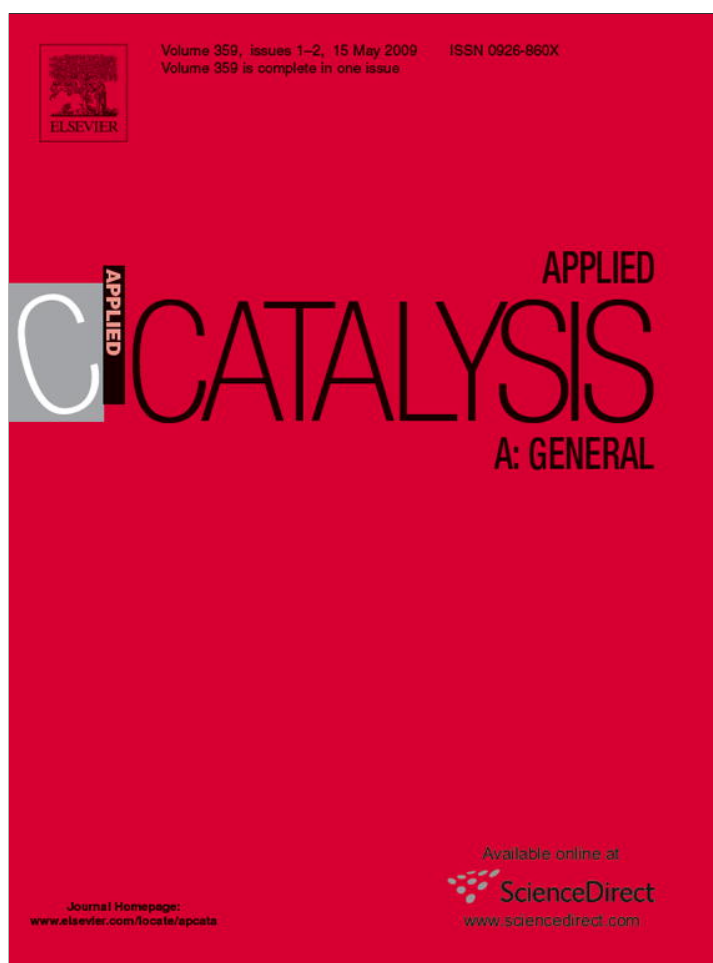


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journal homepage: www.elsevier.com/locate/apcataLiquid phase hydrogenation of crotonaldehyde over Au/CeO₂ catalystsBetiana Campo^a, Gerardo Santori^b, Corinne Petit^c, María Volpe^{a,*}^a PLAPIQUI, Camino La Carrindanga km 7, 8000 Bahía Blanca, Argentina^b CINDECA (UNLP-CONICET), 47N 257, 1900 La Plata, Argentina^c Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse, UMR 7515 CNRS, ECPM/ULP, 25 rue Becquerel, 67087 Strasbourg cedex 2, France

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ABSTRACT

Three Au/CeO₂ catalysts, with different specific surface area (80, 150 and 240 m²/g) were tested for the hydrogenation of crotonaldehyde in liquid phase. Reactions were carried out with molecular hydrogen as the reductant, in a batch reactor using isopropanol as the solvent, at 80 °C and 1 MPa. The high surface area catalyst (Au/CeO₂, 240 m²/g) showed a selectivity towards crotyl alcohol of 29%. This value was much lower than the one previously obtained for the same sample under gas phase conditions (73%) [B. Campo, C. Petit, M. Volpe, J. Catal. 242 (2006) 162]. Under liquid phase the promotional effect of high surface area ceria is lost. The low and middle surface area samples (80 and 150 m²/g respectively) showed meager selectivity to carbonyl hydrogenation due to both the low promotional effect of the support and the relatively large size of gold particles. For the three catalysts the formation of propanol was observed, which decreases catalysts selectivity to crotyl alcohol.

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In last years new heterogeneously catalytic pathway have been studied for their application to a large number of organic synthesis. Conventionally these reactions are carried out with homogeneous catalysts or with stoichiometric transformations. However, heterogeneous catalysts should be preferred to conventional methods mainly because of environmental concerns, but also for technical and economical considerations. In this context, the use of gold based catalysts for the selective hydrogenation of α,β -unsaturated compounds has received great attention in the last years [1–7]. Gold catalysts have shown remarkable selectivity toward the hydrogenation of the conjugated C=O bond, reaching in some cases exceptionally high values of selectivity towards the unsaturated alcohol.

