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Advances in the preparation of supported gold catalysts: Mechanism of deposition, simplification of the procedures and relevance of the elimination of chlorine

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ABSTRACT

The paper focuses on the chemical mechanisms involved during the preparation of gold catalysts supported on alumina and titania and on attempts to simplify the procedures of preparation. Three methods involving the same gold loading (1 wt%) and the same precursor, $HAuCl_4$, were studied: impregnation in excess of solution, anion adsorption and deposition–precipitation with urea. Regarding the first point, we showed that 1 wt% Au corresponds to a gold loading lower than the capacity of adsorption of the supports and that the three methods consist of a first common step of adsorption of anionic hydroxychloro gold complexes. The chemical mechanism involved during deposition–precipitation with urea was compared to that previously proposed for higher gold loading (8 wt%), and it was found that the time of contact between the support and the solution could be drastically shortened (from 16 to 1 h).

Regarding other simplifications of the preparations, the necessity of the washing step to eliminate the chlorine was investigated. In contrast to calcination, thermal treatment in hydrogen of samples still containing chlorine leads to rather small gold particles (<5 nm), but not to chlorine elimination. As in the case of CO oxidation, the presence of chlorine was found detrimental for selective hydrogenation of butadiene. However, chlorine can be eliminated from the samples prepared by impregnation or anion adsorption by washing with ammonia solution of low concentration. In the case of the deposition–precipitation with urea, water washing is sufficient to eliminate the remaining chlorine.

1. Introduction

For many catalytic reactions, supported gold catalysts are more active when metal gold particles are smaller than 5 nm [1]. Narrow size distribution and absence of impurities such as chlorine, sodium and potassium are also highly desirable. Most of the methods of gold catalyst preparation involve gold chloride or chloroauric acid as precursors; they are the most common gold precursors, commercially available, rather easy to handle and soluble in water.

The gold catalysts method of preparation of reference is that developed by Haruta et al. [2,3], which is deposition–precipitation performed at fixed pH by addition of sodium hydroxide, sodium carbonate or ammonia. It requires washing steps to remove the chlorides and does not apply to oxide supports of low point of zero charge (PZC) such as silica. The gold loading is generally limited to ~1 wt%, but the gold particles can be very small (2–3 nm) if pH is properly chosen. The chemistry involved during this procedure of preparation was extensively studied by Moreau and Bond [4–6].

In former works, we investigated several preparation methods of gold catalysts involving chloroauric acid as precursors with the objective of depositing high gold loadings, avoiding the loss of gold in solution and getting small gold particles [7–9].

The simplest one is impregnation with chloroauric acid; it permits the deposition of all gold onto supports whatever the gold loading and the nature of the support. However, the catalysts contain high amount of chlorides and as a consequence lead to large gold particles after calcination treatment. However, if the mere procedure of impregnation is followed by a step of washing with ammonia solution (1 M), small gold particles (3–4 nm) can be obtained after calcination treatment on any type of oxide supports (alumina, titania, silica) [9].

Anion adsorption is also a rather simple method, but the gold loading is limited by the adsorption capacity of the support, and the solution pH must be lower than the PZC of the oxide support. This method requires washing steps to remove a maximum of chlorides, and the gold particles are rather small particles (~4 nm) [7].

Deposition–precipitation with urea (performed at 80 °C to decompose urea so as to gradually increase the pH) is a method that we have developed first to deposit high gold loadings [7,8].

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It is not suitable either for oxide supports of low PZC and requires washing steps, but all gold can be deposited for instance at least up to 8 wt% on a TiO_2 support of 50 $m^2\ g^{-1}$. Small gold particles (2–3 nm) can be obtained after thermal treatment, provided that the time of contact between the support and the gold solution is long enough (4–16 h). A mechanism of deposition was proposed [8].

The goal of this study was multiple: (i) It was to investigate and compare the chemical mechanisms involved in these three methods of preparation, i.e., impregnation in excess of solution, anion adsorption and deposition–precipitation with urea (DPU) in the specific case of $HAuCl_4$ as the precursor and of a targeted gold loading of 1 wt%, which on average corresponds to the usual gold loading used for gold catalysts. As shown in the paper, this gold loading corresponds to a gold amount lower than the adsorption capacity of the alumina and titania supports used in this study. The investigation into these chemical phenomena and of the rate of gold deposition was facilitated by the use of beads of alumina support that could be easily separated from the solutions. (ii) It was an attempt to simplify the procedure of preparation. For impregnation and anion adsorption, the objective was also to look for suitable experimental conditions to obtain small gold particles after activation. For DPU, the goal was rather to find ways to simplify the preparation procedure, so as to make it more competitive with deposition–precipitation performed at fixed pH. We mainly focused on parameters, such as the washing step and the conditions of activation. (iii) The presence of chlorine in gold catalysts is not desirable because it favors gold particle sintering, and apart from that, it is detrimental for activity in CO oxidation; in the present paper, we showed that it was also detrimental for hydrogenation reactions. It is noteworthy that this work was performed within the framework of an extensive catalytic study on selective hydrogenation of butadiene in the presence of excess of propene (propene/butadiene = 100) [10–12], so as to simulate conditions of purification of light alkene cuts. Gold was found 100% selective to butenes at 100% conversion of butadiene. Under our experimental conditions, this occurred at about 170 °C. Above this temperature, alkanes started to form from butenes and propene, but at 300 °C, the conversion to alkanes remained lower that 0.5%.

2. Experimental methods

2.1. Gold catalysts preparation

Batches of 3 g of catalyst with a targeted gold loading of 1 wt% were prepared. The oxide supports used were titania (P25 Degussa, 50 $m^2\ g^{-1}$) and alumina (AluC Degussa, 110 $m^2\ g^{-1}$, δ-type) powders and two types of alumina beads of 2 mm diameters with two different BET surface areas: 40 and 200 $m^2\ g^{-1}$. All the samples were prepared using a parent aqueous solution of $HAuCl_4$, $3H_2O$ (Acros Chemicals) (10 g per liter of distilled water), which was stored in the dark. It is noteworthy that the tetrachloroauric anion, $[AuCl_4]^-$, hydrolyzes in water and forms anionic hydroxychloro gold complexes $[Au(OH)_xCl_{4-x}]^-$ whose x, i.e., the extent of hydrolysis, increases with pH [13–15]. The extent of hydrolysis also depends on the gold and chlorine concentrations, i.e., on the ionic strength of solution [15] and on temperature [16].

Anion adsorption (AA) was performed as follows. A suspension of 3 g of support in 290 mL of distilled water was also introduced into a glass reactor with double walls heated at 80 °C. Then, 6.0 mL of a solution of $HAuCl_4$, $3H_2O$ at 10 g L^{-1} was added dropwise under vigorous stirring. After 1 h of stirring at 80 °C, the solids obtained were separated by centrifugation (11,000 rounds/min for 10 min), washed with water (as described below) and dried at RT. A few of them were directly dried at RT without previous washings.

As for the preparations by Impregnation in Excess of Solution (IES), a suspension of 3 g of support in 24 mL of distilled water was introduced into a flask at RT. Then, 6.0 mL of a solution of $HAuCl_4$, $3H_2O$ at 10 g L^{-1} was added dropwise under vigorous stirring. After 1 h of stirring at RT, the solution was evaporated with a rotating evaporator at 80 °C under vacuum. This step lasted around 1 h.

Note that a few AA and IES samples were also prepared with a targeted gold loading of 4 wt% Au. In these cases, the concentrations of gold solution were four times as high.

The preparations by deposition–precipitation with urea (DPU) were performed as follows. A suspension of 3 g of support in 290 mL of distilled water was introduced into a glass reactor with double walls, allowing water circulation between the walls and therefore a homogeneous and well-controlled temperature of the suspension. The suspension was heated at 80 °C, then 60.0 mg of $HAuCl_4$, $3H_2O$, i.e., 6.0 mL of a solution at 10 g L^{-1}, was added under vigorous stirring followed by 900 mg of urea. A color change was observed within the first minute: the suspension initially yellow turned salmon-orange. The suspension was stirred at 80 °C for 16 h in the absence of light. The solid obtained was separated by centrifugation (11,000 rounds/min for 10 min) and washed with water.

