub>2</sub>.



**Fig. 2b.** X-ray photoelectron spectrum of the energy level 2p of titanium in Au/TiO<sub>2</sub>.

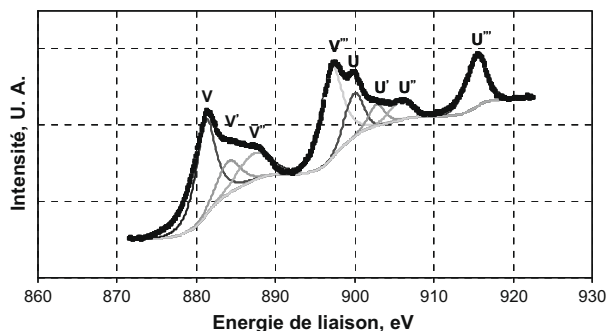


Fig. 2c. X-ray photoelectron spectrum of the energy level 3d of cerium in Au/CeO<sub>2</sub>.

reported in Table 2. In the case of Au/CeO<sub>2</sub> and Au/ZrO<sub>2</sub>, the values of the surface concentration are close to those in the bulk (2.1 instead of 1.32 pour Au/ZrO<sub>2</sub> and 1.91 compared with 1.93 for Au/CeO<sub>2</sub>). Conversely, for Au/TiO<sub>2</sub>, the corresponding value is almost 5 times higher on the surface than on the bulk (7.56 compared with 1.56), which confirms the very broad dispersion of gold on titania as observed by TEM. The quantitative analysis of XPS data is not straightforward as XPS is not strictly surface specific. In this case, the difference in the surface values for gold concentration on Au/TiO<sub>2</sub> and Au/CeO<sub>2</sub> may result from a difference of porosity, although particle shape effect could not be excluded.

### 3.2. CO oxidation

The catalysts were tested and their performance was compared for the CO oxidation reaction. The rates of the reaction expressed in mol CO min<sup>-1</sup> g<sub>Au</sub><sup>-1</sup> at 50 °C are displayed in Table 3 while the results of conversion vs. temperature are presented in Fig. 3.

Au supported on both TiO<sub>2</sub> and CeO<sub>2</sub> proves very active with a conversion of c.a. 40% at room temperature and with total conversion reaching at c.a. 75 °C. Therefore the rates of these reactions must be similar. The behaviour of Au/ZrO<sub>2</sub>, however, is different with the catalyst being less active. The 100% conversion was attained at c.a. 300 °C. As the amount of gold is comparable for the three catalysts, this difference in reactivity results principally from a difference in particle size though a support effect should not be excluded since such effects are known to be among the key parameters in the achievement of an excellent activity from gold catalysts in the oxidation of CO. This effect has been recently rationalised in terms of support reducibility and nature of the Au support interaction [29].

### 3.3. Acetylene oxidation

The conversion of acetylene vs. temperature for Au supported on CeO<sub>2</sub>, TiO<sub>2</sub> or ZrO<sub>2</sub> is presented in Fig. 4. The activity varies according to the nature of the support in the following order Au/CeO<sub>2</sub> > Au/TiO<sub>2</sub> > Au/ZrO<sub>2</sub>. The rates of reaction at 210 °C are reported in Table 3, along with the temperature of 50% conversion (*T*<sub>50</sub>).

The only observed product of reaction was CO<sub>2</sub>, with H<sub>2</sub>O not being measured. The presence of CO was never detected though

**Table 3**  
Rate in CO oxidation at 50 °C (alone) and rate in C<sub>2</sub>H<sub>2</sub> oxidation at 210 °C (alone) and *T*<sub>50</sub> for Au/CeO<sub>2</sub>, Au/TiO<sub>2</sub> and Au/ZrO<sub>2</sub>.

Catalyst	CO <i>r</i> (mol h <sup>-1</sup> g <sub>Au</sub> <sup>-1</sup> )	C <sub>2</sub> H <sub>2</sub> <i>r</i> (mol h <sup>-1</sup> g <sub>Au</sub> <sup>-1</sup> )	C <sub>2</sub> H <sub>2</sub> <i>T</i> <sub>50</sub> (°C)
Au/CeO <sub>2</sub>	1.91	6.15 × 10 <sup>-2</sup>	170
Au/TiO <sub>2</sub>	1.84	5.33 × 10 <sup>-3</sup>	265
Au/ZrO <sub>2</sub>	0.08	1.77 × 10 <sup>-3</sup>	340

