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Crotonaldehyde hydrogenation on supported gold catalysts

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Abstract

Au/Nb_2O_5 and Au/CeO_2 catalysts were studied for the selective hydrogenation of crotonaldehyde, both in liquid (batch reactor, 4 atm, 60 °C, solvent: isopropanol) and in gas (flow microreactor, 120 °C, atmospheric pressure) phases. Samples were characterized by TPR and XRD and tested for the CO oxidation reaction. Large differences in support reducibility between both catalysts were determined from the TPR results. The XRD and CO oxidation results demonstrated that the gold particles were lower than 5 nm. The dependence of the selectivity towards crotyl alcohol and of the conversion on time on stream was measured. The niobia-supported catalyst was mainly unselective, the selectivity towards crotyl alcohol value being 20% for both liquid and gas phases. The Au/CeO_2 catalyst is highly selective in gas phase (78% of selectivity towards crotyl alcohol). Under liquid phase conditions, a high selectivity level was not reached mainly due to secondary reactions.

Keywords: Gold catalyst; Ceria; Niobia; Selective hydrogenation; Crotonaldehyde

1. Introduction

The control of the selective hydrogenation of α,β-unsaturated compounds has been extensively studied over a large variety of catalysts. The desired product, from an industrial viewpoint, is the unsaturated alcohol, which is an important reactant in the synthesis of cosmetic and pharmaceuticals products.

In the following scheme, the possible hydrogenation products of crotonaldehyde are shown (Scheme 1).

It is very difficult to preferentially hydrogenate the C=O bond over the C=C bond using classical hydrogenation catalysts based on Ni, Pd or Pt. Lately, several research groups have reported that the selectivities to the unsaturated alcohol are quite high when gold-supported catalysts are employed [1–7], showing that gold is peculiarly selective towards hydrogenation of the conjugated C=O bond. In addition, there seems to be a certain influence of the nature of the support in the activity and selectivity. For example, Milone et al. [1] studied Au/Fe_2O_3 and Au/Al_2O_3 as catalysts to selectively hydrogenate the C=O bond of *trans*-4-phenyl-3-buten-2-one (benzalacetone) and 4-methyl-3-penten-2-one, 3-penten-2-one. The authors concluded that the reducibility of the support plays an important role: the higher the reducibility of the support the higher is the catalytic performance of gold. Claus and coworkers [3a,3b] investigated the selective hydrogenation of acrolein and of crotonaldehyde over Au/SiO_2, Au/TiO_2, Au/ZrO_2, Au/ZnO and Au–In/ZnO. They found that the selectivity to unsaturated alcohol was in the 23–63% range. They concluded that the support would play a role only in the determination of the morphology of the particles. They suggested that the edges of gold crystallites are the active sites for C=O hydrogenation. In this way, the support would participate indirectly on selectivity, by determining the morphology of the particles.

In the present work, Au/CeO_2 and Au/Nb_2O_5 are studied as catalysts for the hydrogenation of crotonaldehyde, both in liquid and in gas phases. The results obtained in gas phase reactions are important for evaluating the catalysts from a fundamental point of view. On the other hand, tests in liquid phase are more appropriate to evaluate the catalysts under operational conditions more suitable for industrial applications.

Ceria was selected as a support due to its redox properties as well as the fact that it promotes a high metal dispersion [8]. In a previous work, some of us have studied Au/HSA–CeO_2 [9]. In this work it was concluded that gold supported on high-surface

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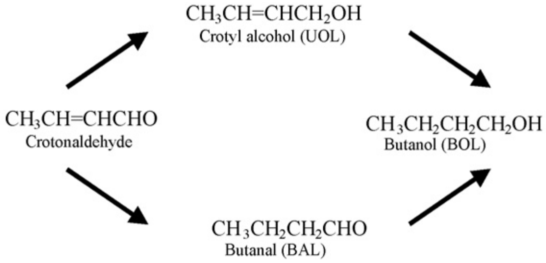

Scheme 1. Hydrogenation of crotonaldehyde.

ceria is highly selective for the hydrogenation of crotonaldehyde in gas phase. Niobia was chosen considering the possibility of achieving a gold catalyst in the SMSI state. Noronha et al. [10] measured a promotional effect of Nb_2O_5 on the catalytic properties of Pd. Yoshitake and Iwasawa [11] reported that the selectivity towards the allylic alcohol, in acrolein hydrogenation over Pt/Nb_2O_5, was higher for the catalysts in the SMSI state than for those reduced at lower temperature.

