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Crotonaldehyde hydrogenation by gold supported on TiO_2: structure sensitivity and mechanism

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Abstract

The catalytic properties of two series of Au/TiO_2 catalysts prepared by deposition-precipitation with NaOH (DP NaOH) (~ 3 wt%) and by deposition-precipitation with urea (DP Urea) (~ 8 wt%) were evaluated for the reaction of crotonaldehyde hydrogenation at atmospheric pressure. There is no difference in activity (mol $g_{Au}^{-1}\,s^{-1}$) and selectivity between the DP Urea and DP NaOH samples for a given activation treatment. This is due to the fact that the DP Urea and DP NaOH samples exhibit a similar gold particle size distribution, although the gold loading in DP Urea catalysts is much higher than in DP NaOH. The DP Urea samples were reduced under H_2 at different temperatures (120–500 °C) or treated in air at 300 °C with various flow rates, to vary the average particle size within a large range, 1.7 to 8.7 nm. The selectivity to crotyl alcohol (selective hydrogenation of the carbonyl bond), in the 5–50% conversion range, is high, 60–70 %, and is independent of the reduction temperature, and almost constant as a function of the particle size. In contrast, the TOF depends on the gold particle size, drastically increasing when the gold particle size is ~ 2 nm. These characteristic features of Au/TiO_2 catalysts in this reaction are compared with those of Pt/TiO_2. The possible adsorption modes of crotonaldehyde are discussed. Hydrogen dissociation is proposed to be the rate-determining step, and to take place on the low-coordinated atoms of the gold particles.

Keywords: Gold; Catalysts; Metal nanoparticles; Titania; Catalyst preparation; Deposition-precipitation; Hydrogenation of crotonaldehyde; Transmission electron microscopy; HRTEM

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1. Introduction

Ni-, Pd-, or Pt-based catalysts are very active catalysts in hydrogenation reactions because of the high ability of these metals to dissociate hydrogen and because the hydrogenation reaction rate (r) is positively dependent on the hydrogen coverage ($r = k\Theta_H^\alpha$ with $\alpha > 0$). In comparison to these metals, gold has been classified as a poor catalyst to dissociate H_2 molecules.

Early studies showed that supported gold can catalyze various hydrogenation reactions, such as those of linear alkenes [1–3], alkynes [3,4], cyclohexene [5,6], and acetone [7]. Then, little attention was paid to the hydrogenation properties of gold, probably because of the very low activity of gold supported on oxides when the metal particles are large. The position of gold in catalysis drastically changed at the end of the 1980s, when Haruta and co-workers were able to prepare small gold particles supported on oxides and discovered that these catalysts were active in CO oxidation at low temperatures [8,9]. Gold has been more recently tested again in hydrogenation reactions, and as reported by Bond and Thompson [10], it also seems a very promising catalyst for this type of reaction.

Indeed, supported gold catalysts were active and selective in partial and selective hydrogenation reactions. Jia et al. [11] showed that Au/Al_2O_3 catalyzed the hydrogenation of acetylene to ethylene with 100% selectivity in the temperature range 40–250 °C and with a maximum activity for an average gold particle size of 3.0 nm. Okumura et al. [12] investigated the reaction of hydrogenation of 1,3-butadiene

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over Au/Al_2O_3, Au/SiO_2, and Au/TiO_2. All the Au catalysts were 100% selective to butenes with 65–75% of selectivity to 1-butene. They found that the reaction was almost insensitive to the size of the Au particles (2.5 and 5 nm) and to the nature of the oxide support.

One of the most studied reactions of hydrogenation with gold catalysts is the selective hydrogenation of α,β-unsaturated aldehydes [12–17]. Indeed, the selectivity in unsaturated alcohols, the desired products, is difficult to achieve (i) because thermodynamics favors the hydrogenation of the C=C over the C=O bond by about 35 $\mathrm{kJ\,mol^{-1}}$ and (ii) because for kinetic reasons, the reactivity of the C=C bond is higher than that of the C=O bond. Hence, on conventional supported hydrogenation catalysts (Pt, Ru, Ni, etc.), the main products are the saturated aldehydes. On supported gold catalysts, interesting selectivities to unsaturated alcohol were found, even if the results obtained from one research group to another are not always fully consistent. The selective hydrogenation of crotonaldehyde (but-2-enal) was first studied by Bailie and Hutchings [14] at atmospheric pressure and 250 °C, with Au/ZnO and Au/ZrO_2 prepared by coprecipitation, and with Au/SiO_2 prepared by impregnation. They found that Au/ZnO was more selective for C=O bond hydrogenation and that the addition of thiophene acted as a promoter for selective hydrogenation. Haruta and colleagues [12] studied the same reaction but at high pressure (1.0 MPa) and 227 °C, with Au/Al_2O_3 and Au/TiO_2 catalysts prepared by deposition-precipitation with NaOH and gold particles sizes of 4.6 and 3.4 nm, respectively, and Au/SiO_2 (5.3 nm) prepared by grafting of gold acetyl acetonate. They also found that the selectivity depends on the nature of the support. The highest selectivity to crotyl alcohol was obtained over Au/TiO_2 ($\approx$ 25% instead of $<$ 10% for the other samples). Bailie et al. [15] studied the influence of the particle size on the selectivity in the Au/ZnO system. Gold particle sizes were increased by increasing the gold loading in the samples (2 wt% (2–4 nm), 5 wt% (4–5 nm), and 10 wt% (bimodal distribution: 1–3 and 6–10 nm)), or by increasing the reduction temperature of the 5 wt% Au/ZnO catalyst (250 °C (4–6 nm), 300 °C (3–8 nm), 350 °C (10–15 nm), and 400 °C (up to 20 nm)). They reported that the selectivity to crotyl alcohol increased when the gold loading or the reduction temperature increased, and they proposed that the active sites for selective hydrogenation of crotonaldehyde to crotyl alcohol were associated with the presence of large Au particles. Claus et al. [16] also studied the effect of the particle size in a series of three Au/TiO_2 catalysts (1.1, 2.0, and 5.3 nm) prepared by three different preparation methods in selective hydrogenation of acrolein under high pressure (2 MPa) and at 240 °C. They observed a drastic decrease in the TOF by two to three orders of magnitude and a decrease of selectivity when the size of gold particles decreased from 2.0 to 1.1 nm, and constant values of TOF and selectivity for average particle sizes of 2.0 and 5.3 nm. They proposed that the structure sensitivity of the reaction in the case of small gold particles was due to quantum size effects, i.e., to alteration of the metallic properties of the smallest gold particles. In a more recent study, Claus and colleagues [17] prepared three Au/ZrO_2 catalysts by the same method of deposition-precipitation, using various pH's, to obtain catalysts with various gold particle sizes (4.0, 6.9, and 7.7 nm). They found that the TOF decreased by nearly one order of magnitude, and the selectivity to allyl alcohol increased (from 15 to 35%) when the particle sizes increased. On the other hand, they observed by HRTEM, multiply twinned particles whose number increased with increasing reduction temperature (300 to 500 °C) or reduction time (3 to 18 h). They pointed out the fact that when the number of multiply twinned particles increased, both the selectivity and the TOF decreased. They attributed the higher activity of Au/TiO_2 compared to that of Au/ZrO_2 (TOF × 2) to the fact that the gold particles were round shaped on TiO_2 and facetted on ZrO_2 (average particle size of $\sim$ 5 nm on both supports). Round-shaped gold particles on TiO_2 would contain a higher proportion of low-coordinated surface sites, which would explain the higher TOF.