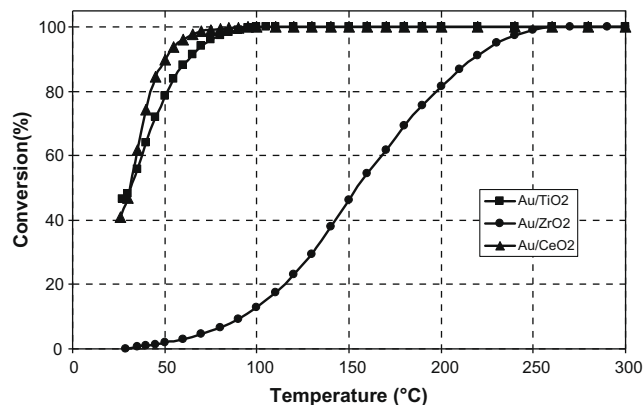


Fig. 3. Conversion of CO vs. *T* °C for Au/TiO<sub>2</sub>, Au/CeO<sub>2</sub> and Au/ZrO<sub>2</sub>.

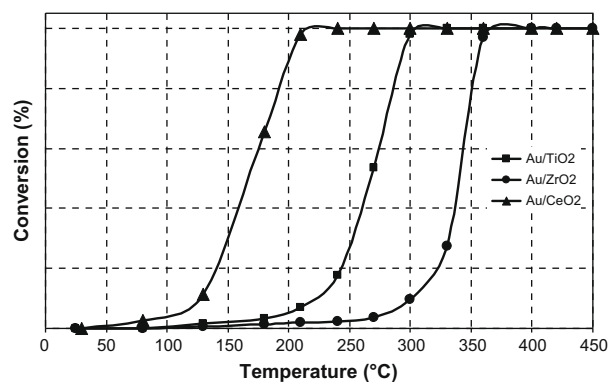


Fig. 4. Conversion of C<sub>2</sub>H<sub>2</sub> vs. *T* °C for Au/TiO<sub>2</sub>, Au/CeO<sub>2</sub> and Au/ZrO<sub>2</sub>.

it has been reported as a transient primary product of reactions during experiments on Pt and on Pt–Rh [9,11,14]. In our study, the subsequent conversion of CO to CO<sub>2</sub> must be a very fast steady-state event. Moreover, the marked ability of gold to catalyse the CO reaction may prevent CO observation in the gas phase, although its formation as an adsorbed intermediate should perhaps not be ruled out.

The most active catalyst is Au/CeO<sub>2</sub> with a *T*<sub>50</sub> value of 170 °C and contrary to the oxidation of CO this catalyst is markedly more active than Au/TiO<sub>2</sub>, while Au/ZrO<sub>2</sub> remains the less active for the oxidation reaction. As particle size for the first two catalysts are equivalent it is clear that this cannot be the only parameter influencing the activity. Indeed, as the reaction occurs at a temperature higher than that of CO oxidation, other factors such as oxygen mobility and the nature of the adsorbed molecular oxygen species may be involved [30]. Another important factor is the fraction of gold surface which is active. Recently, Hutchings et al. have reported that active gold species in CO reaction have a peculiar bilayer cluster which contains only c.a. 10 atoms and are therefore not detectable by conventional TEM [31]. The oxygen storage ability of ceria is well-known and this, allied to the ease with which the surface oxygen can be reduced, may be an influence upon the reaction, in contrast to the non-reducible TiO<sub>2</sub> and ZrO<sub>2</sub>. Indeed, the reducibilities of the Au-supported catalysts were checked by TPR (5% H<sub>2</sub>, not shown). For TiO<sub>2</sub> and ZrO<sub>2</sub> no hydrogen consumption was obtained upto 400 °C, whereas c.a. 42% of Ce<sup>4+</sup> is reduced to Ce<sup>3+</sup> between 130 and 400 °C.

The rates of reaction expressed in Table 3 are c.a. 100 times lower than those obtained for CO oxidation even though the activities were compared at different temperatures. To understand further the kinetics phenomenon implied in both reactions, a study of the simultaneous oxidation of CO and acetylene was undertaken.



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

The catalytic behaviour of each catalyst in the  $C_2H_2$  oxidation was studied by adding 1% CO to the feed while maintaining fixed the flow rate and an equivalent mass of catalyst, i.e.  $75 \text{ cm}^3 \text{ min}^{-1}$  and 0.15 g of catalyst. The conversions in the presence of CO, as represented in Fig. 5a–c, were systematically compared with those obtained in the absence of CO in the feed.