Four washings with water were performed in 300 mL of distilled water, followed by centrifugation. After each step of washing, silver nitrate was used to test the presence of chlorides in the supernatant. Usually, after two or three washings, no trace of chlorides was detected in the DPU and AA samples. $NaBH_4$ was also used to test the presence of gold in the first supernatant, expected to precipitate as dark gold metal particles. These tests were always negative for the DPU and AA samples, except for the AA samples prepared with 4 wt% Au.

All the samples were dried under vacuum at RT for 12 h (except the IES samples) and stored under vacuum in a desiccator, in the dark in order to prevent any uncontrolled reduction of gold [17].

The *as-prepared* gold samples (i.e., obtained after drying) were reduced either under hydrogen at 300 °C (~100 mg of catalyst under 100 mL min^{-1} H_2 with a heating rate of 2 °C min^{-1} then a 2 h plateau at 300 °C) or calcined under air at 300, 400 or 500 °C (100 mL min^{-1}, heating rate of 2 °C min^{-1} then a 2 h plateau at 500 °C). In both cases, according to former studies [7,18], gold is fully reduced. For the sake of convenience, thermal activation under air is called *calcination* and activation under hydrogen is called *reduction*.

2.2. Techniques

Chemical analyses of Au, Cl and Al or Ti were performed on the as-prepared samples by inductively coupled plasma atom emission spectroscopy at the CNRS Centre of Chemical Analysis (Vernaison, France). From the percentages obtained from chemical analyses, the Au weight loadings of the samples were expressed in gram of Au per gram of support: wt% Au = $[m_{Au}/(m_{TiO2\ or\ Al2O3})] \times 100$, and the Cl content in the same way, i.e., wt% Cl = $[m_{Cl}/(m_{TiO2\ or\ Al2O3})] \times 100$.

The dried samples (150 mg) were reduced by temperature programmed reduction (TPR) in a quartz gas flow reactor, from room temperature to 600 °C, with a heating rate of 7.5 °C min^{-1}, under a stream of 5% v/v H_2 in argon (total flow rate = 25 mL min^{-1}) at atmospheric pressure. Hydrogen consumption was detected with a thermal conductivity detector.

TEM analysis was performed using a JEOL JEM-100 CX II microscope operating at 100 kV. Gold particle size measurement was performed using ITEM software on digitized micrographs. Note that particles were measured one by one and not automatically. The limit of size detection was about 1 nm, and it was easier to measure gold particles on titania than on alumina because they were more visible. The average metal particle sizes, d_{Au}, were determined from the measurement of at least 300 particles and were expressed as the arithmetic mean: $d_{Au} = \Sigma n_i d_i / \Sigma n_i$, where n_i is the number of particles of diameter d_i.

XRD analysis was carried out with a Siemens D500 diffractometer with Cu Kα radiation.

Infrared spectroscopy was performed with an IFS 66 V Bruker spectrometer using a DRIFTS cell (collector from Spectratech). The sample compartment of the cell was filled with the *as-prepared* gold samples (~10 mg), which was reduced *in situ* from room temperature to 300 °C, with a heating rate of 2 °C min^{-1}, under a stream of 5% v/v H_2 in argon (total flow rate = 50 mL min^{-1}) then for 30 min at 300 °C. The cell was cooled to RT under the same mixture, then purged with He before introduction of a mixture containing 1% v/v CO in He. A reference spectrum was recorded in He, and the intensity of the spectrum in CO/He atmosphere was expressed as $\mathrm{Log}(I_{CO}/I_{ref})$.

Liquid Raman spectra were recorded with a commercial RAMAN RXN1 analyzer from Kaiser Optical Systems, Inc. (KOSI) under a laser working at 785 nm and a power of 400 mW. The spectrometer incorporated a CCD detector providing full spectral collection of Raman data from 200 to 3500 cm^{-1} with a resolution of at least 4 cm^{-1} and holographic notch filters.

As mentioned at the end of the Introduction, the samples were tested in the reaction of selective hydrogenation of butadiene, in fact in the presence of a large excess of propene to mimic the conditions of alkene purification. The reaction conditions are reported in Refs. [10–12]. In short, the reaction of hydrogenation was carried out with 100 mg of catalyst in a plug flow microreactor. The catalysts were activated *in situ* under pure H_2 or air (100 mL min^{-1}) from RT to 300 °C (2 °C min^{-1}) and maintained at 300 °C for about 30 min. Then, the reaction mixture consisting of 0.3% butadiene, 30% propene and 20% hydrogen was introduced at RT (50 mL min^{-1}, GHSV = 20,000 h^{-1}) while the catalyst was heated up to 300 °C at a rate of 1 °C min^{-1}. Gas analysis was performed by gas chromatography. The activities of the catalysts expressed in $\mu mol\ s^{-1}\ g_{metal}^{-1}$ were compared at 60 °C, i.e., at low conversion of butadiene (<5%); at this temperature, propene was not hydrogenated, only butenes were formed, mostly 1-butene and *cis*-2-butene, and the catalyst does not deactivate [11].

3. Results and discussion

3.1. Anion adsorption and impregnation in excess of solution

3.1.1. Anion adsorption capacity of the supports and rate of adsorption

The capacity of titania and alumina for the adsorption of anionic gold complexes was investigated in experiments performed at 80 °C and at natural pH, i.e., at a pH lower than the PZC of the two supports ($PZC_{TiO2} \sim 6$ and $PZC_{Al2O3} \sim 7–8$). Two gold loadings were targeted, the standard one of 1 wt% and a larger one of 4 wt% to determine the extent of the adsorption capacity. The solution volume was fixed to 100 mL $g_{support}^{-1}$, so this implies two different gold concentrations and two different initial pHs.

The amounts of gold and chlorine adsorbed onto the supports (without and after subsequent washing) are gathered in Table 1. For the preparations at 1 wt% Au, the whole gold was deposited on the two supports, whereas for the 4 wt% Au, only 1.4 wt% Au was deposited on titania (yield: 35%) and 1.9 wt% on alumina (yield: 50%). Table 1 shows that washing with water maintains the gold content of the four samples. This is an indication that gold is in strong interaction with these supports, in agreement with literature data, which showed that gold is strongly adsorbed on supports such as alumina [19] or titania [7]. On the other hand, washing with water does not lead to the complete elimination of the chlorines; about half of them remain in the samples. The chlorides are known to strongly adsorb on alumina [20] and titania [21], but they probably also remain in the coordination sphere of the gold complexes.

The fact that for each support the amount of chlorine is the same for the two gold loadings is consistent with the fact that the pH of the suspension is the same for the two gold concentrations: 2.3 for titania and 4.2 for alumina, because of the strong buffering effect of these oxide supports. Note that the pH does not significantly vary either along with the contact time and that the pH of the suspension is lower for titania than for alumina because the PZC of titania is lower than that of alumina. On the other hand, the amount of chlorine left in the samples (unwashed) is higher with alumina (~0.9 wt%) than with titania (0.4 wt%). This is probably because the gold chloride complexes are more extensively hydrolyzed at pH 4.2 with alumina than at pH 2.3 with titania, so more chlorides are released in solution at pH 4.2 and can adsorb on alumina, which as mentioned above also exhibits a higher surface area.

Anion adsorption is expected to occur through electrostatic interaction with protonated hydroxyls on the support surface (OH_2^+). The larger amount of gold adsorbed on alumina than on titania may result from the presence of more numerous surface hydroxyls because of the larger surface area of alumina (100 $m^2\ g^{-1}$) than that of titania (50 $m^2\ g^{-1}$). This may also result from different OH_2^+/OH ratios on the two supports; however, without the curves of the zeta potential versus pH, it is not possible to predict which support has the largest number of OH_2^+.

An AA preparation (1 wt% Au) was also performed on alumina beads (2 mm diameter and specific surface area of 200 $m^2\ g^{-1}$) under the same conditions as for alumina powder. After addition of the beads to the gold solution, the solution, initially pale yellow, became colorless within 5 min of mixing, while the beads became pale yellow. A $NaBH_4$ test confirmed the absence of gold remaining in solution. These observations indicate a very fast adsorption of gold.