Finally, it is important to state that the reactions were carried out under the same experimental conditions corresponding to previous studies on Pt-based samples [12], in order to perform a comparison between Au and Pt catalysts.

The samples were characterized by XRD and TPR measurements and they were tested for the CO oxidation reaction.

2. Experimental

2.1. Catalyst preparation

Ceria (240 m^2/g) was from Rhône Poulenc, while niobia (52 m^2/g) was kindly provided by CBMM, Brazil. Previous to gold introduction both supports were calcined, ceria at 300 °C and niobia at 800 °C.

Au/CeO_2 was prepared by deposition–precipitation method using sodium bicarbonate. At 70 °C approximately 5 g of support were contacted with 500 ml of an aqueous solution of $HAuCl_4$ (10^{-3} M). The pH of the solution was kept at 8 by adding a 0.1 M solution of Na_2CO_3 drop by drop. Afterwards, the solid was filtered and the catalyst precursor was washed with a 4 M NH_3 solution and with hot water in order to eliminate Cl^- and Na^+ ions. Finally, the solid was dried at 100 °C for 12 h and then calcined under air at 300 °C (1 °C/min) for 4 h.

Au/Nb_2O_5 was prepared following the method developed by Ivanova et al. [13]. Approximately 5 g of the support were contacted with an aqueous solution of $HAuCl_4$ (10^{-3} M) at 70 °C. The suspension was vigorously stirred for 2 h. Then, a concentrated solution of NH_3 was added and 30 min later, the solid was filtered and washed with hot water in order to eliminate Cl^- and NH_4^+ ions. The catalyst was then dried at 100 °C for 12 h and calcined under air at 300 °C (1 °C/min) for 4 h.

Caution/safety note: the contact of ammonia with a gold solution could provoke the formation of gold ammonia complexes which are explosive [14]. The use of this procedure is not dangerous if the gold complexes are strongly attached to the support. The assurance that there remains no gold in the solution prior to the introduction of ammonia is a pre-requisite.

The Au loading in the catalysts was determined by atomic absorption spectroscopy.

2.2. Catalysts characterization

An X-ray diffraction (XRD) analysis of the Au/Nb_2O_5 and Au/CeO_2 catalysts reduced at 120 °C, was carried out on a Siemens D 5000 polycrystalline diffractometer using Cu Kα radiation.

The reducibility of the catalysts was studied by temperature-programmed reduction (TPR) in a homemade apparatus.

The activity of the catalysts was tested using the CO oxidation reaction. Tests were carried out in a fixed bed quartz microreactor, at atmospheric pressure. The catalyst mass was 50 mg, while the reactive mixture was 1.5 and 5.0% of CO and O_2, respectively, diluted in He. The concentration of CO and CO_2 were measured by Rosemount infrared detectors. The reaction temperature was in the 20–300 °C range. The temperature required to obtain a 50% conversion, T_{50}, was taken as a relative measurement of the size of gold particles. It is well known that the gold crystallites in nanometric range lead to low reaction temperatures for CO oxidation [13,15].

2.3. Crotonaldehyde hydrogenation in gas and liquid phases

The reaction in gas phase was carried out in a quartz microreactor, at atmospheric pressure. In a typical run, the sample (200 mg) was reduced *in situ* at 120 °C for 1 h. The crotonaldehyde (Fluka puriss, 100–200 μl) was introduced in a trap, set before the reactor tube, and was maintained at 0 °C to achieve a constant crotonaldehyde partial pressure of 1.6 kPa. Two catharometers, inserted in the line at the input and output of the reactor, respectively, measure the reactant pressure all along the experiment. When crotonaldehyde was injected, the reactor was kept closed to avoid air contamination. Approximately 20 min later, the reactor was opened. If no adsorption occurs on the catalyst, the output signal should recover to its initial level in about 30 s, the time for gas to reach the catharometer.

The reaction products were analyzed each 20 min by gas chromatography with a FID detector and a DB-Wax column operating at 40 °C.

The reaction in liquid phase was carried out in a Parr reactor, operating in batch conditions at 60 °C and 4 atm of H_2. In a typical experiment, a sample of 100–150 mg was reduced *ex situ* at 300 °C and then introduced to the reactive mixture (crotonaldehyde in isopropanol, 0.1 M) in H_2 flow. Then, the reactor was pressurized at 4 atm of H_2. Finally, the stirring rate was set at 500 rpm and the reaction was considered to be started. Samples of the reactive mixture were taken from the reactor at 20 min intervals. Crotonaldehyde and product concentrations were measured by gas chromatography, using a FID detector and a Chrom PAW column operating at 35 °C.