In the case of Au/CeO<sub>2</sub>, acetylene reacts in a similar way across the temperature domain in the presence or absence of CO (Fig. 5a). The situation is somehow different with Au/TiO<sub>2</sub>; the presence of CO delays slightly the reaction of acetylene combustion, as proven by an increase in the  $T_{50}$  value of c.a. 80 °C, when compared with the value observed when acetylene is the sole gas in the combustion mixture (Fig. 5b). The case of Au/ZrO<sub>2</sub> is also different from the two previous ones. Indeed, the value of the  $T_{50}$  is decreased by c.a. 60 °C, revealing a positive effect of CO (Fig. 5c). For all the three catalysts, the CO oxidation reaction starts only after the  $C_2H_2$  oxidation. This delay in reactivity could signify that CO is adsorbed onto the same sites as  $C_2H_2$  only when these sites are vacated by the acetylene molecules or from the latter's reaction products. Here again, a support effect in the competitive reaction between CO and  $C_2H_2$  is decisive; therefore, this support effect was studied in a great detail by a kinetics analysis in order to find a possible explanation for its role of the support in the reaction.

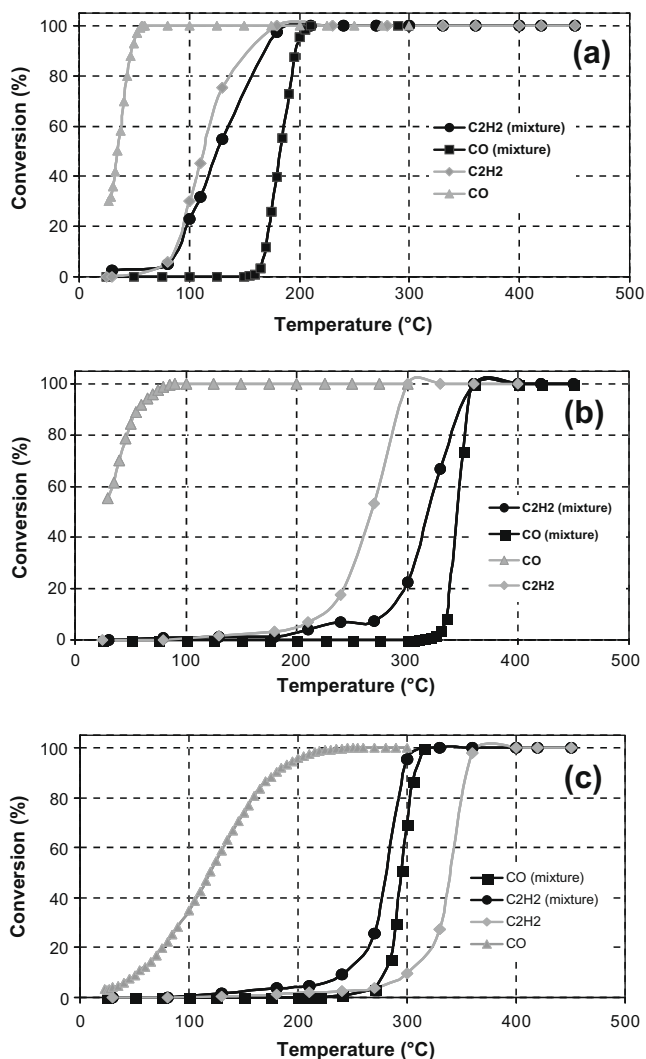


Fig. 5. Influence of CO on  $C_2H_2$  conversion: (a) Au/CeO<sub>2</sub>, (b) Au/TiO<sub>2</sub>, (c) Au/ZrO<sub>2</sub>.

Table 4

Kinetics data for acetylene oxidation: orders of reaction towards  $C_2H_2$  and  $O_2$  (without CO).

	T (°C)	Order $C_2H_2$	Order $O_2$
Au/CeO <sub>2</sub>	100	0.2	0.0
	130	0.2	0.0
	270	-0.3	0.5
Au/ZrO <sub>2</sub>	300	-0.2	0.5
	300	0.0	0.8
Au/TiO <sub>2</sub>	330	0.0	0.7
	330	0.0	0.8
	360	0.0	0.8

### 3.3.2. Kinetics study

The activity measurements were completed by a kinetic study undertaken by varying the partial pressure of acetylene at constant oxygen pressure and vice versa in order to determine the apparent order of reaction for Au supported on CeO<sub>2</sub>, ZrO<sub>2</sub> and TiO<sub>2</sub>, respectively. Each order was measured at different temperatures in the kinetic regime; the orders for both  $O_2$  and  $C_2H_2$  are not temperature dependent in these sets of experimental condition. In a number of cases a variation of  $\pm 0.1$  in unit was observed depending upon the temperature, but was considered as being experimentally insignificant, proving that mass transfer is not limiting. The orders of reaction towards  $O_2$  or  $C_2H_2$  are displayed in Table 4.