As shown above, the influence of the gold particle size and of the nature of the support on the activity and selectivity for the hydrogenation of α,β-unsaturated aldehydes is not clear, yet. To attempt to clarify the influence of the first parameter, we decided to investigate the dependence of the catalytic properties with gold particle size in Au/TiO_2 catalysts prepared by a single method, the deposition-precipitation with urea [18]. The main advantage of this method over the method of deposition-precipitation with NaOH developed by Haruta and colleagues [19,20] is that all the gold of the solution is deposited on TiO_2, so higher gold loading can be reached with the same gold particle size as with Haruta's method, and the gold loading of the catalysts can be easily controlled. The results obtained are therefore compared with those obtained on Au/TiO_2 catalysts prepared by deposition-precipitation with NaOH. The reaction studied is the hydrogenation of crotonaldehyde (CH_3–CH=CH–CH=O) at atmospheric pressure, under the same experimental conditions as those used in former studies for Pt/TiO_2 catalysts [21,22]. Hence, comparisons of the catalytic behavior between platinum and gold catalysts could be made, especially the influence of the particle size and that of the reduction temperature, since these two parameters are the key parameters which govern the activities and selectivities of Pt/TiO_2 catalysts.

2. Experimental

2.1. Catalyst preparation

Titania Degussa P25 was used as support (45 $\mathrm{m^2\,g^{-1}}$, nonporous, 70% anatase and 30% rutile, purity $>$ 99.5%) and solid $HAuCl_4 \cdot 3H_2O$ (Acros) as gold precursor. Before preparation, TiO_2 was previously dried in air at 100 °C for at least 24 h.

Table 1
Au/TiO_2 catalysts used in the present study

Sample	Conditions of preparation	Au loading (wt%)
DP Urea 1 h	DP urea for 1 h at 80 °C	6.9
DP Urea 2 h	DP urea for 2 h at 80 °C	7.5
DP Urea 16 h	DP urea for 16 h at 80 °C	7.5
DP Urea 16 h/90	DP urea for 16 h at 90 °C	7.3
DP NaOH 2 h	DP NaOH for 2 h at 80 °C	2.8

2.1.1. Preparation by deposition-precipitation with NaOH (DP NaOH samples)

One hundred milliliters of an aqueous solution of $HAuCl_4$ (4.2×10^{-3} M) was heated to 80 °C. The pH was adjusted to 7 by dropwise addition of NaOH 1 M, 1 g of TiO_2 was dispersed in the solution, and then the pH was readjusted to 7 with NaOH. The suspension thermostated at 80 °C was vigorously stirred for 2 h.

2.1.2. Preparation by deposition-precipitation with urea (DP Urea samples)

One gram of TiO_2 was added to 100 ml of an aqueous solution containing $HAuCl_4$ (4.2×10^{-3} M) and urea (0.42 M). The initial pH was ~ 2. The suspension thermostated at 80 °C was vigorously stirred for 1, 2, or 16 h. Urea decomposition leads to a gradual rise in pH.

These sequences of preparation in solution were performed in the dark, in blackened flasks, since light is known to decompose the gold precursors and to reduce them. The solids gathered after centrifugation were washed with water, centrifuged four times, and then dried under vacuum at 100 °C for 2 h in the dark, according to the procedure reported in [18]. The samples were stored away from light under vacuum in a desiccator or under Ar for transportation to Strasbourg where the catalytic reaction was performed. According to Zanella et al. [23] gold is still mainly in oxidation state III after drying.

Table 1 summarizes data for the various Au/TiO_2 catalysts used in this study.

2.2. Techniques

Chemical analysis was performed by inductively coupled plasma atomic emission spectroscopy at the CNRS Center of Chemical Analysis (Vernaison, France). The Au weight loading of the samples was expressed in grams of Au per gram of sample calcined at 1000 °C: wt% Au = $[m_{\mathrm{Au}}/(m_{\mathrm{Au}} + m_{\mathrm{TiO_2}})] \times 100$.

The average size of gold particles in the various samples, analyzed after the catalytic reaction, was determined by transmission electron microscopy (TEM) with a Jeol 2000FX electron microscope. The histograms of particle sizes were established from the measurement of 300 to 1000 particles. The size limit for the detection of gold particles on TiO_2 was about 1 nm. The average particle diameter d_s was calculated using the following formula: $d_s = \sum n_i d_i^3 / \sum n_i d_i^2$ where n_i is the number of particles of diameter d_i.

XANES (X-ray absorption near-edge structure) measurements of the Au/TiO_2 samples were performed at the Au L_{III} edge at the XAS 13 beam line of the DCI storage ring (operating with positrons at 1.85 GeV and a mean ring current of 300 mA) of the LURE synchrotron radiation facility (Orsay, France). The samples were diluted with cellulose and pressed into a pellet. The XANES spectra were recorded at room temperature, in transmission mode using two argon-filled ionization chambers and a channel-cut Si(111) monochromator. For each sample, the XANES spectra were scanned twice with 0.5 eV steps from 11,870 to 12,020 eV. The energy was calibrated using a Au metal foil. The XANES spectra of references, gold foil, and $Au(OH)_3$ were also recorded. After background correction, the XANES spectra were normalized at the end of the first EXAFS oscillation.

Activation treatments and catalytic reactions were carried out in a glass flow reactor, operating at atmospheric pressure as described elsewhere [24]. Before catalytic experiments, each catalyst (10–50 mg) was reduced at various temperatures, between 120 and 500 °C, either under H_2 flow (50 ml min^{-1} for 10 min at RT, heating (5 °C min^{-1}), 1 h at the chosen temperature, and cooling down to the reaction temperature, 120 °C) or under air flow (50, 35, or 2 ml min^{-1}, 10 min at RT, heating (2 °C min^{-1}), 4 h at 300 °C, and cooling down to RT). In the latter, catalysts were afterward purged with Ar at RT and then submitted to a treatment at 120 °C under H_2, as described above.

Crotonaldehyde supplied by FLUKA puriss and stored in argon was used as received. Experiments were performed with a crotonaldehyde/H_2 pressure ratio fixed to 8/752 (Torr).

The reaction products were analyzed on line by gas-liquid FID chromatography (GLC, with a 30-m-long and 0.5461-mm-diameter DB-Wax column (J&W Scientific) heated at 85 °C). The relative sensitivity factors using the FID detector are taken from the Dietz Tables [25] as 1 for crotonaldehyde, crotyl alcohol, butanal, and butanol and 1.4 for hydrocarbons.

The reaction activities (µmol $\mathrm{s}^{-1}\,\mathrm{g}_{\mathrm{Au}}^{-1}$) were calculated according to the following formula: $A = \alpha F/\omega$, where α is the crotonaldehyde conversion, F, the crotonaldehyde flow rate in mol s^{-1}, and ω, the weight of gold in grams. The turnover frequency (TOF), number of molecules of crotonaldehyde converted per surface atom of gold particles and per second, was calculated with the assumption that gold particles were cuboctahedral with a hexagonal face in contact with the titania surface. The selectivities to the different products, crotyl alcohol, butanal, butanol, and hydrocarbons were expressed as the molar ratio of the selected product to the all products formed. The crotonaldehyde, used without further purification, contained 0.1–0.3% butanal; therefore, the selectivity values were always compared at conversions higher than 4% to minimize the errors.

No activity was observed on the support alone tested under the same experimental conditions as Au/TiO_2 catalysts, more precisely in the 80–160 °C temperature range. The comparison of the catalytic behavior of all the Au/TiO_2 catalysts was made for a reaction temperature of 120 °C. The weight of catalyst and the flow rate of the products were consequently adjusted to convert 5–10% products in order to compare the activities and selectivities in a similar range of conversions.