The procedure of preparation by impregnation in excess of solution (IES) differs from that of anion adsorption: (i) the solution volume was smaller, 10 instead of 100 mL $g_{support}^{-1}$, so the pH was very low (<1), and the gold chloride complexes must be less hydrolyzed (see Experimental); (ii) the preparation was performed at RT

Table 1
Capacity of adsorption of gold by alumina and titania, in the conditions of anion adsorption at natural pH and 80 °C; gold and chlorine loadings in samples washed with water or unwashed.

Catalyst	pH	Nominal Au loading (wt%)	Unwashed		Washed	
			Au (wt%)	Cl (wt%)	Au (wt%)	Cl (wt%)
Au/TiO_2	2.3	1	1.0	0.4	1.0	0.2
		4	1.4	0.4	1.4	0.2
Au/Al_2O_3	4.2	1	0.9	0.8	0.9	0.4
		4	1.9	0.9	1.9	0.6

instead of 80 °C, which does not favor the hydrolysis of the gold species [16] (see Experimental); (iii) the solution was removed by evaporation at 80 °C, so the solution pH gradually decreased during this step, and all the cations and anions were deposited on the support. In the specific case of the impregnation of 1 wt% of gold, a phenomenon of anion adsorption must be involved as in the case of AA preparation, all the more that the pH of impregnation is lower than that of AA, so more numerous OH_2^+ sites must be available. This is confirmed by these two experiments:

(1) Washing with water of the IES 4 wt% Au/TiO_2 led to gold leaching down to 1 wt%, i.e., down to the gold loading corresponding to the anionic adsorption capacity of titania (see Table 5);

(2) As in the case of the anion adsorption, when the IES procedure was performed with alumina beads, the pale yellow solution also became colorless and the alumina beads turned pale yellow within 5 min of stirring. In this case as well, the $NaBH_4$ test confirmed the absence of gold remaining in solution. Note that after reduction at 300 °C and breakage of the beads prepared either by AA or by IES, one could observe a ~0.2-mm-thick pink shell, indicating that gold was located only on the external surface of the beads. The average sizes of the gold particles examined by TEM after reduction at 300 °C were roughly the same as those obtained on alumina powder.

3.1.2. Influence of the activation step on chloride content and gold particle size

The goal of these experiments was to determine whether sample washing, i.e., chlorine elimination, was really necessary to get small gold particles. The unwashed AA catalysts reduced at 300 °C under H_2 contain rather small gold particles (2.9 nm on TiO_2 and 3.2 nm on Al_2O_3 in Table 2 and Fig. 1b and d) in spite of the rather large amount of Cl present in the *as-prepared* samples. Note that chlorine is still present after reduction, but in lower amount. In contrast, when the samples are calcined, the gold particles are much larger on both supports (>10 nm in Table 2 and Fig. 1a and c). This is due to the presence of chlorine since smaller gold particles can be obtained when the AA samples are washed and contain a lower amount of chlorine (e.g., gold particles of 5.6 nm for Cl content of 0.07 wt% [7]). Ivanova et al. [22,23] also reported gold particles as large as 16 nm after calcination at 300 °C of Au/Al_2O_3 samples prepared by "direct anionic exchange", washed with water, and still containing almost the same chlorine amount (0.3 wt% Cl) as in our samples. The mobility of chloride-containing precursors impregnated on oxide supports is known to induce gold sintering during activation in air or oxygen [24–26]. Note that the presence of chlorine in the samples after calcination is in agreement with reports that showed that calcination under air up to 600 °C does not lead to the total elimination of chlorines from gold catalysts [22,27].

The same type of results was obtained with the IES samples. The gold particles in the H_2-reduced IES samples (Table 3) are as small (2.7 nm on TiO_2 and 3.0 nm on Al_2O_3) as in the AA samples (Table 2) in spite of higher chlorine content. Calcination temperatures of 300 or 400 °C were not high enough to reduce gold in the IES Au/TiO_2 or Au/Al_2O_3 samples; this was attested by the color of the samples, which remained very pale yellow. After calcination at 500 °C, Au/Al_2O_3 turned pink-red and Au/TiO_2 turned purple, indicating that gold or at least a fraction of it has been reduced. This was confirmed by XRD, the diffractograms of which revealed the presence of metallic gold with large particles, 45 nm on alumina and 18 nm on titania, in agreement with most of the literature data on gold samples prepared by impregnation [1]. It is noteworthy that 1 wt% Au/TiO_2 prepared by impregnation to incipient wetness (no excess of solution) behaved differently since gold could be reduced during calcination at 300 °C, also leading to large gold particles (>10 nm) [7].

All these results indicate that thermal treatments under hydrogen are greatly beneficial to obtain small gold particles in samples still containing chlorines (Tables 2 and 3). However, they do not lead to the total elimination of the chlorines. This is in contrast with the Haruta's assessment [28] that reduction under H_2 leads to the removal of chlorine as HCl.

3.1.3. Influence of chlorine on hydrogenation of butadiene and chlorine elimination by washings

As mentioned in the Introduction, chlorides in gold catalysts are known to inhibit the catalytic activity in oxidation such as CO oxidation [1], so it is necessary to get rid of them. Their presence is also detrimental for the activity in the case of the reaction of hydrogenation of butadiene. This is illustrated in Table 4, which compares AA and IES samples with different chlorine contents (entries 1–3) with samples (prepared by DPU) that do not contain chlorine, but have gold particles of the same size as in the AA and IES samples (entries 4–6). One can see that for a given average gold particle size, the catalytic activity in selective hydrogenation of butadiene is lower when the catalyst contains chlorine. Note that our former paper [11] showed that the activity (at 60 °C as here and also expressed per g of catalyst) decreased as gold particle size increased and that the product distribution in 1-butene, *cis*-2-butene and *trans*-2-butene at a given conversion depended on neither the gold particle size nor the chlorine content.

Previous studies have shown that chlorides could be eliminated when catalysts were washed with ammonia solutions. This was shown first by Xu et al. [19], then by Ivanova et al. [22,23,29] and also by Li et al. [30] with a NH_3 gas treatment. Ivanova et al. found that washings with ammonia (4 and 25 mol L^{-1}) lowered the chlorine content down to less than 150 ppm in Au/Al_2O_3 samples prepared by anion adsorption. Ammonia was proposed to be able to transform gold hydroxychlorides into gold hydroxide or hydroxy species [19,23]. In a former work, some of us [9] also observed that lower concentration of ammonia $(1\ \text{mol}\ L^{-1}, 30\ \text{mL}\ g_{cata}^{-1})$ could efficiently eliminate the chlorides from samples prepared by impregnation to incipient wetness (IWI) on various oxides with almost no gold leaching. The absence of gold leaching during ammonia washing of IWI 4 wt% Au/TiO_2 and Au/Al_2O_3 (i.e., with gold loading exceeding the adsorption capacity of supports) was interpreted as resulting from the formation of ammino-hydro-

Table 2
Preparations by anion adsorption (AA): influence of the activation treatment on the gold particle size in unwashed samples.