In previous works [6,8] some of us investigated on the gas phase hydrogenation of crotonaldehyde over gold supported on ceria. It was concluded that the high surface area catalyst (Au/HSA-CeO₂, with 240 m²/g) at 120 °C and atmospheric pressure, is active and highly selective towards the hydrogenation of the C=O bond. The high selectivity is an intrinsic characteristic of gold nanoparticles (with particle size lower than 4 nm), though ceria plays an important role as a result of its redox and acid–base properties. Other Au/CeO₂ catalysts, with 80 and 150 m²/g as specific surface area, showed rather low selectivity. The diminution of the desired selectivity when decreasing the support specific surface area was

mainly attributed to the relatively large gold particle size (higher than 9 nm) obtained for the low and middle surface area ceria supports.

Since in organic synthesis reactions are carried out in a solvent for various reasons, in the present work we have decided to test Au/CeO₂ in liquid phase conditions. We have measured the activity and selectivity of samples with different specific surface area: 240 (in our previous work named as HSA-CeO₂), 150 and 80 m²/g for the hydrogenation of crotonaldehyde. We have compared the results with the ones corresponding to gas phase test, focusing on the yield to crotyl alcohol and secondary products as well as in the role of ceria by its own right. In a previous study [9] we have tested gold supported on ceria for the liquid phase hydrogenation of crotonaldehyde, but too low conversion levels were attained. For this reason, in the present work, both reaction temperature and hydrogen pressure were increased. To our knowledge, except for our previous work [9], it is the first time that Au/CeO₂ is employed under liquid phase for the hydrogenation of crotonaldehyde in liquid phase.

1. Experimental

1.1. Preparation and characterization of the gold supported catalysts

Three gold catalysts previously prepared [6,8] were studied. The specific surface areas of the sample were 80, 150 and 240 m²/g. Briefly, the supports were dried under chromatographic air flow at 500 °C for 1 h. Gold was fixed from an aqueous solution of HAuCl₄

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following the direct anionic exchange (DAE) method [10]. In solution the gold species is $\text{Au}(\text{OH})_2(\text{Cl})_2$ and a concentration corresponding to a target 2 wt% of gold was employed. The solids were treated with NH_4OH after grafting to eliminate the chlorine residues [11]. The samples were labeled as $\text{Au}/\text{CeO}_2/240$ (in a previous work [6] named as $\text{Au}/\text{HSA}-\text{CeO}_2$), $\text{Au}/\text{CeO}_2/150$, $\text{Au}/\text{CeO}_2/80$. An additional sample, prepared with a concentration of HAuCl_4 corresponding to a target 5 wt% of gold was named as $\text{Au}5/\text{CeO}_2/240$.

Two 2% Pt catalysts were prepared on high surface CeO_2 (240 m^2/g) and on SiO_2 (210 m^2/g). Both samples were prepared by impregnation of the supports with solutions of HPtCl_6 with a target gold concentration of 2 wt%. The precursors were calcined for 4 h at 400 °C and reduced at the same temperature and during the same period of time under H_2 .

The catalysts were characterized by transmission electron microscopy (TEM) on a Jeol 100 CX2 (Tokyo, Japan) apparatus.

1.2. Hydrogenation of crotonaldehyde in liquid phases

Hydrogenation of crotonaldehyde in liquid phase was studied in a batch reactor at 80 °C and 1 MPa of H_2 . Before reaction 0.2 g of the catalyst were reduced under flowing H_2 , increasing the temperature from 20 to 120 °C, and holding it for 1 h. The catalysts were handled without exposing to the air. Care was taken to avoid trace of oxygen in the system. The aldehyde was introduced into the stirred reactor dissolved in isopropyl alcohol (60 ml of a 0.04 M solution of crotonaldehyde). The progress of the reaction was followed by sampling a sufficient number of microsamples. The composition of the samples was analyzed by means of a Varian GC 3400 gas chromatograph, equipped with a 30 m J&W DB-WAX capillary column and a flame ionization detector. The sensitivity factors were taken from Dietz tables [12] as 1 for crotonaldehyde (CAL), crotyl alcohol (UOL), butanal (BAL) and butanol (BOL), 1.4 for hydrocarbons (HC), 0.5 for ethanol (EOL). The conversion and selectivity towards the different products were measured. The rate, expressed as moles of crotonaldehyde converted per gram of gold and per second was calculated. The stirring rate was varied in the range 300–900 rpm. Within this range the conversion/selectivity pattern of the $\text{Au}/\text{CeO}_2/240$ catalyst was the same for the different stirring rates. Thus the lack of external diffusion limitations was confirmed.