3. Results

3.1. General features on activity and product distributions

All the catalysts (DP Urea and DP NaOH) show a deactivation period during the first 30–40 min of time on stream as reported in Fig. 1 for DP Urea 16 h reduced under H_2 at different temperatures. The product distributions are also the same for all the catalysts, with crotyl alcohol and butanal as main products, and butanol and butenes as minor products. They remain quasi constant with the time on stream, even during the deactivation period (Fig. 2). From a kinetic point of view, the constant distribution of reaction products indicates that the deactivation process is independent of these products. Therefore, the activity evolutions could be fitted by curves following the exponential equation, $A_t = a_3 + a_1 * \exp(-a_2 * t)$, where a_i are only related to the deactivation constants. This was detailed elsewhere for a Pt catalyst, which exhibited the same features [26]. Examples of curve fittings are shown on Fig. 1. The activities reported in Tables 2 and 3, and further discussed, correspond to the activity in the steady state, calculated from the equation with $t = \infty$ (Activity $= A_\infty = a_3$).

3.2. Catalyst regeneration and reproducibility

We checked that the deactivation was reversible with catalyst DP Urea 16 h reduced at 300 °C under H_2. After about 45 min of reaction, i.e., deactivation, the catalyst treated again under H_2 for 1 h at 300 °C exhibits exactly the same behavior on stream as the fresh catalyst (Fig. 3a). This indicates that deactivation is due to adsorbed species and not to metal sintering during the reaction. It can be deduced that the gold particles that were measured after reaction are of the same size as just after thermal pretreatment.

We also checked the reproducibility of the experiments of reactivity. The curves of activity versus reaction time of two DP Urea 2 h samples arising from the same batch and reduced at 300 °C under H_2 are superimposable (Fig. 3b). Noteworthy is the fact that the conditions of sample storage described under Experimental are the determining ones to obtain reproducible experiments, because of the trend of gold particles toward sintering under ambient air.

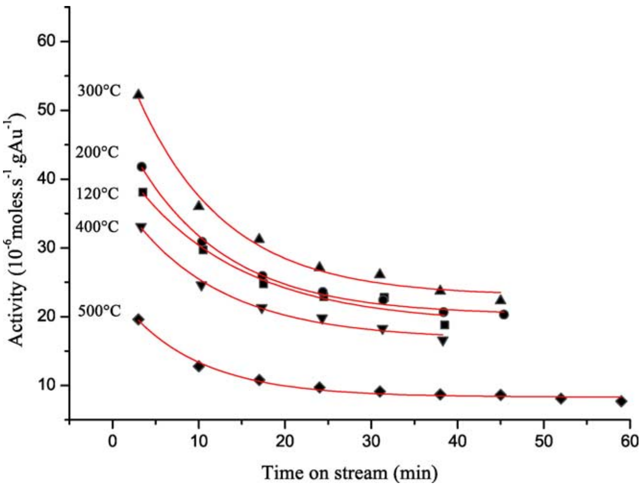


Fig. 1. Hydrogenation of crotonaldehyde ($P_{H_2} = 752$ Torr, $P_{\text{crotonaldehyde}} = 8$ Torr, $T_{\text{reaction}} = 120\,°C$). Activity versus time on stream of DP Urea 16 h reduced under H_2 at different temperatures (experimental points + curve fittings (continuous lines)).

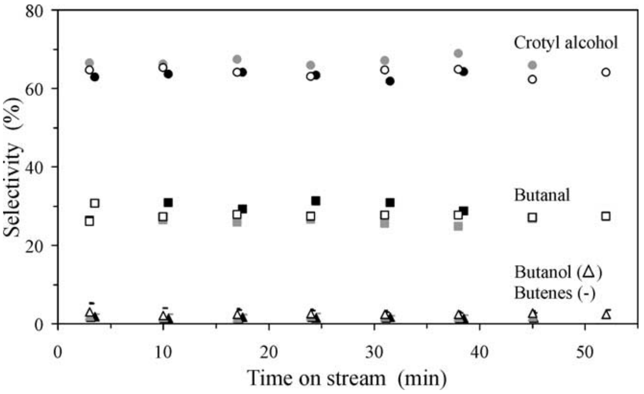


Fig. 2. Hydrogenation of crotonaldehyde ($P_{H_2} = 752$ Torr, $P_{\text{crotonaldehyde}} = 8$ Torr, $T_{\text{reaction}} = 120\,°C$). Selectivities versus time on stream of DP Urea 16 h reduced under H_2 at 120 °C (black symbols); at 300 °C (gray symbols); at 500 °C (white symbols).

3.3. Product distributions and activation energy

The product distributions obtained with the Au/TiO_2 catalysts are remarkable since they consist of 60–70% of crotyl alcohol, whatever the studied Au/TiO_2 catalyst and the temperature of pretreatment (Fig. 2). A selectivity-conversion diagram was obtained for catalyst DP Urea 16 h in gradually decreasing flow rates during the time on stream in order to increase the conversion (Fig. 4). This diagram shows that the selectivity to butanal remains unchanged up to 50% conversion while those in butenes and butanol slightly increase at the expense of that in crotyl alcohol.

To check if butanal could be formed by isomerization of crotyl alcohol as observed on Pt-based catalysts [27], the hydrogenation of crotyl alcohol was investigated for the DP Urea 16 h catalyst. It was observed that crotyl alcohol reacted at a similar rate as crotonaldehyde, to give rise to 90% of butenes, 3.9% of butanal, and 6.1% of butanol. The

Table 2
Gold particle size and catalytic activity in hydrogenation of crotonaldehyde of DP Urea16 h and DP NaOH 2 h as a function of the reduction temperature under H_2

Catalysts	Reduction temperature (°C)	Average particle size d_s (nm)	Standard deviation on d_s (nm)	Activity (10^{-6} mol g_{Au}^{-1} s^{-1})	TOF (10^{-3} s^{-1})	$S_{\text{crotyl alcohol}}$ (%)
DP Urea 16 h	120	1.7	0.40	19.9	6.4	65
	200	1.7	0.49	20.3	6.5	66
	300	1.9	0.46	22.4	7.8	67
	400	2.1	0.59	16.7	6.3	68
	500	2.6	0.58	8.3	3.7	64
DP NaOH 2 h	120	1.3	0.31	22.8	6.0	66
	200	1.7	0.40	19.8	6.3	66
	300	1.8	0.41	20.7	6.9	69
	400	2.1	0.54	13.2	5.0	70
	500	2.5	0.60	6.3	2.7	62

Table 3
Gold particle size and catalytic activity in hydrogenation of crotonaldehyde as a function of the DP Urea samples, pretreated at 300 °C in H_2 or air

Catalysts	Pretreatment	Average particle size d_s (nm)	Standard deviation on d_s (nm)	Activity (10^{-6} mol g_{Au}^{-1} s^{-1})	TOF (10^{-3} s^{-1})	$S_{\text{crotyl alcohol}}$ (%)
DP Urea 1 h	H_2 (50 ml min^{-1})	2.4 and 6.7		5.1		59
DP Urea 2 h		2.1	0.50	12.1	4.6	65
DP Urea 16 h		1.9	0.46	22.4	7.8	67
DP Urea 16 h/90		1.6	0.37	18.8	5.6	68
DP Urea 2 h	Air (50 ml min^{-1})	2.8	0.58	5.2	2.5	60
	Air (12 ml min^{-1})	3.5	0.74	2.9	1.7	60
	Air (5 ml min^{-1})	4.0	0.86	2.3	1.5	53
DP Urea 1 h	Air (50 ml min^{-1})	8.7	2.76	0.7	0.9	nd[a]

[a] The value was not reliable due to the too low conversion (~ 1%) (see experimental section).