AA catalyst (unwashed)	Experimental loading		Activation		After activation		
	Au (wt%)	Cl (wt%)	*T* (°C)	Gas	Average gold particle size (nm)	Standard deviation (nm)	Cl (wt%)
Au/TiO_2	0.8	0.3	300	H_2	2.9	2.2	0.2
			300	Air	11.4	3.4	0.2
Au/Al_2O_3	0.9	0.7	300	H_2	3.5	1.7	0.4
			300	Air	12	4.8	0.4

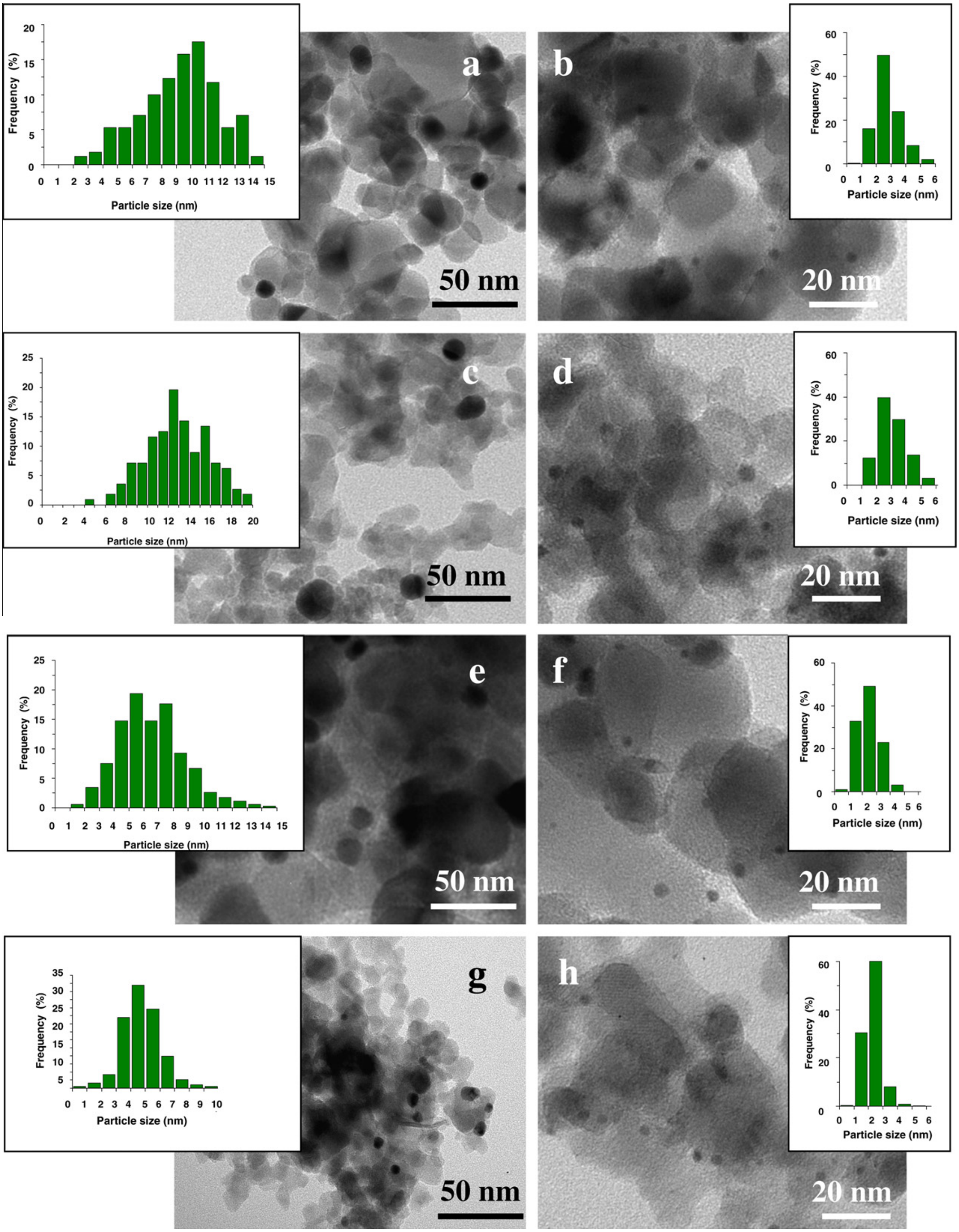

Fig. 1. Histograms of gold particle sizes and TEM micrographs of (a) unwashed AA Au/TiO_2 calcined in air at 300 °C; (b) unwashed AA Au/TiO_2 reduced in H_2 at 300 °C; (c) unwashed AA Au/Al_2O_3 calcined in air at 300 °C; (d) unwashed AA Au/Al_2O_3 reduced in H_2 at 300 °C; (e) unwashed IES Au/TiO_2 reduced in H_2 at 300 °C; (f) IES Au/TiO_2 washed with ammonia solution (0.01 M) then reduced in H_2 at 300 °C; (g) unwashed DPU Au/Al_2O_3 calcined in air at 300 °C; (h) washed DPU Au/Al_2O_3 reduced in H_2 at 300 °C.

xo-aquo gold complex, $[Au(NH_3)_2(H_2O)_{2-x}(OH)_x]^{(3-x)+}$ (*gold–ammonia* complex in the following), able to strongly interact with the surface of the support, which is negatively charged at basic pH ($>PZC_{support}$).

In the present paper, in addition to washing with 1 mol L^{-1} of ammonia, we also tested less concentrated ammonia solutions (0.1 and 0.01 mol L^{-1}, 100 mL g_{cata}^{-1}) on IES 4 wt% Au/TiO_2 and 1 wt% Au/Al_2O_3 samples. Table 5 shows that even for low ammonia

Table 3
Preparations by impregnation in excess of solution (IES): influence of the activation treatment on the gold particle size.

IES catalyst	Experimental loading		Activation		After activation		
	Au (wt%)	Cl (wt%)	Gas	T (°C)	Average gold particle size (nm)	Standard deviation (nm)	Cl (wt%)
Au/TiO_2	1.1	0.9	H_2	300	2.7	1.0	0.4
			Air	300	Non-reduced		–
			Air	400	Non-reduced		–
			Air	500	~18[a]	5.9	–
Au/Al_2O_3	0.8	1.0	H_2	300	3.0	1.2	1.0
			Air	300	Non-reduced		–
			Air	400	Non-reduced		–
			Air	500	~45[a]	–	0.6

[a] Estimation by XRD.

Table 4
Influence of the chlorine in gold catalysts on the catalytic activity at 60 °C in selective hydrogenation of butadiene.

Entry	Catalyst	Experimental loading		Activation		After activation	Activity
		Au (wt%)	Cl (wt%)	Gas	T (°C)	Average gold particle size[a] (nm)	($\mu mol\ s^{-1}\ g_{métal}^{-1}$)
1	IES Au/TiO_2	1.1	0.88	H_2	300	3.4	2.4
2	AA Au/Al_2O_3	0.9	0.81	H_2	300	4.0	0.6
3	IES Au/Al_2O_3	0.8	0.98	H_2	300	4.9	0.3
4	DPU Au/TiO_2	1.1	<0.02	Air	300	3.4	4.5
5	DPU Au/TiO_2	1.1	<0.02	Air	400	3.9	4.2
6	DPU Au/Al_2O_3	1.1	<0.02	Air	500	4.4	3.9
7	DPU Au/Al_2O_3	0.9	<0.02	H_2	300	2.7	5.0
8	Unwashed DPU Au/Al_2O_3	0.9	0.04	H_2	300	4.1	2.6

[a] Volumic mean: $d_{Au} = \Sigma n_i d_i^3 / \Sigma n_i d_i^2$.

Table 5
Influence of ammonia washing on the gold and chlorine contents and the gold particle size of samples prepared by impregnation in excess of solution (IES).

IES sample	Washing solution	Experimental loading after washing		After reduction	
		Au (wt%)	Cl (wt%)	Average gold particle size (nm)	Standard deviation (nm)
4 wt% Au/TiO_2	–	3.6	2.7	7.9	2.4
	NH_3 (1 M)	3.6	<0.02	3.7	1.0
	NH_3 (0.1 M)	3.0	<0.02	2.8	0.8
	NH_3 (0.01 M)	3.4	0.03	2.8	0.7
	H_2O	0.9	0.2	3.3	0.9
1 wt% Au/Al_2O_3	–	0.8	1	3.0	1.2
	NH_3 (1 M)	0.8	<0.02	2.6	0.5
	NH_3 (0.1 M)	0.9	0.03	2.4	0.9

concentration, most of chlorides are eliminated without significant gold leaching, leading to smaller gold particles after reduction (compare Fig. 1f with Fig. 1e). As mentioned above, water washing of the IES 4 wt% Au/TiO_2 leads to gold leaching down to a gold loading of 1 wt% corresponding to the anionic adsorption capacity of titania (Table 5).

Note that the use of ammonia solutions with gold may lead to the formation of fulminating gold (not well-formulated solid gold compounds containing nitrogen) [1,31,32]. Even though the teams who performed ammonia washings did not report burst, this method is probably not usable at large scale.