2. Results and discussion

2.1. Preparation and characterization of the catalysts

OH groups and oxygen vacancies are possible anchoring sites for gold precursor on ceria surface. Surface OH would be exchanged by Cl, while oxygen vacancies would fix the gold precursor by incorporation of Cl (see the scheme in Fig. 1). The mechanism is

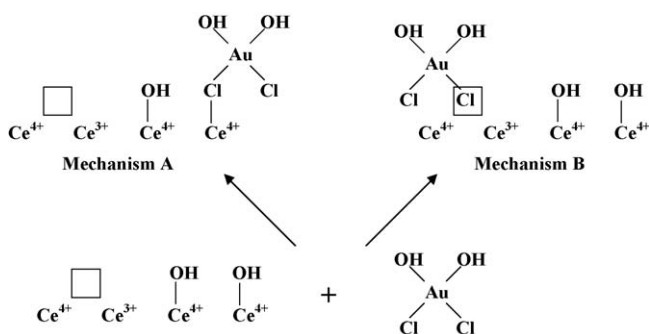


Fig. 1. Possible mechanism for the fixation of HAuCl_4 on ceria surface.

similar to the one proposed by Force et al. for the interaction between rhodium complexes on ceria surface [13].

The $\text{CeO}_2/240$ support took 1.83 wt% of gold after NH_4OH treatment. A high gold dispersion is achieved for this catalyst, with a metal particle size lower than 4 nm, as previously determined from XRD analysis [6]. Even more, gold nanostructures on $\text{CeO}_2/240$ are resistant to sintering, since only negligible size growing was observed after reducing the sample at 300 °C [6]. Oxygen vacancies are considered to be stabilization sites for gold crystals [14,15]. The stability of the gold nanoparticles supported on high surface area ceria seems to indicate that mechanism B (see Fig. 1) governs the anchoring of gold for the case of $\text{CeO}_2/240$.

It is interesting to note that if concentration of the solution of HAuCl_4 is increased to a value corresponding to a target 5% of gold, the amount of the metal retained by the high surface is 4.5% (corresponding to $\text{Au}5/\text{CeO}_2/240$).

$\text{CeO}_2/150$ and $\text{CeO}_2/80$ retained 1.5% of gold for a target concentration 2%. If the concentration of the solution of the gold precursor is increased in order to obtain a target 5% of gold, the metal loading retained by both middle and low surface area ceria keeps constant at 1.5%. This result shows that a saturation of the ceria anchoring sites would occur. A similar phenomena had been observed during the preparation of Au supported on ZrO_2 , possessing different specific surface areas (Petit et al., unpublished results).

Previous result [8] showed that gold particle size of $\text{Au}/\text{CeO}_2/80$ and $\text{Au}/\text{CeO}_2/150$ catalysts was approximately 10 nm, as measured by TEM and XRD. A representative TEM micrograph of the $\text{Au}/\text{CeO}_2/80$ sample is shown in Fig. 2. The low contrast between the ceria support and the metal particles can be clearly observed. However, in this image some particles with diameter of 9 nm are detected.

Gold particles on low and middle surface area ceria undergo a sintering process when a reduction at 300 °C under H_2 is carried out [8]. The low stability indicates that the nature of gold particles on $\text{CeO}_2/80$ and $\text{CeO}_2/150$ is different from that corresponding to high surface area ceria. It could be supposed that for low and middle surface area ceria gold species are fixed not only on vacancies (mechanism B) but by exchanging OH groups, following mechanism A.