For both liquid and gas phase reactions, the conversion of crotonaldehyde and the selectivity to the different products were measured as a function of time. The ratio between the selectivity towards the hydrogenation of the carbonyl bond and the selectivity towards the hydrogenation of the olefinic bond was calculated as: $(C{=}O/C{=}C) = (S_{\text{crotyl alcohol}} + S_{\text{butanol}})/(S_{\text{butanal}} + S_{\text{butanol}})$.

3. Results and discussion

3.1. Catalyst preparation

Gold concentrations on Au/CeO_2 and Au/Nb_2O_5 catalysts were 1.9 and 1.5 wt%, respectively for an initial solution containing the amount of gold corresponding to a preparation of 2% of gold on the support. For both samples, the amount of chlorine species was lower than 200 ppm, showing that the NH_4OH treatment effectively eliminates the precursor ligands.

3.2. Catalyst characterization

Fig. 1 shows the XRD diffractograms corresponding to Au/CeO_2. The fluorite oxide-type diffraction pattern is observed according to the CeO_2 structure. No line corresponding to gold compounds was detected indicating that the noble metal particles are smaller than 5 nm, the particle size limit for the XRD analysis.

The TPR profiles of ceria and the corresponding Au/CeO_2 catalyst are shown in Fig. 2. For the pure support, two consumption peaks were observed at 430 and 850 °C. The first one is assigned to the reduction of surface oxygen species (O^{2-} and O^{-} anions) [16], while the other could be due to the reduction of bulk oxygen and to the formation of Ce^{3+}.

The presence of gold introduces a strong modification of ceria TPR profile (see Fig. 2) because only one peak at a relative low temperature (123 °C) was detected. This result indicates that gold enhances ceria reduction, as was already reported by Andreeva and coworkers [17].

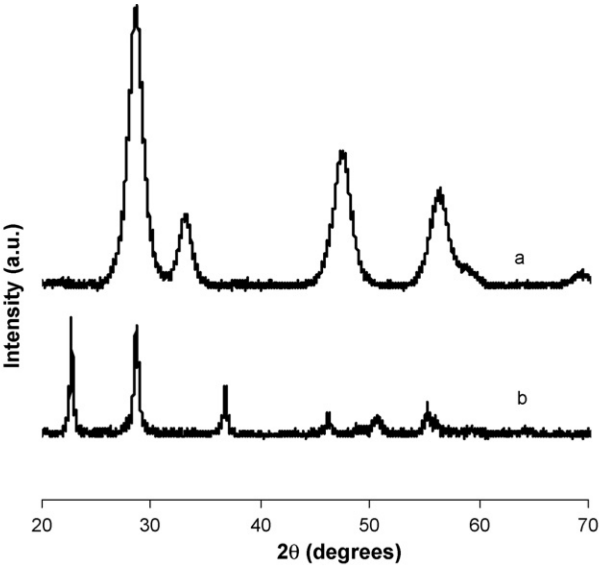

Fig. 1. XRD diffractograms: (a) Au/CeO_2 and (b) Au/Nb_2O_5.

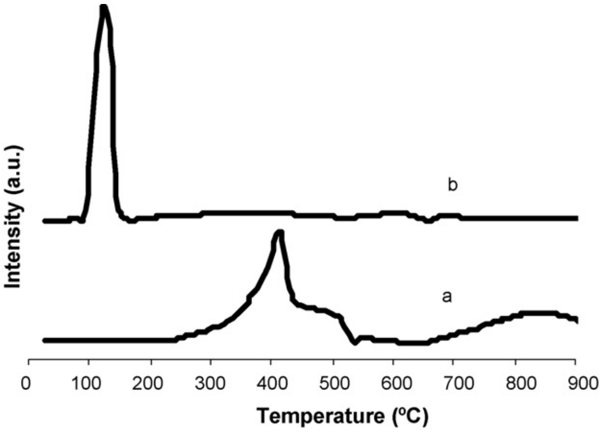

Fig. 2. TPR profiles: (a) CeO_2 and (b) Au/CeO_2.