3.2. Preparation by deposition–precipitation with urea (DPU)

3.2.1. Influence of the nature of the support, the gold loading and the conditions of activation on gold particle sizes; reproducibility and upscaling of the preparation

Note that in this section, all the samples were washed with water according to the procedure described in Experimental. A first set of DPU preparations was performed on different oxide supports (TiO_2, Al_2O_3 and also ZrO_2 (Rhodia, 21 $m^2\,g^{-1}$) and CeO_2 ceria (HSA5, Rhodia, 200 $m^2\,g^{-1}$) with the objective of depositing 1 wt% Au. The gold loadings reported in Table 6 confirm former results obtained on highly loaded samples (4 and 8 wt% Au) [7,8] that all gold is deposited onto these supports. This was also confirmed with the test of addition of $NaBH_4$ to the supernatant after centrifugation, which did not reveal the presence of gold. The slightly lower gold loading on alumina and the slightly higher gold loading on titania may be due to a problem of accuracy of the chemical analyses since the same parent gold solution was used. All the 1 wt% Au samples contain less than 200–300 ppm of chlorine, which is the detection limit.

Table 6 also shows that the sizes of the gold particles obtained after reduction under hydrogen at 300 °C are all of 2 nm in average (Fig. 1h) and are independent on the gold loading and the nature of the support. The case of ceria is peculiar since gold particles are not visible on this substrate by TEM (see Experimental). XRD does not show any diffraction peak of metallic gold either on Au/CeO_2. However, since the activity and selectivity in selective hydrogenation of butadiene of this catalyst are the same as for the three other gold catalysts [11], it can be anticipated that the gold particle size is also the same.

The influence of the conditions of thermal activation to reduce gold was also studied with DPU 1 wt% Au on alumina and titania.

Table 6
Preparations by deposition–precipitation with urea (DPU): influence of oxide supports and gold loadings on the average gold particle size (after reduction under H_2 at 300 °C).

DPU catalyst	Theoretical Au loading (wt%)	Experimental loading		Average gold particle size (nm)	Standard deviation (nm)
		Au (wt%)	Cl (wt%)		
Au/Al_2O_3	1	0.9	<0.02	2.3	0.9
	2	1.7	<0.03	2.1	0.7
	4	3.1	<0.03	2.2	0.8
Au/TiO_2	1	1.1	<0.02	2.1	0.7
	7	6.8	<0.03	1.9	0.7
Au/ZrO_2	1	0.9	<0.02	2.1	0.7
Au/CeO_2	1	1.0	<0.02	<5[a]	–

[a] XRD result.

Table 7
Preparations by deposition–precipitation with urea (DPU): influence of the activation temperature and the nature of the gas on the gold particles size.

DPU catalyst	Activation gas	Activation temperature (°C)	Average gold particle size (nm)	Standard deviation (nm)
Au/TiO_2	Air	300	2.9	0.8
	Air	400	3.2	1.0
	Air	500	3.9	1.0
	H_2	300	2.2	0.7
	H_2	500	2.1	0.6
Au/Al_2O_3	Air	300	2.1	0.6
	Air	500	2.3	0.7
	H_2	300	2.2	0.8
	H_2	500	1.8	0.5
	H_2	300[a]	1.8	0.6
	H_2	300[b]	2.1	0.7

[a] Heating rate: 10 °C min^{-1}.
[b] Plateau at 300 °C for 10 min only.

The results in Table 7 show that they have a stronger influence on the gold particle sizes of Au/TiO_2 than of Au/Al_2O_3. For the latter, the gold particles have almost the same size, ~2 nm, whatever the nature of the gas and the temperature, 300 or 500 °C. For Au/TiO_2, ~2 nm gold particles were also obtained after H_2 reduction and independently of the temperature, but larger particles were obtained under air and size increased with temperature (from 3 to 4 nm between 300 and 500 °C). The evolution of the gold particle size on titania with the temperature of calcination compares well with that obtained with calcined 8 wt% DPU Au/TiO_2 [33]. In contrast, the evolution with the reduction temperature is slightly different: with 8 wt% DPU Au/TiO_2, the average gold particle sizes slightly increased from 1.9 nm at 300 °C to 2.6 nm at 500 °C [33]. We have no explanation for these small differences.

The reproducibility of the DPU method of preparation was evaluated. This is an important issue since it is known that it is not always straightforward to control all the preparation parameters. Table 8 shows that the samples are the same in terms of gold and chlorine loadings and of gold particle size even when different bench scientists performed preparation. This leads to similar catalytic activity in selective hydrogenation of butadiene as shown in Table 8, which confirms the reproducibility of the preparations.

We also attempted to upscale the amount of gold catalyst prepared (1 wt% Au). Preparations performed with 10 and 50 g of alumina (both in one liter of solution) provide the same type of samples as the preparations with 3 g (Table 8).

3.2.2. Toward a simplification of the DPU preparation

As mentioned above, DPU is a rather heavy method of preparation because it requires a long time of contact between the support and the gold solution (16 h), then washing steps and activation treatment. Attempts for simplifying the procedure of DPU preparation were investigated.

Table 7 shows that it is possible to increase the heating rate from 2 to 10 °C min^{-1} and to shorten the duration of the plateau at 300 °C from 2 h to ~10 min without modifying the gold particle size on alumina.

Whether the DP time is 16 h (Experiments 1 and 4) or only 1 h (Experiments 2 and 5 in Table 9), all gold is deposited as in the case of a preparation with 8 wt% Au samples [7,8]. However, the difference with 8 wt% Au samples is that the gold particle sizes in 1 wt% are roughly the same after 1 or 16 h of preparation, whereas they are very different in 8 wt% Au/TiO_2 (6.9 nm after 1 h and 2.3 nm after 16 h of DPU) [7].

Table 8
Preparations by deposition–precipitation with urea (DPU): reproducibility of the preparation of Au/Al_2O_3 and influence of the amount of support/upscaling of the preparation (gold particles obtained after reduction under H_2 at 300 °C).

Mass of alumina support (g)	Experimental loading		Average gold particle size (nm)	Standard deviation (nm)	Activity ($\mu mol\ s^{-1}\ g^{-1}_{métal}$)
	Au (wt%)	Cl (wt%)			
3	–	–	1.9	0.5	–
3	0.9	<0.02	2.1	0.6	4.9
3[a]	0.8	<0.03	2.0	0.6	5.1
3[b]	–	–	1.9	0.4	5.2
10	0.9	<0.02	2.2	0.8	–
50	0.9	<0.02	2.0	0.7	–

[a,b] Catalysts prepared by two other bench scientists.

Table 9
Preparations by deposition–precipitation with urea: influence of different parameters of preparation on the gold particle size (activation under H_2 at 300 °C).

DPU catalyst	Experiment number	Condition of preparation	Final pH	Au loading (wt%)	Average gold particles size (nm)	Standard deviation (nm)
Au/Al_2O_3	1	80 °C/16 h (Standard)	7.6	0.9	2.2	0.8
	2	80 °C/1 h	4.5	0.9	2.2	0.7
	3	RT/1 h	4.2	0.8	3.4	1.0
Au/TiO_2	4	80 °C/16 h (Standard)	7.4	1.1	2.2	0.4
	5	80 °C/1 h	3.9	1.1	3.0	1.2
	6	RT/1 h	2.7	1.0	2.4	0.8

When preparation is performed at RT for 1 h, all gold is also deposited. On titania (Experiment 6), the gold particles are as small as in the standard conditions (Experiment 4), whereas on alumina (Experiment 3), they are larger (Experiment 1).

These results show that the DPU preparation of 1 wt% Au samples can be shortened by decreasing the DPU duration to 1 h and that it is also possible to increase the heating rate from 2 to 10 °C min^{-1} and to reduce the duration of the plateau at 300 °C without modifying the gold particle size.