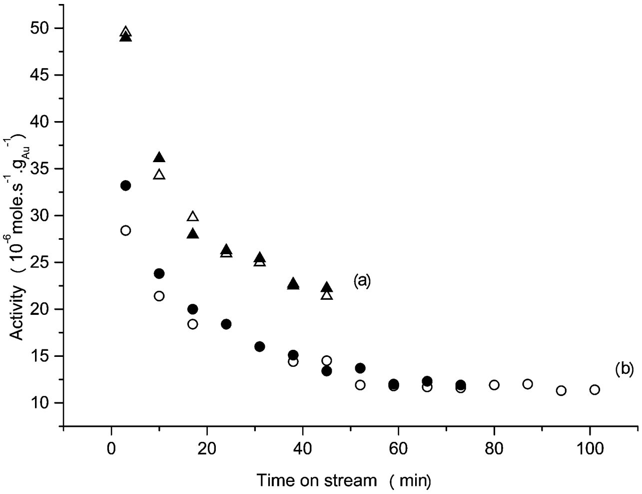


Fig. 3. Experiments of (a) regeneration of DP Urea 16 h reduced at 300 °C under H_2 and of (b) reproducibility of the catalytic reaction with DP Urea 2 h reduced at 300 °C under H_2; white symbols for the first experiment and black symbols for the second one.

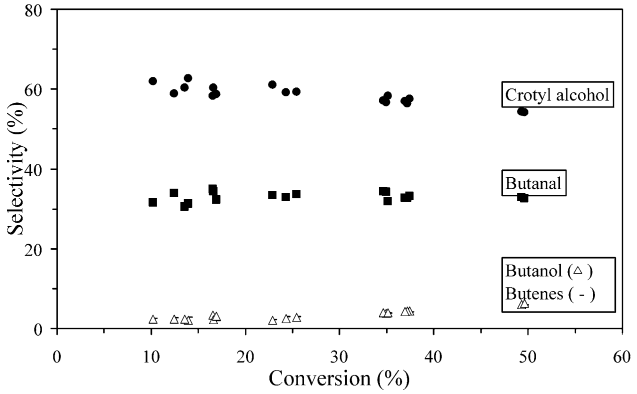


Fig. 4. Hydrogenation of crotonaldehyde ($P_{H_2} = 752$ Torr, $P_{\text{crotonaldehyde}} = 8$ Torr, $T_{\text{reaction}} = 120$ °C). Selectivities versus conversion on DP Urea 16 h/90 reduced under H_2 at 120 °C.

butenes formed from crotyl alcohol consisted of 73% of but-1-ene, 7% of *trans*-but-2-ene, and 20% of *cis*-but-2-ene. This butene distribution is similar to that obtained from butadiene hydrogenation on the same catalyst (unpublished results). These results suggest that crotyl alcohol transforms by dehydration into butadiene, which further hydrogenates into butenes. This could explain the increased of selectivity to butenes at the expense of that in crotyl alcohol when the conversion of crotonaldehyde increased. This also indicates that the butanal observed in the crotonaldehyde hydrogenation products is directly formed from the reactant since the isomerization of crotyl alcohol into butanal is a minor reaction. Scheme 1 can be proposed.

The activation energy of the crotonaldehyde hydrogenation was deduced from the experiments performed in the 80–160 °C temperature range. A value of 36.3 kJ mol^{-1} was

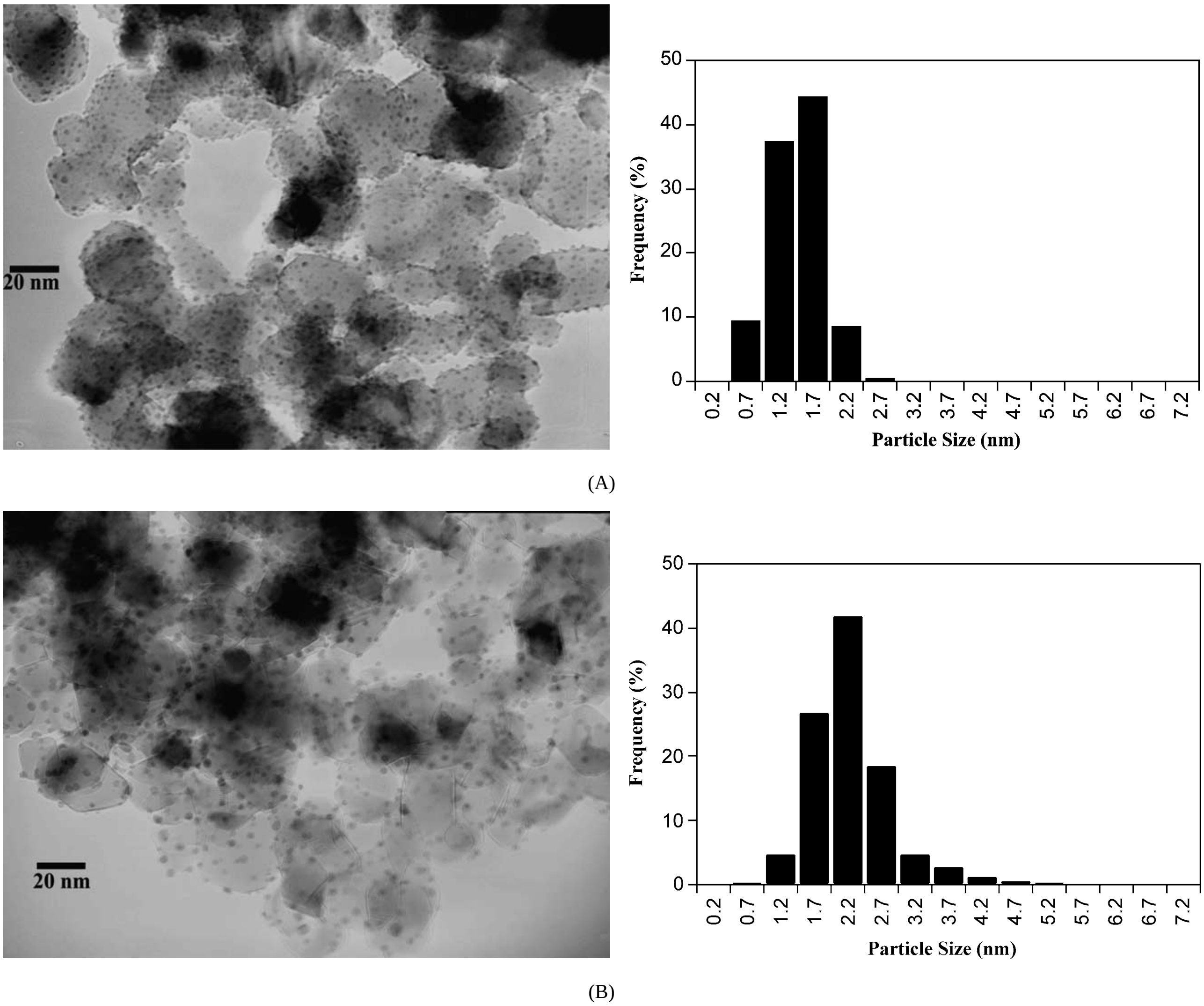
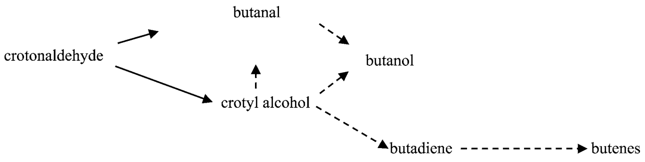


Fig. 5. TEM images and size histograms of gold particles of DP Urea 16 h reduced under H_2 at 120 °C (A) and at 500 °C (B).



Scheme 1. Reaction pathway of the hydrogenation of crotonaldehyde with Au/TiO_2 catalysts; plain and dotted arrows represent the primary and secondary reactions, respectively, and the lengths of the arrows are roughly proportional to the reaction rates.

found, which is slightly higher than the 21–34 $kJ\,mol^{-1}$ reported by Vannice and Sen [28] or 28 $kJ\,mol^{-1}$ reported by Raab and Lercher [29], obtained on Pt/TiO_2 catalysts for the same reaction.