To further investigate on the nature of gold particles supported on different surface area ceria a XPS study was carried out over the $\text{Au}/\text{CeO}_2/80$ catalyst submitted to a reduction at 120 °C. The corresponding 4f7/2 and 4f5/2 transitions are shown in Fig. 3. The peaks result from the convolution of two contributions corresponding to two different gold species, Au^0 (83.2 and 87 eV) and Au^{n+} (85.3 and 89.1 eV). On the other hand, previous characteriza-

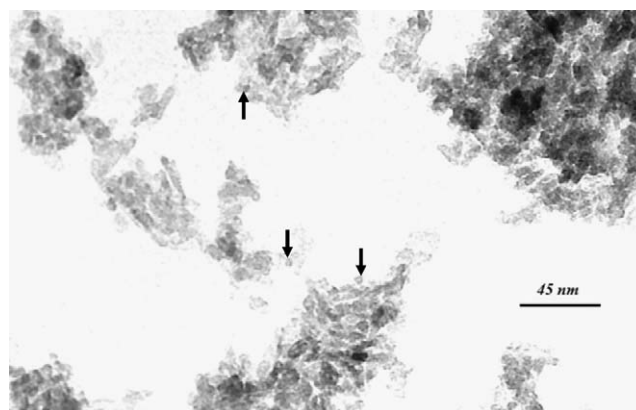


Fig. 2. TEM image for the $\text{Au}/\text{CeO}_2/80$ catalysts with arrows pointing to gold particles.

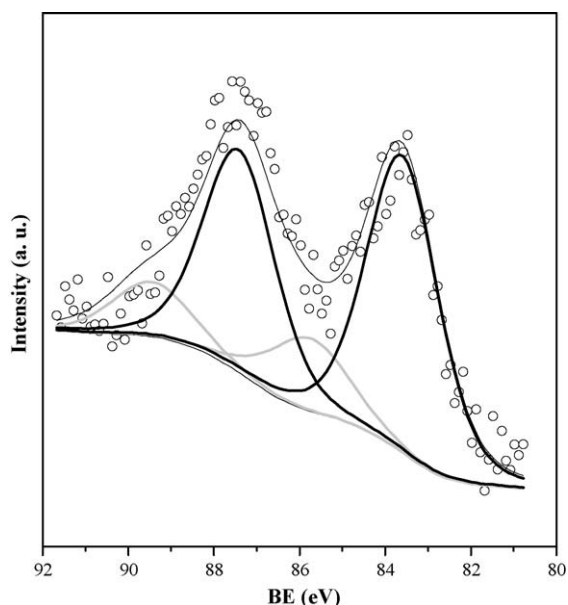


Fig. 3. XPS analysis of Au/CeO₂/80 reduced at 120 °C.

tion of reduced Au/CeO₂/240 [6] showed that only one gold species is present on this sample. Thus the XPS results indicate that the nature of gold nanoparticles supported on ceria depends on the specific surface area of this oxide. The different chemical nature of gold species on low and on high surface area ceria would be created during the very first step of the preparation of these samples.

2.2. Hydrogenation of crotonaldehyde under liquid phase conditions

In previous studies (unpublished results) the hydrogenation of crotonaldehyde in liquid phase was carried out over Pt based catalyst employing different solvents: hexane, tetrahydrofuran and isopropanol. It was concluded that isopropanol was the best solvent in order to obtain the highest selectivity towards the desired product, crotyl alcohol. This alcohol was selected as the solvent for the selective hydrogenation reaction over gold catalysts.

Firstly the bare support CeO₂/240 was tested for the hydrogenation of crotonaldehyde at 80 °C. No appreciable activity was detected, even after 24 h of reaction time. Even more, the support was almost inactive when the reaction temperature was raised up to 180 °C. Only minor amount of propanol were detected at this temperature.

It is known that dehydrogenation or dehydration of an alcohol could occur over acid or base sites respectively [16]. Thus propene and acetone could be obtained from the solvent (isopropanol) taking into account that ceria surface present both acid and basic sites. However, no acetone was detected during the reaction, showing that the dehydrogenation activity of ceria base sites is negligible under the present reaction conditions.

On the other hand a low formation of propanol was observed for the reaction performed over high surface area ceria. We suggest that the solvent is dehydrated to propene over ceria acid sites. In a second step, the hydration of the olefin would originate propanol.