In order to eliminate the chlorides, the DPU catalysts are usually washed four times with 100 mL g_{cata}^{-1}. It was interesting to check whether this washing step was really necessary to get small gold particles and active catalysts. Indeed, in contrast to the AA and IES samples, for which part of the chlorides is adsorbed onto the oxide support and the other part acts as ligands of adsorbed hydroxychloride gold complexes, the chlorides in the DPU samples are supposed to be located onto the support, and not in the coordination sphere of Au(III) since Au(III) is coordinated by urea or product of decomposition of urea [8] (see also Section 3.2.3). They are not in strong interaction with the support since they can be easily eliminated during washing with water. Table 10 compares the average size of gold particles on alumina and titania for unwashed and washed samples after activation under air or hydrogen. The gold particles on alumina and titania have the same average size (~2 nm) after reduction with hydrogen, whether the samples are washed or not. As in the case of the AA and IES samples (Tables 2 and 3), the gold particles are larger after calcination when the samples contained chlorides (Fig. 1g). The chlorides present in the unwashed samples also lead to less active catalyst in selective hydrogenation of butadiene than washed samples for the same gold particle size of 4 nm (Table 4). These results confirm that the DPU samples must be carefully washed to remove the chlorides.

3.2.3. Revisited mechanism of deposition–precipitation with urea

The mechanism of deposition–precipitation with urea proposed in Ref. [8], which is reminded below, was deduced from the following observations performed during the preparation of samples containing high gold loadings of 4–8 wt% [7,8]:

1. In the absence of support, there is no precipitation of gold as long as the solution is not heated; our interpretation was that there is no precipitation as long as urea does not start decomposing during heating;
2. At 80 °C, all gold precipitates onto the support at pH between ~2 (the initial pH) and ~3;
3. According to XAFS measurements, the gold compound deposited on oxide support at 80 °C is the same as the amorphous precipitate obtained in the absence of support under the same conditions. Its chemical composition was $AuN_{2.2}O_{1.2}C_{0.9}H_{4.2}Cl_{0.1}$, which formally corresponds to Au(III) coordinated by one urea molecule. XAFS does not allow distinguishing O from N ligands; however, we found that the Au-1st neighbor distance of 2.03 nm was consistent with a Au–N distance. Raman showed that the Au–Cl and Au–OH bands of the initial hydroxychloro gold complexes disappeared during DPU, and IR and Raman performed on the gold precipitate showed the presence of NH_x, OH, carbonate and isocyanate groups. We deduced that the formation of the precipitated compound arises from a reaction of complexation between hydroxychloro gold complexes in solution and products of hydrolysis of urea or urea, but we could not go further in the characterization. In the following, the gold species deposited on supports during DPU is designated as *gold–urea* species.

The chemical mechanism proposed in Ref. [8] was the following: part of the anionic gold species present in solution at pH between ~2 (initial pH) and ~3 (pH of precipitation) adsorbs on the OH_2^+ sites on the oxide support (pH < PZC) and acts as nucleation sites for the precipitation of the orange *gold–urea* compound at pH ~3. This interpretation was also based on the fact that this method of preparation did not work properly with silica support (all gold was not deposited), because its low PZC (~2) does not permit the adsorption of anionic gold species. The decrease in the size of the gold particles after calcination, as the contact time between the solution and the support increased, was explained by a decrease in the size of the particles of the *gold–urea* precipitate due to peptization-type phenomenon: As pH increases because of urea decomposition, the density of negative surface charges of these

Table 10
Preparations by deposition–precipitation with urea: influence of the step of washing with water on the gold particles size as a function of the support (TiO_2 and Al_2O_3) and the activation gas (air or H_2).

DPU catalyst	Water washing	Experimental loading		Activation gas	Average gold particles size (nm)	Standard deviation (nm)
		Au (wt%)	Cl (wt%)			
Au/Al_2O_3	No	0.9	0.04	H_2	1.9	0.5
	Yes	0.9	<0.02	H_2	2.0	0.6
	No	0.9	0.19	Air	4.9	1.7
	Yes	0.9	<0.02	Air	2.1	0.6
Au/TiO_2	No	1.1	0.74	H_2	2.2	0.6
	Yes	1.1	<0.02	H_2	2.2	0.7
	No	1.1	0.74	Air	4.7	1.1
	Yes	1.1	<0.02	Air	3.1	0.8

particles increases, inducing repulsive forces that lead to particle fragmentation.

In contrast, in samples containing 1 wt% Au, the gold particle size is the same whether the contact time is 16 or 1 h (Table 9). This is because the gold loading is lower than the adsorption capacity of both alumina and titania (Table 1). Our interpretation is that all the hydroxychloro gold complexes can adsorb before the formation of the *gold–urea* complexes, and there is no phenomenon of precipitation. This is emphasized by the following experiments.

The same color changes are observed during DPU of the 1 wt% Au samples as in the case of the DPU preparation of 8 wt% Au samples: after the addition of urea to the suspension of the support in the chloroauric acid solution at 80 °C, the pale yellow color of the suspension turns pale orange within less than 1 min for both TiO_2 and Al_2O_3. Note that the initial pH of the suspension is the same whether urea is added or not added: 2.3 for titania and 4.2 for alumina (Table 1). According to our previous works [8], this attests fast change in gold speciation from hydroxychloro gold to *gold–urea* complexes. In that paper, we made Raman experiments of the solution used for the DPU preparation of an 8 wt% Au sample, i.e., containing 4.2×10^{-3} M of $HAuCl_4$ and 0.42 M of urea. The Raman spectrum of the solution mixture performed at RT revealed two Au–Cl Raman bands at 322 and 347 cm^{-1}, which disappeared when the solution was heated at 80 °C and became orange, and when gold started to precipitate. As reported above, the analysis of the precipitate revealed the quasi-absence of chloride and the presence of urea.

Since gold is not supposed to precipitate at 80 °C when the nominal gold loading is 1 wt%, attempts were made to perform the DPU at RT. Although urea does not decompose, all gold could be deposited on the two supports, and the gold particles were roughly of the same size as at 80 °C (Table 9). During DPU at RT with titania (Experiment 6), the same change of color as at 80 °C was observed but occurred much slower (within 1 h), and the final pH was 2.7 (initial pH 2.3). With alumina (Experiment 3), the sample remained pale yellow, and the final pH remained equal to 4.2. Experiment 3 was performed again, but the pH of the suspension of alumina was lowered to pH 2.7 by addition of HCl, and after 1 h of stirring at RT, the suspension had turned orange as in the case of titania. According to our earlier work [8], these color changes indicate that *gold–urea* complexes formed at RT, and faster at pH 2.3–2.7 than at pH 4.2. To check again the relationship between color and gold speciation, new Raman experiments were performed. A solution of $HAuCl_4$ (4.2×10^{-3} M – conditions of the 8 wt% Au sample, initial pH 2.4) was used again because Raman is not sensitive enough for the observation of the Au–Cl bands in solution 5×10^{-4} M used for the preparations of the 1 wt% Au sample. With the $HAuCl_4$ solution (4.2×10^{-3} M), the two Au–Cl Raman bands were indeed clearly observed at 322 and 347 cm^{-1} as in Ref. [8]. After addition of urea (0.42 M, pH 2.6) at RT, the yellow solution gradually turned orange-yellow within around 10 min and the two Au–Cl bands slightly decreased in intensity ($I/I_0 = 0.95$); after 1 h, the solution was orange, and the two Au–Cl bands had significantly decreased ($I/I_0 = 0.65$) while pH remained unchanged. Although this experiment was not performed in the conditions of concentration for the preparation of 1 wt% Au sample, it clearly shows that at constant pH, the gold speciation is modified by the presence of urea and that *gold–urea complexes* probably formed. Our interpretation regarding the color changes observed during DPU at RT is the following: Since color changes with titania and alumina are not fast during DPU at RT, the hydroxychloro gold species can first interact with the support before being gradually transformed into gold urea species. The changes of speciation occur faster at pH 2.6 with titania than at pH 4.2 with alumina. Since after reduction the gold particles have roughly the same size as when DPU is performed at 80 °C, it can be anticipated that the same phenomenon occurs at RT as at 80 °C, although slower. So, our conclusion is that when DPU is performed at 80 °C with 1 wt% Au, the first step is the adsorption of hydroxychloro gold species and is rapidly followed by a change of speciation into adsorbed *gold–urea* complexes.