On Au/TiO_2 catalysts, the product distributions were also independent of the reaction temperature in the studied temperature range (80–160 °C). However, at 160 °C, the consecutive reaction of crotyl alcohol became detectable, since the butene selectivity slightly increased from 2 to 6 % at the expense of the crotyl alcohol selectivity.

3.4. Influence of the reduction temperature under H_2

The influence of the reduction temperature under H_2 (120 to 500 °C) on the catalytic properties was studied with catalysts DP Urea 16 h and DP NaOH 2 h. Both Au/TiO_2 catalysts show the same evolution of the catalytic properties versus the reduction temperature with roughly the same activities and TOFs (Table 2). They exhibit almost the same activities and TOF's whether they have been reduced at 120, 200, and 300 °C, and lower activity and TOF after reduction at 400 and 500 °C.

It is important to note that the average sizes of gold particles in both catalysts are very close to each other. In addition, the average sizes of both types of catalysts are almost the same for reduction temperatures between 120 and 400 °C (~ 1.8 nm), and slightly larger after reduction at 500 °C (~ 2.5 nm). Figs. 5A and 5B show the TEM images and the size histograms of gold particles of DP Urea 16 h reduced under H_2 at 120 and 500 °C, respectively.

We checked by XANES that gold is already fully reduced at a pretreatment temperature as low as 120 °C for both types of catalysts. Indeed, the XANES spectra of DP Urea 16 h and DP NaOH 2 h reduced under H_2 at 120 or 200 °C are the same, and they are similar to that of the Au^0 reference of gold foil (Fig. 6).

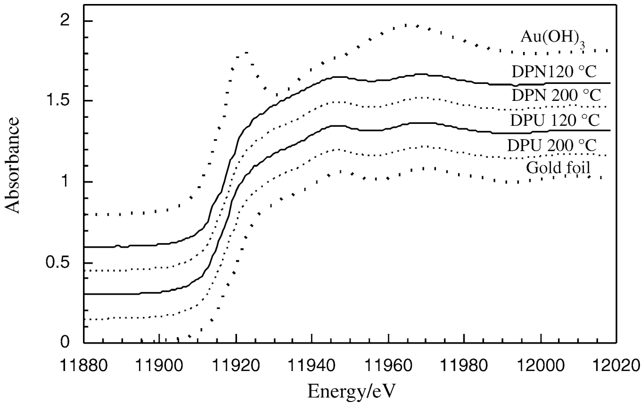
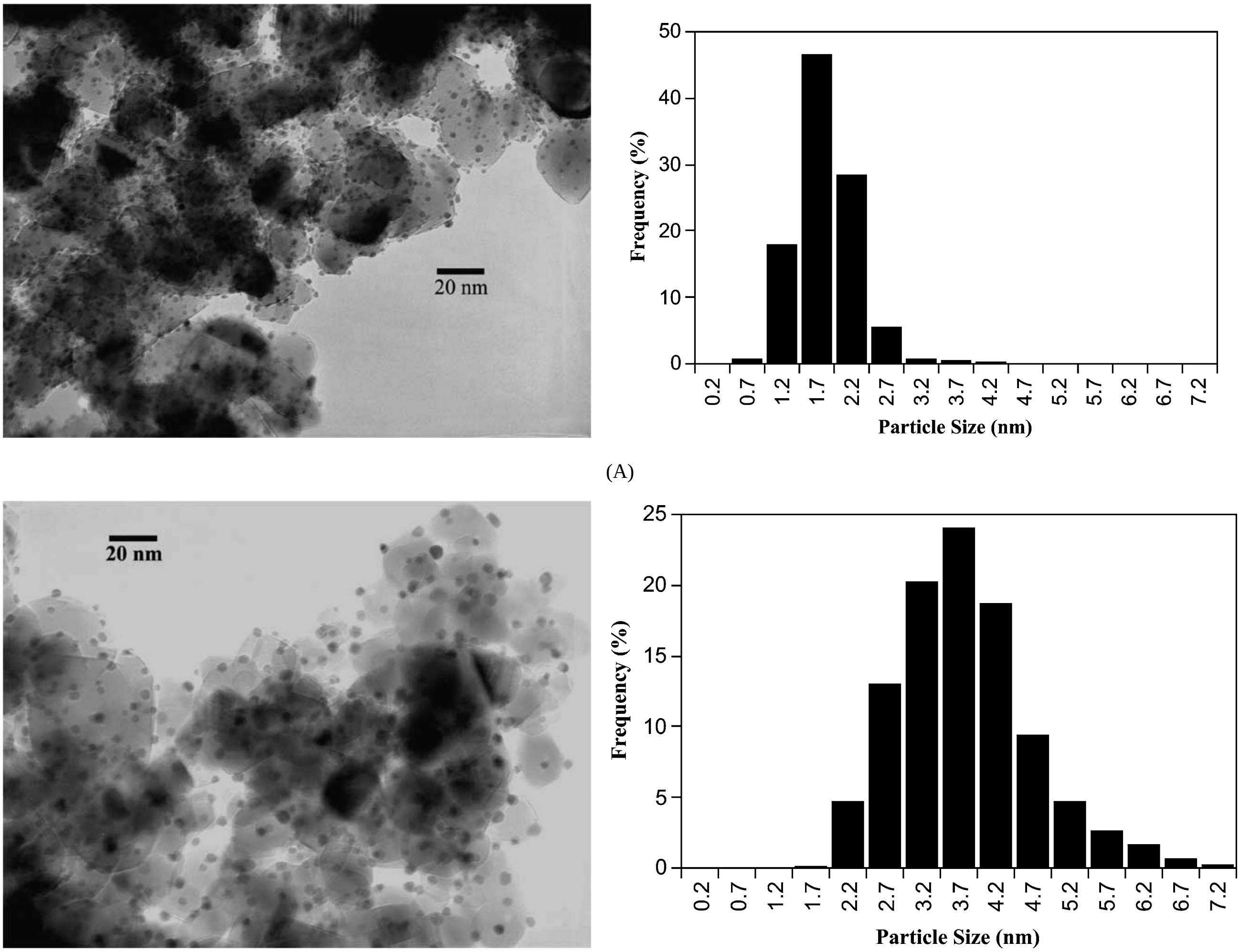


Fig. 6. XANES spectra of DP Urea 16 h and DP NaOH 2 h reduced under H_2 at 120 and 200 °C and XANES spectra of references, $Au(OH)_3$, and Au metal foil.

3.5. *Influence of the gold particle size*

The influence of the gold particle size on the catalytic properties was systematically investigated with a series of DP Urea catalysts prepared during various deposition-precipitation times (1, 2, and 16 h) and temperatures (80 or 90 °C) and pretreated at 300 °C. As shown in Table 3, for the series of catalysts reduced under H_2, the average particle size decreases when the deposition-precipitation time or the preparation temperature increases, in the same way as when the samples were treated under air [18]. DP Urea 1 h, which contains the largest gold particles, shows the lowest activity in the hydrogenation of crotonaldehyde. The bimodal size distribution did not make possible the calculation of the average particle size, and therefore that of the TOF. However, DP Urea 1 h gives a monomodal size distribution (8.7 nm) when it is pretreated with air at 300 °C. Intermediate particle sizes (2 to 4 nm) were obtained with DP Urea 2 h pretreated



(A)

(B)

Fig. 7. TEM image and size histogram of gold particles in DP Urea 2 h pretreated at 300 °C under H_2 (A) and under air (B).