It is interesting to note that bare high surface area ceria was active for the hydrogenation of crotonaldehyde in gas phase conditions at 120 °C [6]. Crotyl alcohol was produced at early reaction time (selectivity of 82%), showing that ceria presents redox active sites for hydrogenation of the carbonyl bond. For steady state conditions mainly a secondary product (a C8 aldehyde originated by a condensation of crotonaldehyde) was produced over basic and acid support site.

Summing up it could be considered that on gas phase conditions both redox and acid–base sites of ceria are active, while for liquid phase conditions only a minor concentration of acid sites remains active for producing propanol. The much lower activity of the support under liquid phase than in gas phase is probably due to the relative low reaction temperature for the former case (80 °C against 120 °C in liquid and in gas phase respectively). Furthermore, probably the solvent plays a role in the diminution of the activity of the catalyst under liquid phase conditions. The solvation of the different species (alcohols, aldehydes, etc.) by isopropanol and its effect on the reaction mechanisms cannot be clearly understood in the present study. This conclusion, about the unclear role of the solvent in the alteration of mechanistic aspects was commented in the detailed work of Mukherjee and Vannice on the liquid phase hydrogenation of citral over Pt/SiO₂ [17].

The hydrogenation of crotonaldehyde in liquid phase was studied over the three catalysts: Au/CeO₂/80, Au/CeO₂/150 and Au/CeO₂/240. The product distribution was monitored as the conversion increased with time. A representative behavior is illustrated in Fig. 4. In an additional experiment, carried out in the absence of hydrogen, no hydrogenation activity was detected. Therefore, hydrogen transfer from the solvent can be ruled out.

The reaction shows an induction period (30–40 min), probably related to a delay in the diffusion of the substrate from the solution to the catalyst surface. Afterwards the conversion level increased with time on stream up to approximately 60%.

The activity for the hydrogenation of crotonaldehyde over gold ceria catalysts is reported in Table 1, as rate of reaction per gram of gold and per second, calculated from the conversion at 240 min of reaction time. The samples showed similar activities, though those of high surface area ceria catalysts (Au/CeO₂/240 and Au/5CeO₂/240) were slightly lower than the corresponding to the other two samples. Considering that Au/CeO₂/240 showed the lowest particle size, it should be expected to present the highest activity (expressed as crotonaldehyde converted per gram of gold). We will revert to this matter later.

Since the solvent was isopropanol, aldol condensation could take place and the formation of acetals should be expected. However, for the present reaction conditions, no detectable amount of these side products was observed.

For the three catalysts the following products were detected: butanal, butanol, crotyl alcohol and, propanol. The latter product is not hydrogenation one but would be originated from the solvent, as discussed above. Propanol was not considered for calculating the selectivity of the different catalysts.

For early reaction times, for all the samples, the main product was butanal. The selectivity to the saturated aldehyde decreased with time on stream for Au/CeO₂/240 and Au/CeO₂/150, while it was constant for gold supported on low surface area ceria, Au/CeO₂/80. On the other hand the selectivity to crotyl alcohol increased, reaching 29% and 20% for high and middle surface area ceria. For the Au/CeO₂/80 catalyst the selectivity to crotyl alcohol was low (9%). The reason why the selectivity to crotyl alcohol is the highest for the Au/CeO₂/240 catalyst is related to a high gold dispersion (particle size lower than 4 nm). Opposing, the selectivity to the unsaturated alcohol is the lowest for the catalyst with the highest particle size, Au/CeO₂/80 (approximately 10 nm). These results would indicate that relatively large gold particles are unselective, as it was reported for the case of the hydrogenation of crotonaldehyde [5,8], and of cinnamaldehyde [18] over gold supported catalysts.