A series of DPU preparations was also performed with the alumina beads at 80 °C. The DPU procedure applied to alumina beads of high surface area (200 $m^2\,g^{-1}$) shows that gold interacts very quickly with the support. Indeed, the yellow solution becomes colorless within the first 5 min of contact with the alumina beads, which become pale orange. After reduction at 300 °C and breakage of several beads in two hemispheres, one can observe that gold is located only at the periphery of the beads, forming a ~0.2-mm-thick pink shell, as for the AA and IES samples, and that the size of the gold particles is roughly the same as those on the alumina powder. In contrast, when alumina beads of low surface area (40 $m^2\,g^{-1}$) are used, the suspension becomes blurry 5 min after the introduction of gold and urea. After decantation, a fine orange precipitate is observed apart from the alumina beads, which are hardly colored. This precipitate is probably the same as that observed when DPU was performed in the absence of support, i.e., the *gold–urea* compound [8]. Then, the DPU procedure was slightly modified. After addition of the beads (40 $m^2\,g^{-1}$) to the gold solution heated at 80 °C, the urea solution (0.9 g urea in 20 mL water) was added dropwise within about 1 h using a "syringe pump". After decantation, the beads were orange, and the suspension almost transparent and colorless, indicating that most of the gold had interacted with the support. These results reveal that the phenomenon of gold deposition–precipitation on alumina is controlled by the rate of formation of the *gold–urea* complexes and by the number of adsorption sites (OH_2^+) easily accessible on the external surface of the beads. Indeed, when the alumina surface area is high (200 $m^2\,g^{-1}$), all gold is rapidly deposited because the number of adsorption sites is high enough to allow all gold complexes to interact rapidly with these sites. In contrast, when the surface area is low (40 $m^2\,g^{-1}$), the number of easily accessible adsorption sites is smaller, so *gold–urea* compound precipitates in solution. However, if the formation of the *gold–urea* complexes is controlled by a slow addition of urea, the hydroxychloro gold complexes have time to diffuse into the beads before the formation of *gold–urea* complexes, so precipitation in solution can be avoided. These results are consistent with the conclusion drawn above that during DPU preparation of samples containing 1 wt% Au, i.e., a gold loading lower than the adsorption capacity of the oxide support, urea replaces the chlorides in the gold coordination sphere after the hydroxychloro gold complexes have been adsorbed.

3.3. Comparison and relationship between the three methods of preparation

3.3.1. TPR

The reducibility of gold in Au/Al_2O_3 and Au/TiO_2 prepared by the three different methods, DPU, AA and IES, washed and dried was compared through the TPR profiles. On alumina, gold of DPU catalysts reduces at 160 °C, while gold of AA and IES samples is less reducible (~200 °C) (Fig. 2A). On titania, the DPU and AA catalysts show gold reduction peaks at the same temperature, ~100 °C, while gold in the IES catalyst shows three broader and smaller peaks at higher temperatures, 130, 190 and 205 °C (Fig. 2B).

The results show that both the nature of the support and the amount of chlorine have an influence on the reducibility of gold. Indeed, gold in DPU samples, which do not contain chlorine (Table 6), reduces at lower temperature and more easily on titania than on alumina. This has been already observed by other groups [34,35]. Gold in the IES samples, which contain the largest amounts

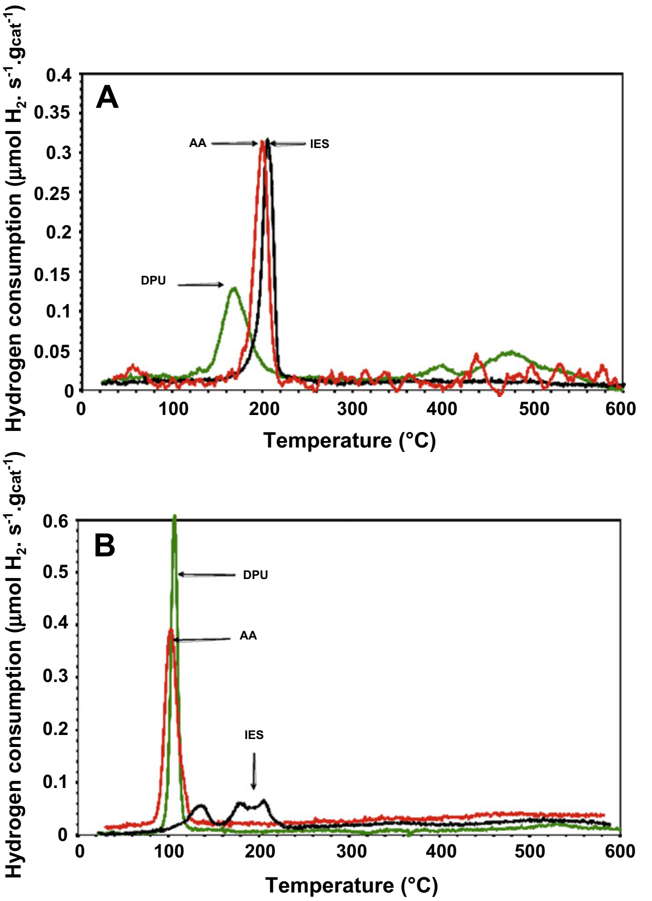

Fig. 2. TPR profiles of Au/Al_2O_3 (A) and Au/TiO_2 (B) catalysts supported on alumina and prepared by DPU, IES and AA.

of chlorine (~1 wt%, Table 3), is the least reducible whatever the support; this result is also consistent with the fact that gold in these samples is not reduced after calcination at either 300 or 400 °C (Table 3). The AA Au/TiO_2 sample, which contains relatively little chlorines (0.36 wt% Cl) (Table 2), shows a TPR profile close to that of the DPU sample, whereas AA Au/Al_2O_3, which contains more chlorine (0.81 wt%), has a reduction profile closer to that of IES Au/Al_2O_3.

Gold complexes containing chlorides are therefore more stable and less reducible than complexes containing hydroxyl or nitrogen ligands. This is in agreement with several papers, which report that chlorine inhibit the reducibility of Au(III) [11,35–38].

3.3.2. IR study

Two Au/Al_2O_3 catalysts were characterized by DRIFTS, a DPU one, which contains very low amount of chlorine (Table 10) and an IES one, which contains a high Cl amount (Table 3). Both samples were *in situ* reduced at 300 °C under hydrogen, cooled down to RT, then CO was adsorbed at RT (see Experimental).

In the range of the CO vibration bands (Fig. 3), the spectrum of DPU Au/Al_2O_3 sample shows a single intense band at 2105 cm^{-1}, which has been previously assigned to CO linearly adsorbed on low coordination sites of metallic Au nanoparticles [39–41].

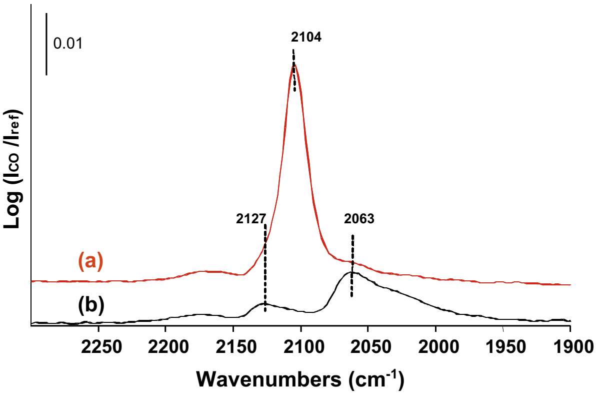

Fig. 3. DRIFT spectra of Au/Al_2O_3 prepared by DPU and IES after *in situ* reduction at 300 °C and CO adsorption at RT.