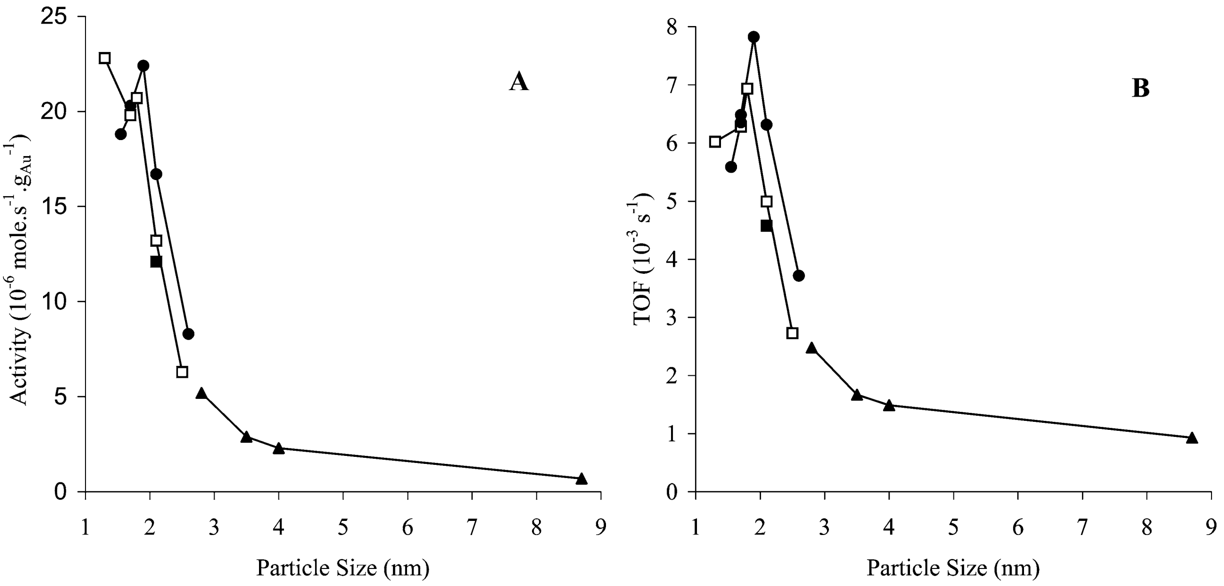


Fig. 8. Activity (A) and TOF (B) versus the average particle size of DP Urea 16 h pretreated under H_2 (●), DP Urea 2 h pretreated under H_2 (■), DP Urea 2 h and DP Urea 1 h pretreated under air (◆), and DP NaOH 2 h pretreated under H_2 (□).

with air at various flow rates (Table 3). Figs. 7A and 7B show the TEM images and the size histograms of gold particles of a DP Urea 2 h sample pretreated under H_2 and under air at 300 °C, respectively. It shows that the H_2 pretreatment leads to smaller gold particles than the air pretreatment. Table 3 shows that the catalytic activity increases when the particle size decreases, which is consistent with the increasing metal surface area.

Figs. 8A and 8B report the activity and TOF, respectively, versus the average particle size of all the DP Urea and DP NaOH catalysts described above (from Tables 2 and 3). This figure clearly shows that both activities and TOFs decrease when the average gold particle size increases, and that both of them are much higher when the Au/TiO_2 catalysts contain gold particles with average sizes of ~ 2 nm. It also indicates that there is no effect of the preparation method, or of the conditions of reduction on the catalytic properties, in agreement with a previous study on the reaction of CO oxidation [23].

Concerning the product distributions, we can note a slight decrease in the selectivity to crotyl alcohol from 60–70 to 50–60% when the average particle size increases (Tables 2 and 3).

3.6. HRTEM observations

The morphology, structure, and orientation of the gold particles on the TiO_2 support after different reduction temperatures have been determined by HRTEM. Fig. 9A shows a 2-nm gold particle from a DP Urea sample pretreated at 200 °C under H_2. The interface is not completely flat. Among all the observed particles, no preferential orientation could be observed. The particles are single crystals and present some tiny facets and round parts. They are stable under the electron beam. Fig. 9B corresponds to particles from the same initial preparation after pretreatment at 500 °C under H_2. The particle sizes are now perfectly facetted with facets corresponding to the (111) and (100) planes. They are also stable under electron beam irradiation. The shape is the same on all the observed particles, and the interface is flat. On Fig. 9B, the gold particle is in epitaxy on the TiO_2 substrate. The (111) plane of gold is parallel to the (110) plane of the rutile phase of the support.

4. Discussion

The main features observed during this study on crotonaldehyde hydrogenation over Au/TiO_2 catalysts are the following.

(i) Regarding the reaction.
  - The Au/TiO_2 catalysts are highly selective to crotyl alcohol, which arises from the selective hydrogenation of the C=O bond: 60–70% for particle sizes lower than 4 nm and a slightly lower selectivity when the particle size increases (Tables 2 and 3).
  - The selectivities do not depend on the conversion, at least up to 50% (Fig. 4), or on the time on stream, i.e., on the state of deactivation of the catalysts (Fig. 2), or on the reduction temperature (Tables 2).
  - Both the activity and the TOF increase when the gold particle size decreases (Fig. 8).

(ii) Regarding the catalysts.
  - There is no influence of the preparation method, deposition-precipitation with NaOH or urea, on the catalytic properties since similar trends are obtained in deactivation, and the DP Urea and DP NaOH catalysts show the same TOF, activity (expressed per

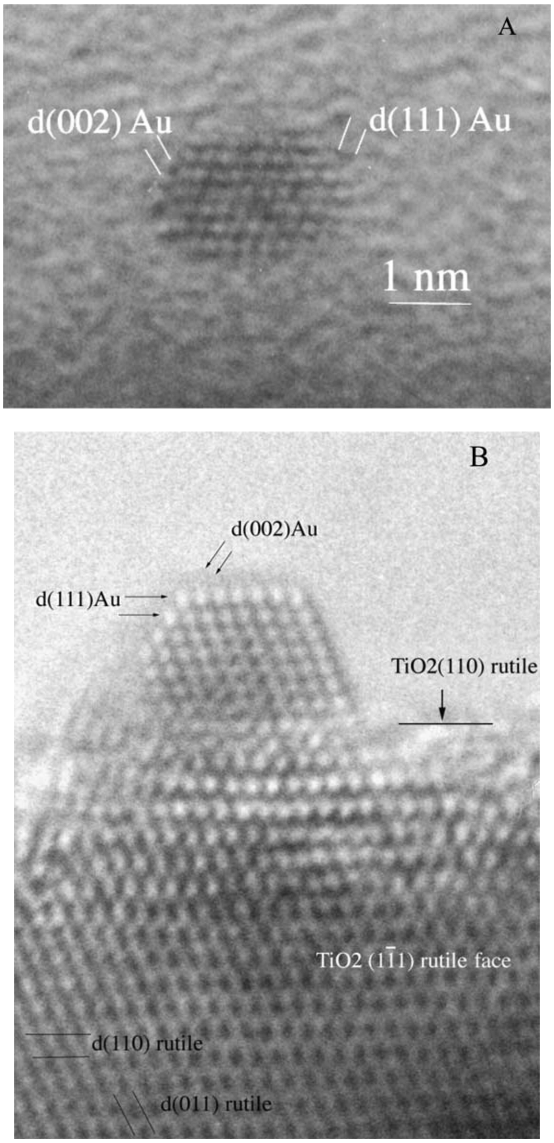


Fig. 9. HRTEM image of a gold particle seen in profile view of DP Urea after calcination under H_2 at (A) 200 °C, (B) 500 °C (the view axis, perpendicular to the image, is in the [110] direction).

gram of Au), and product selectivities. This was also observed in a previous study on the reaction of CO oxidation [23]. Noteworthy is that if the activities are expressed per gram of catalyst, the DP Urea samples are more active since they contain a higher Au loading ($\sim$ 8 wt%) than the DP NaOH samples ($\sim$ 3 wt%).