On all the catalysts, it must be stressed that acetylene and  $O_2$  may adsorb on different types of site. For Au/CeO<sub>2</sub>, at low temperature, i.e. below 130 °C, and therefore at low conversion, there is no variation in the conversion of acetylene with an increase of  $P_{O_2}$ . In this range, the order towards acetylene is slightly positive while a zero order towards oxygen is obtained, suggesting that the rate does not depend upon oxygen pressure. The situation is rather different for the other two catalysts and particularly for oxygen. The order towards acetylene remains close to zero. Nevertheless, here the variations are significant, in the case of ZrO<sub>2</sub>, the order towards acetylene is slightly negative with a value of -0.2 suggesting that during the course of the reaction the catalyst surface is covered by strongly adsorbed acetylene. The order towards oxygen is positive and equal to 0.5 which means that the rate is only dependent on oxygen partial pressure and might suggest a dissociation of oxygen on the surface. Finally, for Au/TiO<sub>2</sub>, a zero order towards  $C_2H_2$  is observed which means that the surface is covered by acetylene and the order towards  $O_2$  is equal to 0.8 proving that the rate of reaction is a function of the oxygen pressure and not of acetylene in this set of experimental conditions.

## 4. Discussion

The oxidation reaction of CO is systematically inhibited in the presence of acetylene. However, this is not the case with acetylene which behaves differently in the presence of CO according to the support used. The behaviour could be summarised by the following observations:

- On Au/CeO<sub>2</sub> there is no influence of CO in the  $C_2H_2$  oxidation;
- the  $C_2H_2$  oxidation is inhibited by the presence of CO on Au/TiO<sub>2</sub>;
- the  $C_2H_2$  oxidation is enhanced by the presence of CO on Au/ZrO<sub>2</sub>.

This offers an indication of the mechanism of oxidation – the adsorption of acetylene and CO most probably occurs on the same active site. The adsorption is competitive in favour of acetylene according to CO. The acetylene is strongly adsorbed to the surface at room temperature and occupies all adsorption sites which do not allow an adsorption of CO. However, it does provoke an increase in the temperature required for acetylene conversion with

an increase of around 50 °C over a whole range of temperatures compared with the conversion of acetylene alone. Once the oxidation of acetylene is complete the oxidation of CO can begin. The delay in the oxidation of CO indicates that CO could adsorb and react only on those sites vacated by acetylene or its oxidation products.

Acetylene is characterised by its very strong adsorption on the surface of noble metals [15], due to its high capacity as an electron donor, this characteristic is verified by this experiment where inhibition of CO oxidation is systematically observed in the presence of C<sub>2</sub>H<sub>2</sub>. This strong adsorption may result from the acidic character of the acetylene molecule as conferred by the sp hybridisation which gives 50% of s-character to the molecule. A particular type of affinity of acetylene for gold has been postulated by DFT calculations when comparing adsorption capacity of either acetylene or ethylene by Segura et al. [32]. Our experience in acetylene hydrogenation, indicates that this observation is valid in the presence of both oxygen and hydrogen [33].

It is known that the reaction order of a surface-catalysed reaction is strongly affected by the degree of coverage achieved by a reactant. The variation of order found in the oxidation of the three catalysts of this study may be the result of a difference in the adsorption strength. A significant result is that the orders of reaction in oxygen and acetylene depend upon the type of support. The order of oxygen is never negative, while the order in HC is zero or slightly positive for Au/TiO<sub>2</sub> and Au/CeO<sub>2</sub>, respectively, and is slightly negative for Au/ZrO<sub>2</sub> indicating that, in this latter case, HC is strongly bonded on the surface and therefore could reflect a competitive adsorption with other reactant or other intermediate. It reacts with difficulty and could account for the comparatively reduced activity for this catalyst. However, only a small variation of the HC order is observed. Although significant, (experimental error being of ±0.1), it does not seem that the difference in the behaviour of the three catalysts results from a difference in the acetylene adsorption and/or reaction in adsorbed phase. The difference in the orders of reaction towards oxygen is much more significant and indicates that the mode of adsorption and/or reaction depends only on oxygen.