It could be suggested that the more plausible species of crotonaldehyde adsorbed on gold surface is planar η_4 (depicted in Fig. 5a). On the other hand, other species as those postulated for crotonaldehyde adsorbed on Pt surfaces [19] (depicted in Fig. 5b

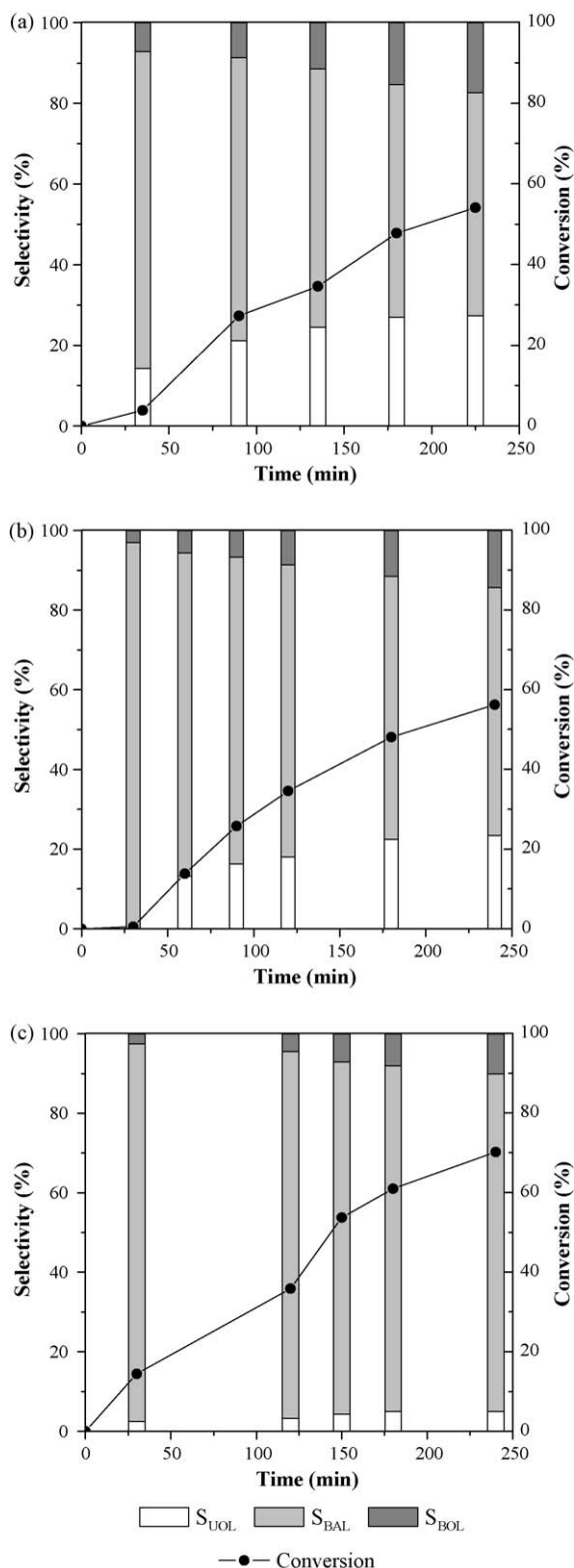


Fig. 4. Hydrogenation of crotonaldehyde in liquid phase. Dependence of conversion and selectivity on time on stream for: (a) Au/CeO₂/80, (b) Au/CeO₂/150, (c) Au/CeO₂/240.

and c) would not be formed over gold surfaces. Species “a” gives rise to either butanal or crotyl alcohol, depending on the properties of gold particles. For relatively large particles (as those present in the Au/CeO₂/80 and Au/CeO₂/150 samples) the hydrogenation of C=C would be favored over that of C=O due to the relative low

Table 1

Catalytic properties of gold ceria catalysts at 240 min of reaction time for the hydrogenation of crotonaldehyde under liquid phase.

Catalysts	Metal (wt%)	Particle size ^a (nm)	Activity ^b 10 ⁵	S% ^c	Propanol production ^d
Au/CeO ₂ /80	1.53	10	2.28	10	89,102
Au/CeO ₂ /150	1.52	9	2.18	20	120,345
Au/CeO ₂ /240	1.83	<4	1.41	29	134,761
Au5/CeO ₂ /240	4.72	–	1.52	26	140,007
Pt/CeO ₂ /240	2.1	–	–	17	93,203
Pt/SiO ₂	2.3	–	–	0	0

^a Data from Ref. [8].

^b Total activity: mmol of crotonaldehyde converted per gram of Au and per second.

^c Selectivity to crotyl alcohol measured at 4 h of reaction time (only primary hydrogenation products were considered).

^d Chromatographic area measured at 4 h of reaction time.

electronic density of d orbitals. The growth in the density of d electrons when decreasing particles size favors the backbonding interaction with $\pi^*C=O$, promoting C=O adsorption and thus increasing the desired selectivity.