- For a given temperature, the metal gold particles are smaller when the catalysts are pretreated under hydrogen than under air (Table 3). In addition, gold is already fully reduced at 120 °C under hydrogen (Fig. 6) whereas under air, a temperature of 200 °C must be reached to obtain fully reduced gold particles [23].
- The average particle sizes in the catalysts do not drastically increase when the reduction temperature increases (Tables 2). This is remarkable since nanoparticles of gold are supposed to melt at a much lower temperature than bulk gold, $\sim$ 330 °C for particles of $\sim$ 2 nm instead of 1060 °C for bulk [30], and since they are very close to each other, especially in the DP Urea samples because of the high Au loading (average distance between the particles of $\sim$ 5 nm; Figs. 5 and 7). It may be noted that in the case of Au/ZnO prepared by coprecipitation, Hutchings and colleagues [15] reported evidence for particle sintering, from 4 to 20 nm, when the reduction temperature increased from 250 to 400 °C.
- The size of the gold particles is not affected by the reaction, and catalyst deactivation is not due to metal sintering. This has also been reported by Hutchings and colleagues [15] in the case of Au/ZnO for the same reaction.

In order to interpret the catalytic results, it is desirable to compare these results with the catalytic behavior of the Pt/TiO_2 catalysts in the selective hydrogenation of crotonaldehyde.

4.1. Comparison with Pt/TiO_2 in crotonaldehyde hydrogenation

Compared to Pt/TiO_2, which was studied under the same reaction conditions (R. Touroude, unpublished results and Ref. [21]), it must be pointed out that the Au/TiO_2 catalysts are much less active, by about two orders of magnitude. In contrast, the selectivities to unsaturated alcohol are higher with gold catalysts, and the evolution with the reduction temperature and the particle size is completely different. Indeed, Vannice and Sen [28], and then other groups [21,29,31], showed that both the selectivity and TOF increased when the reduction temperature of Pt/TiO_2 increased up to 500 °C, which is not the case with Au/TiO_2. However, on Pt/TiO_2, the selectivity to crotyl alcohol did not exceed 40–50% after high-temperature reduction. The interpretation, generally admitted, proposed first by Vannice and Sen [28] is that the carbonyl bond of the unsaturated aldehydes is activated on the sites located at the Pt^0–TiO_x interface, involving oxygen vacancies. These sites result from the so-called strong metal support interactions (SMSI) which are described as the migration of TiO_x entities onto the Pt^0 particles [32]. These sites exist on Pt/TiO_2 after reduction at a low temperature (200 °C), and their number increases when the reduction temperature increases up to 500 °C. An additional interpretation was proposed by Lercher and colleagues [21] who attributed the higher selectivity and activity found in catalysts containing large Pt particles, i.e., after high-temperature reduction, to the fact that large particles contain a high fraction of Pt atoms on face (111). This face would favor the adsorption of crotonaldehyde via the carbonyl bond to the detriment of the adsorption via the olefinic bond. In a former theoretical work [33], Delbecq and Sautet had already proposed that face (111) better adsorbs the C=O bond than the C=C one.

On Au/TiO_2 catalysts, the evolution of the activity and selectivity versus the reduction temperature and the particle size is completely different. The same high selectivity (60–70%) was obtained for all the reduction temperatures between 120 and 500 °C (Table 2), and whether the thermal pretreatments were performed under hydrogen or air (Table 3). This last point deserves a comment. Lin and Vannice [34] established by O_2 chemisorption that oxygen vacancies were present on titania after Au/TiO_2 reduction under H_2, and that their concentration markedly increased with the reduction temperature. The fact that our catalytic results do not show any dependence with the gas used for reduction (H_2 or air) indicates that the oxygen vacancies play no role in the crotonaldehyde hydrogenation on Au/TiO_2 catalysts. It may also be noted that the HRTEM images (Fig. 9) do not show any decoration of the gold particles by TiO_x entities. Moreover, in contrast to Pt/TiO_2 catalysts, the activity and TOF of Au/TiO_2 catalysts significantly decrease when the particle sizes increase (Fig. 8), and the selectivities are only slightly smaller for the largest particles (50–60%) (Table 3). Therefore, it turns out to be difficult to apply the concepts proposed for Pt/TiO_2 catalysts, to explain the high selectivity to crotyl alcohol for Au/TiO_2 catalysts.

4.2. Comparison with published data on the effect of gold particle size on selective hydrogenation of α,β-unsaturated aldehydes

As reported in the Introduction, several teams have attempted to correlate the hydrogenation properties with the gold particle sizes [15,16]. The results presented in this paper, which cover a large range of particle sizes, from 1.7 to 8.7 nm, with monomodal size distributions, are somewhat different from the published results.

First, we observed a significant increase of activity and TOF when the gold particle size decreases, especially in the 1–2 nm range (Fig. 8). The only study covering this range of small sizes is that of Claus et al. [16] on Au/TiO_2 catalysts (1.1, 2.0, and 5.3 nm), but, as noted in the Introduction, they obtained the opposite results, i.e., a large decrease of activity for the smallest particle sizes. However, it may be noted that the authors proposed an alternative explanation for the low activity of the samples containing 1-nm particles, the burying of the metal particles into the support, due to the fact that the sample had been prepared by the sol–gel method.

Second, a constant selectivity to unsaturated alcohol (60–70%) was obtained within a large size range, and whatever the gold loading and the conditions of reduction. Our results drastically contrast with the conclusion of Hutchings and colleagues [15], that the active sites for the selective hydrogenation of crotonaldehyde to crotyl alcohol are associated with the presence of large Au particles. It may be noted that their study did not cover the same particle range (4 to 20 nm). In addition, they used a different support, ZnO, which may also have an influence on the reactivity of gold. Indeed, in the case of supported Pt catalysts, one of us [35] showed that Pt/ZnO exhibits a larger crotyl alcohol yield than Pt/TiO_2 because of the easy formation of a PtZn alloy and of the presence of remaining chlorine atoms on the support.

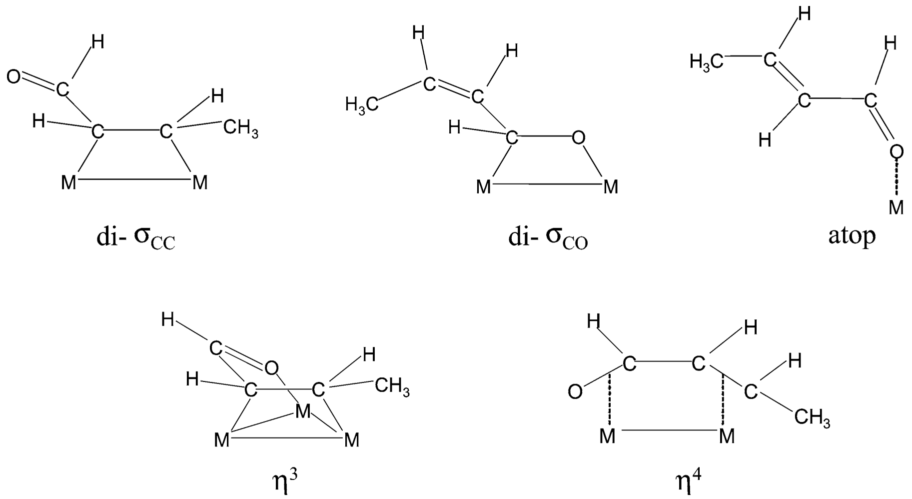
Hence, the results obtained by Hutchings and colleagues [15], Claus et al. [16], and us are not consistent from the point of view of the influence of the gold particle size, but the nature of the support in [15] and the experimental reaction conditions [15,16] (temperature and/or pressure) are not similar either. Now, let us go further with a few more comments regarding our results.