There is a particular interest in comparing the behaviour in the presence of H<sub>2</sub> where strongly adsorbed acetylene forms an acetylene residue and a hydrogen atom. This process depends mainly upon the support whereas in the presence of hydrogen, adsorbed acetylene tends to form carbonic species [34] which is specific of dispersed gold [33]. The results proposed here underline a similarity between the reactions of acetylene with either H<sub>2</sub> or O<sub>2</sub> and implies a peculiar ability of gold to undergo a carbon-carbon rupture. However, the role of oxygen remains predominant in the oxidation reaction, the question being how and in which form?

A first effect observed is the role of the support which is evidenced by the superiority of CeO<sub>2</sub> over the two other supports which may result from the fact that ceria generally serves as a reservoir for oxygen in the oxidation reaction, though this effect is usually observed above 300 °C [35,36]. For Harmsen et al. [10], the role of ceria is determinant for the mechanism they have proposed which suggests that the oxidation occurs via a bi-functional reaction between adsorbed acetylene and oxygen from the ceria. Although realistic on a Pt-Rh catalyst, this mechanism cannot be the sole possibility in our case, for while the reaction is promoted with ceria, it is not necessarily the only form of active oxygen as both Au/ZrO<sub>2</sub> and Au/TiO<sub>2</sub>, although less active than ceria, nevertheless exhibit a relatively high activity when compared with other metals such as Pt and Rh [8].

It is not the first time that the role of oxygen is evoked particularly in oxidation reactions over gold nanoparticles [37]. Generally, particle size is involved because for small particles gold loses its metallic character due to an increase of the d-electron density and also to a high degree of surface de-saturation which leads to

a higher reactivity; but what our results show is that the size is not the only factor of importance but intriguingly it results directly from the support itself, modifying the kinetics parameter. In particular, when the order towards oxygen changes this is an indication that there is a different mechanism according to the support. Although this work does not completely explain this effect, several assumptions can be made; the electronic factor could be eliminated since as in all cases gold is purely metallic, no ionic gold was detected, even following an oxidation in air. The support effect may result from a structuring influence of the support on the particle, either by epitaxy or by the creation of different particle shapes which could subsequently produce geometrical effects. Indeed previous work enabled us to discuss this type of effect on gold particles supported on alumina, which in this case were preferentially adopting a cubo-octahedric shape (packing) leading to an interesting reactivity towards oxygen. The chemisorption of oxygen does not occur on massive gold, but there are several references in the literature which report that chemisorption and/or dissociation of oxygen become feasible on small gold particles [38–40], the location of oxygen from the support vacancies, on the particle, at the interface being dependent on the support itself. The recent work of Hutchings et al. emphasises the role of shape and morphology in the case of gold catalysts. They have shown that a fraction only of gold surface which is active, and that this active fraction is mainly under the form of bilayer clusters that are c.a. 0.5 nm in diameter with a number of atoms not exceeding 10, and therefore not detectable by classical microscopy [31]. Then our work supports this idea, the support playing an essential role in the formation of these very active particles.

## 5. Conclusions

The present study on acetylene oxidation has revealed several features characteristic of gold catalysts. First of all, the oxidation of acetylene which usually is a difficult reaction on metal becomes quite feasible on gold due to the very strong interaction between acetylene and gold nanoparticles. This confirms the extreme versatility of gold catalysis for oxidation reactions as observed for other contaminants such as CO and volatile organic compounds. The activity is a function of the nature of the support with the following order of activity: Au/CeO<sub>2</sub> > Au/TiO<sub>2</sub> > Au/ZrO<sub>2</sub>. The oxidation of CO is systematically inhibited by the presence of C<sub>2</sub>H<sub>2</sub>; this indicates that the adsorption competition is strongly in favour of C<sub>2</sub>H<sub>2</sub>. However, in the case of the reaction of C<sub>2</sub>H<sub>2</sub> oxidation, the situation is different: CO has no effect on Au/CeO<sub>2</sub>, the reaction is poisoned for Au/TiO<sub>2</sub> and promoted for Au/ZrO<sub>2</sub>. The reason lies in a different kinetic behaviour, mainly for the mode of adsorption and/or reaction of oxygen proven by a variation in the kinetic order, as there is no difference in the order of reaction towards C<sub>2</sub>H<sub>2</sub> for the three catalysts. The effect of oxygen is not clearly elucidated but a change of mechanism resulting from the kinetics is postulated which might be the result of a different structuring of the gold particles according to the nature of the support.

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