The spectrum of IES Au/Al_2O_3 is completely different; it is characterized by a broad band at 2063 cm^{-1} with a lower intensity than that of DPU Au/Al_2O_3, and a much weaker and broad band at 2127 cm^{-1} (Fig. 3), as if the band at 2105 cm^{-1} was split into two bands in the presence of chlorides. The presence of a band at ~2060 cm^{-1}, i.e., at wavenumber lower than that of CO linearly adsorbed on metallic Au (~2100 cm^{-1}), has been previously observed [42–47]. Its attribution to bridged CO species can be discarded as they are expected to give rise to bands at still lower wavenumbers (2000–1950 cm^{-1}) [42,44]. Bands in the 2050–2080 cm^{-1} range have been ascribed either to CO adsorbed on metallic sites at the support–particle interface [43,45] or to CO adsorbed on negatively charged $Au^{\delta-}$ sites [43,46]. We are more in favor with the second band assignment: the presence of $Au^{\delta-}$ in IES Au/Al_2O_3 could be the consequence of the presence of chlorides remaining after reduction (Table 3); they could induce an electron transfer toward the gold particles. Indeed, a recent paper on computer modeling showed that when Cl^- is adsorbed on a gold atom site of Au (1 1 1) surface, the Cl atom becomes slightly positively charged (+0.05), while the gold adsorption site becomes negatively charged (-0.19) as well as the neighbored surface gold atoms (−0.05 to −0.08) [48]. According to other papers [38,49,50], the chlorides could be located either on the alumina support in close proximity to the gold particles or directly on the gold particles. Finally, the weak band at 2127 cm^{-1} can be assigned either to CO adsorbed with a low coverage on metallic Au [51–53] or to CO–$Au^{\delta+}$ species [54–57]. The first interpretation is the most consistent with what has just been discussed above, i.e., that Cl could interact with gold particles and reduce the CO coverage. What is relevant in this IR study is that the presence of chlorine in the samples modifies the frequency of the vibration band of CO adsorbed on metallic gold, i.e. the electron properties of gold.

3.3.3. Relationship between the three preparation methods

Whether anion adsorption, impregnation in excess of solution or deposition–precipitation with urea is performed, the first step of preparation consists in a common step of stirring the oxide support in acidic gold solution at pH <PZC of alumina or titania. During this step, the hydroxychloro gold complexes $[Au(OH)_xCl_{4-x}]^-$ adsorbs on alumina or titania surfaces. As mentioned in Experimental, the x value depends on pH, gold and chlorine concentrations, and temperature. According to the literature [13–15], the main gold speciation in solution is $[AuCl_4]^-$ at pH < 4, i.e., in the solutions used for IES (pH < 1), for AA and DPU preparations (pH = 2.3 with titania and 4.2 with alumina). When the gold complex enters the double layer around the particles of support and adsorbs, the gold speciation probably transforms into $[Au(OH)_1Cl_3]^-$ or $[Au(OH)_2Cl_2]^-$ because of the higher local pH. We have shown that the anion adsorption capacity of titania and alumina is high enough to easily incorporate the targeted gold loading of 1 wt% Au, i.e., the whole gold. The adsorption of gold is very fast, as attested by the simultaneous fast decoloration of the solution and fast coloration taken by the alumina beads (200 $m^2\,g^{-1}$) during DPU, AA and IES. Under our conditions, the nature of the support does not seem to have an influence on the kinetics of adsorption. In contrast, the surface area of the oxide support is a relevant parameter since alumina beads of 40 $m^2 g^{-1}$ combining low BET surface area and small external surface are not able to rapidly adsorb 1 wt% Au. The consequence in the case of DPU is that when the *gold–urea* complex forms, it precipitates in solution, as attested by the blurry solution (see Section 3.2.3).

As a general rule, the three preparation methods of supported gold catalysts can be rationalized as follows. When the preparation is an anion adsorption, 100% of gold can be deposited provided that the nominal gold loading is lower than the adsorption capacity of the support. Otherwise, the excess of non-interacting gold species is eliminated during the washing step. When the preparation is an impregnation in excess of solution or to incipient wetness, this anion adsorption also proceeds, but the excess of gold is deposited during drying without specific interaction with the support, as well as all the chlorides contained in the solution. When the preparation is a deposition–precipitation with urea, again if the gold loading is lower than the adsorption capacity of the support, the hydroxychloro gold complexes adsorb and transform into *gold–urea* complexes, but if the gold loading is higher, the excess of gold precipitates as a *gold–urea* compound on the gold already adsorbed on the support, which acts as nucleation site, as already reported in Ref. [8] and reminded in Section 3.2.3. In the latter case, the time of contact of the support with the solution must be long enough (several hours), i.e., the final pH high enough, to lead to the redispersion of the gold precipitate (peptization, see Section 3.2.3). In contrast, if the gold loading is lower than the adsorption capacity of the support, the DPU duration can be shortened to about 1 h.

One conclusion is that when one has to perform a preparation of supported gold catalyst, it is relevant to wonder whether the targeted gold loading is lower or higher than the adsorption capacity of the oxide support.

The gold particle size obtained after thermal treatments depends on the preparation method (Tables 2, 3 and 6), and the differences are due to the different chlorine contents. Even after washings, the Cl loading is much higher in the AA samples (Tables 1 and 2) than in the DPU ones (Tables 6 and 9) because of the different gold speciation, hydroxychloro gold and *gold–urea* complexes, respectively. The logical consequence should be that the gold particles must be larger in the IES and AA samples because of the higher chlorine content since Cl is known to favor gold sintering. This is true when the samples are thermally treated under air (compare Tables 3 and 6). Moreover gold in the IES samples is not reduced after calcination below 500 °C (Table 3); this is consistent with the fact that gold in the IES samples is also less reducible under hydrogen (Fig. 2). The results are different after activation under hydrogen, the gold particles have roughly the same small size in all samples, but chlorides remain present in the IES and AA samples; as already mentioned, this is detrimental for some catalytic reactions. This is known for CO oxidation [1], and this is true also for selective hydrogenation of butadiene (Table 4). This can be related to the fact that the presence of Cl in the samples modifies the electronic properties of gold as attested by the IR results (Fig. 3) and by the fact that gold is less reducible in the presence of chlorides (Fig. 2).

A way to get rid of the chlorides is to wash the AA and IES samples with ammonia (Table 5). Ammonia washings change the gold speciation with the replacement of the chloride ligands by ammonia and change of the complex charge, from $[Au(OH)_xCl_{4-x}]^-$ to $[Au(OH)_x(NH_3)_{4-x}]^{3-x}$ [9]. The consequence is that the gold particles are smaller after thermal activation under H_2 (Table 5). In the present paper, we have shown that it is not necessary to wash the samples with concentrated ammonia solutions as this was proposed in previous works [22,23]. The concentration can be as low as 0.1 or 0.01 M, because of the strong affinity between Au(III) cations and ammonia.

4. Conclusion

In this paper, we have shown that the preparations of gold catalysts (1 wt% Au) on alumina and titania supports by anion adsorption, impregnation in excess of solution and deposition–precipitation with urea were all determined by a first common step of adsorption of hydroxychloro gold anionic complexes. This results from the targeted gold loading of 1 wt%, which is lower than the adsorption capacity of these supports.

In the case of the deposition–precipitation with urea, this step is followed by a change in speciation of adsorbed gold into *gold–urea* species. The consequence of the preparation at this low gold loading of 1 wt% is that the procedure of DPU preparation initially developed for higher gold loadings can be simplified; the time of contact between the support and the solution can be lowered from 16 to 1 h without incidence on the final gold particle size, which is ~2–3 nm after thermal treatment. Under these conditions, the procedure of DPU preparation becomes competitive in terms of preparation time with respect to deposition–precipitation performed at fixed pH by the addition of NaOH or $NaCO_3$ (see Section 1).

In the case of the samples prepared by anion adsorption and impregnation in excess of solution, i.e., containing adsorbed gold hydroxychlorides, it is also possible to get reasonably small gold particles (<5 nm) if gold reduction is performed under hydrogen and not under air. However, chlorides are not totally eliminated and this can be detrimental for catalysis, as shown in this paper for the reaction of selective hydrogenation of butadiene. Nevertheless, the chlorides can be eliminated by washing the samples with ammonia solutions of low concentrations (0.01 or 0.1 M).

All the results show that the nature of the gold complexes deposited onto the oxide support —hydroxychloro gold complexes for anion adsorption and impregnation, *gold–ammonia* when these samples are washed with ammonia, and *gold–urea* complexes deposition–precipitation with urea— has an influence on the gold particle size after thermal treatment.

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