Let us now compare the present results obtained for gold supported on ceria catalysts under liquid phase conditions with those corresponding to gas phase (previously reported in Ref. [8]). The general trend is that the selectivity to crotyl alcohol measured in liquid phase is much lower than the one obtained for the same catalyst under gas phase. To label, the selectivity was 73% for the Au/CeO₂/240 sample for gas phase experiments [6], while this value was lower than 30% for any reaction time for liquid phase conditions. For explaining the strong diminution of the selectivity, it should be considered that the activity of gold supported on ceria for producing propanol is in some way detrimental for the hydrogenation activity towards crotonaldehyde. The reason would be a competitive adsorption of propene against crotonaldehyde over selective gold–ceria interface sites. The poisoning effect of this adsorption leads to a diminution of the selectivity to crotyl alcohol. The adsorption of propene would also decrease the activity of gold to convert crotonaldehyde. Thus, the higher the production of propanol, the lower the specific activity of the sample. In line with this the activity of the gold catalysts supported on ceria follows the increasing order Au/CeO₂/80 > Au/CeO₂/150 > Au/CeO₂/240. Still another interpretation for the low production of crotyl alcohol in liquid phase could be given: the role of the solvent (commented above, when discussing the catalytic pattern of bare ceria).

It has been established that the activity of ceria by its own right (due to redox and acid–base properties) is much more lower in liquid phase than in gas phase. Concomitantly the promotional effect of the support that has been observed in gas phase [6] is not effective when reaction is performed in liquid phase.

Two Pt based catalysts were tested for the hydrogenation of crotonaldehyde in liquid phase at 120 °C using isopropanol as the solvent. The data corresponding to Pt/SiO₂ and Pt/CeO₂/240 are reported in Table 1. Firstly it can be observed that the activity of Pt samples are higher than the one measured over Au catalyst. The reason is the low capacity of gold to dissociate H₂ [20] which only occur on gold surface defects (corners, kinks, etc.) [21]. Besides, the selectivity to crotyl alcohol is extremely low over the Pt/SiO₂

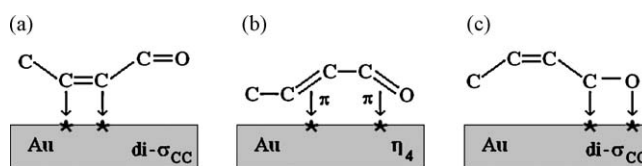


Fig. 5. Possible adsorbed structures of crotonaldehyde on Au particles.

sample, as should be expected. Regarding the modes of adsorption presented in Fig. 5, the “a” species corresponds to the mode of adsorption of crotonaldehyde on Pt surface. No activation of C=O occurs for Pt/SiO₂ considering the inert nature of the support. On the contrary, for Pt/CeO₂ the selectivity measured was 12%, showing that ceria support presents a promotional effect and the carbonyl group is probably activated by Ce³⁺.

The selectivity measured over Pt/CeO₂240 is lower than the one corresponding to Au/CeO₂240, showing that both, gold intrinsic selectivity towards C=O hydrogenation and the promotional effect of high surface area ceria are needed to obtain a selective catalyst. The same trend is observed when comparisons are performed between Pt/CeO₂240 and Au/CeO₂150. On the contrary, the low surface area ceria, Au/CeO₂80, showed a lower performance than Pt/CeO₂240. One should ascribe the meager selectivity of gold supported on low surface ceria to the lack of redox ceria sites as well as to the rather large gold particle size.

3. Conclusions

The catalytic performance of gold supported on ceria for the hydrogenation of crotonaldehyde in liquid phase, with isopropanol as the solvent depends on the specific surface area of the support. Only for high surface area ceria (240 m²/g) appreciable selectivity to crotyl alcohol was measured, due to a high gold dispersion achieved for this carrier.

The promotional effect of high surface area ceria over the catalytic properties of gold previously observed for gas phase is notably diminished when the hydrogenation is carried out with the solvent. The diminution of the selectivity is due to the competitive adsorption of propanol on selective sites and/or to a solvent effect.

Gold supported on high surface area ceria shows a higher selectivity to crotyl alcohol than the corresponding to platinum catalyst.

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