4.3. Comments on the reaction mechanism of crotonaldehyde hydrogenation on Au/TiO_2 catalysts

The selectivity to C=O versus C=C hydrogenation is mainly dictated by the extent of activation of the C=O group [15]. Therefore, the adsorption mode of crotonaldehyde is the determining factor, which orientates the selectivity toward the formation of the monohydrogenated products. The possible adsorption modes of α,β-unsaturated aldehydes on monocrystalline metal surfaces were described by Delbecq and Sautet [33,36]. If the adsorption is restricted to that of the C=C moiety of the molecule (η^2_{CC} of di-σ_{CC}-type) (Scheme 2), hydrogenation would only lead to butanal. Conversely, if the adsorption is restricted to that of the C=O bond (η^2_{CO} of di-σ_{CO}-type), or to that of the oxygen lone pair (atop), only crotyl alcohol could form. In the case of gold catalysts, both products are formed, and we must then assume either the coexistence of two independent C=C and C=O (or O atop) adsorption modes or a unique adsorption mode involving both C=C and C=O (or O), such as the η^3 or η^4 modes (Scheme 2).

In contrast to platinum-based catalysts, the presence of sites, which would hydrogenate the C=C bond only ($\eta^2{}_{CC}$ structure), is unlikely on gold catalysts. Indeed, gold catalysts are active for the partial hydrogenation of butadiene [12,37–41] or acetylene [11], but very poorly active for the hydrogenation of butene or ethylene. We found for the DP Urea 16 h catalyst that butadiene reacted twice as fast as crotonaldehyde under the same conditions of pressure and temperature, but this catalyst was totally inactive for butene hydrogenation (unpublished results). This last result makes unlikely the $\eta^2{}_{CC}$ adsorption mode of olefin on gold particles, and therefore, that of crotonaldehyde.

On the other hand, the fact that the selectivities to crotyl alcohol and butanal are almost constant whatever the gold particle size and the reduction temperature is not in favor of the coexistence of two types of adsorption modes involving two types of catalytic sites whose proportions depend on the structure/size of the gold particles. Therefore, we rather propose that a single mode of adsorption of crotonaldehyde governs the selectivity, either η^3 or η^4 adsorption mode (Scheme 2), and that the addition of two hydrogen atoms gives rise to both butanal and crotyl alcohol. The selectivities to each product would be determined by the relative



Scheme 2. Adsorption modes of the molecule of crotonaldehyde on metal, from Ref. [36].

probabilities of addition of the hydrogen atoms to the different positions in the molecule (O, C_α, C_β, C_γ).

The dramatic increase of the TOF when the particle size decreases (Fig. 8) suggests that the gold atoms involved in the hydrogenation process are those located on edges and corners. For instance, the relative number of low-coordinated sites in cubooctahedral-shape particles [42] varies in the same way as the TOF versus the particle size (Fig. 8). Besides this pure size effect, the evolution of the particle morphology observed on the HRTEM micrographs with the reduction temperature leads to the same conclusion: the gold particles obtained after reduction at 200 °C (Fig. 9A) do not exhibit well-developed facets while those obtained after reduction at 500 °C (Fig. 9B) are perfectly facetted with low index planes. Therefore, the proportion of low-coordinated sites is much lower after pretreatment at 500 °C than at 200 °C, and the decrease in catalytic activity and TOF when the reduction temperature increases from 200 to 500 °C is attributed to the smoothing of the outer surface of the gold particles, i.e., to the decrease in the number of low-coordinated sites. This is in agreement with the interpretation of Claus and colleagues [17] where they attributed the higher activity of Au/TiO_2 compared to that of Au/ZrO_2 to the fact that the gold particles were round shaped on TiO_2 and facetted on ZrO_2. In another work [43] on selective decoration of the faces of gold particles by indium, they proposed that the active sites favoring the adsorption of the C=O group of acrolein are the edges of the gold nanoparticles.

However, these low-coordinated sites are not prone to favor the η^4-adsorption mode for which the reactant structure is rather planar or the η^3-adsorption mode for which multiple metallic sites are involved (Scheme 2), but they might be more adapted to dissociate the hydrogen molecule. Therefore, we propose that the activity of gold catalysts in hydrogenation is determined by the dissociation step of molecular hydrogen. The apparent activation energy calculated in the present work, 36.3 $\mathrm{kJ\,mol^{-1}}$, is the same as that reported by Buchanan and Webb [37] for the selective hydrogenation of butadiene on Au/Al_2O_3 catalysts, 36.5 $\mathrm{kJ\,mol^{-1}}$. This could support the hypothesis that butadiene and crotonaldehyde hydrogenation kinetics are governed by a common rate-determining step, the hydrogen dissociation. In [37], the Au/Al_2O_3 catalysts were prepared by impregnation (1 wt% of Au) and exhibited a broad distribution of particle sizes up to 80 nm with the largest population of size in the 0–10 nm range. Because of the complete absence of activity of the support in butadiene hydrogenation, Buchanan and Webb proposed a mechanism where hydrogen dissociated on alumina and migrated to gold particles to hydrogenate the adsorbed butadiene. However, they did not exclude the fact that the activation of H_2 could take place on tiny gold particles, which could not have been detected by electron microscopy (the smallest particle size they could detect with their microscope was not reported in their paper).

The poor catalytic activity in hydrogenation with gold catalysts compared to Pd or Pt catalysts has been generally attributed to the fact that gold hardly dissociates molecular H_2, as it has been established experimentally and theoretically [44–46]. However, several authors have unexpectedly observed the dissociative chemisorption of H_2 (D_2) on gold films. For instance, Okada et al. [47], who studied the adsorption and reaction of hydrogen (deuterium) on thin gold film grown on Ir (111), noted that surprisingly H_2 (D_2) can dissociatively adsorb on these Au films. They attributed this property to locally relaxed surface features like defects. On thin gold film deposited on Pyrex glass, Stobinski et al. [48] also found that H_2 dissociative chemisorption occurs, providing that the thin Au films were deposited at a low temperature (78 K) and were not sintered afterward. They concluded that H_2 chemisorption occurs only on surface atoms of low-coordination number. These conclusions support our proposals for the hydrogenation mechanism.

5. Conclusion

Thanks to the method of deposition-precipitation with urea, it has been possible to prepare a series of Au/TiO_2 samples with the same gold loading (~ 8 wt%), and various average particle sizes (1.7 to 8.7 nm), either by varying the duration of the preparation, or by changing the conditions of reduction (nature of the gas, temperature, flow rate). With this series of Au/TiO_2 catalysts, it has been possible to study systematically the influence of the gold particle size on their catalytic properties in the hydrogenation of crotonaldehyde, under mild experimental conditions ($\sim 100\,^{\circ}\mathrm{C}$, 0.1 MPa), already used in former studies on Pt-based catalysts. The selectivity to carbonyl bond hydrogenation (crotyl alcohol formation) was twice as high as for olefinic bond hydrogenation (butanal formation). The selectivity was not sensitive to the reduction temperature, as was the case for platinum catalysts whose selectivity to crotyl alcohol was generally much lower ($< 50\%$) than that for gold. The gold catalysts led to very reproducible results. It must be pointed out that the Au/TiO_2 catalysts were much less active by about two orders of magnitude than Pt/TiO_2 catalysts. The structure sensitivity of the Au/TiO_2 catalysts for the hydrogenation of crotonaldehyde was clearly shown by the significant increase in activity and TOF for gold particles of ~ 2 nm. The possible role of the oxygen vacancies of TiO_2 at the metal-support interface, whose number is known to increase with the reduction temperature, was not evident as in the case of Pt/TiO_2. It is proposed that the dissociation of hydrogen on the low-coordinated sites of gold particles (edges and corners) is the rate-determining step of this reaction, and that crotonaldehyde is adsorbed on gold particles through a η^3 or η^4 mode of adsorption.

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