Au/CeO_2 was tested for the oxidation of CO. This test reaction was selected in order to characterize the samples since the activity of gold particles for the oxidation of CO strongly depends on the gold particle size, its morphological characteristic and the presence of metal–support interactions [18]. Fig. 3 presents the variation of the conversion of CO with the temperature for the Au/CeO_2 sample. The T_{50} value (see Table 1) is relatively low, in comparison with those obtained for other gold-supported catalyst. For example, a value of 98 °C was reported for T_{50} of Au/Al_2O_3, for which gold particle size was 8.6 nm [18]. The high activity of the Au/CeO_2 catalyst for the CO oxidation reaction shows that gold is forming nanoparticles on ceria. Since gold becomes active in many reactions when it is well dispersed on metal oxides [15,19,20], we can assume that this sample would be active for the hydrogenation reaction.

Regarding Au/Nb_2O_5 catalyst, the corresponding XRD diffractogram (Fig. 1) shows the pattern of TT (Shäffer notation) phase. No lines due to gold species were detected, as in the case of ceria-supported catalysts. For this reason it could be concluded that Au crystallites are smaller than 5 nm.

The TPR results corresponding to niobia and the niobia-supported catalyst are reported in Fig. 4. Both profiles are

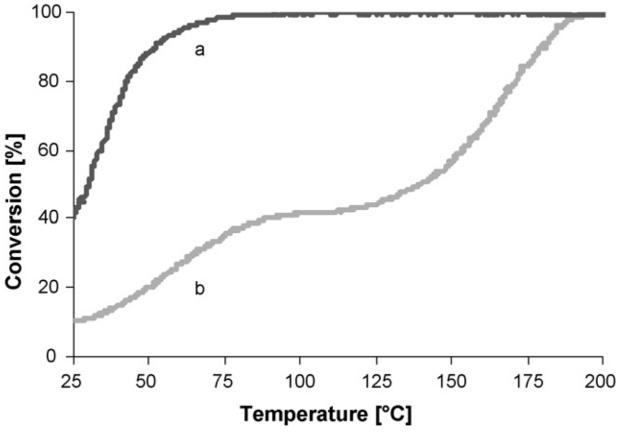

Fig. 3. CO oxidation. Dependence of the conversion on the reaction temperature: (a) Au/CeO_2 and (b) Au/Nb_2O_5.

Table 1
Conversion and selectivity into crotyl alcohol measured at 2 and 24 h of reaction time for gas and liquid phases conditions, respectively

Catalysts and reaction conditions	Conversion of crotonaldehyde (%)	S_{UOL}(%)	C=O/C=C	T_{50} (°C)[a]
Au/CeO_2 gas phase	7	70	2.73	35
Au/CeO_2 liquid phase	20	16	0.98	–
Au/Nb_2O_5 gas phase	2	0	0.12	140
Au/Nb_2O_5 liquid phase	24	19	0.95	–

[a] Temperature required to obtain a 50% of conversion.

identical, showing a low consumption peak at approximately 600 °C, which could be assigned to a phase transition, and a huge consumption up to 800 °C corresponding to dehydroxylation process. The fact that no change in niobia reduction being induced by gold particles was observed is a great difference with Au/CeO_2.

The results corresponding to CO oxidation performed over Au/Nb_2O_5 are reported in Fig. 3 and in Table 1. The conversion values obtained in the 25–200 °C range were lower than those obtained for Au/CeO_2. The value of T_{50} for the latter sample was much lower than that of gold particles supported on niobia showing that Au/Nb_2O_5 is less active than Au/CeO_2. Furthermore, the shape of the profile of the dependence of conversion with the temperature for the CO oxidation over Au/Nb_2O_5 catalyst was completely different from that corresponding to the Au/CeO_2 sample. This result strongly suggests that the nature of gold particles on ceria is very different from those supported on niobia. The shape of the curve corresponding to the CO oxidation over Au/Nb_2O_5 suggests that a bimodal distribution of gold particle size should exist. Thus, the smaller crystallites are reactive towards CO at lower temperature than the higher ones. Sintering of small particles would occur due to the increase of temperature, giving rise to an S-shape curve for the dependence of the conversion of CO on the temperature. Another explanation is possible: niobia would adsorb CO at relative low temperature, depleting the reaction of CO over gold surface. This phenomenon would be overcome at relative high temperature. This hypothesis was also invoked to explain CO oxidation results over Au/Al_2O_3 catalysts [15].

Summing up, from the characterization results it can be established that both Au/Nb_2O_5 and Au/CeO_2 catalysts are systems formed by gold nanoparticles supported on a non-reducible and a reducible oxide carrier, respectively. The reactivity of the particles (as measured by CO oxidation test reaction) is quite different for both cases, probably due to an influence of the support on the nature of gold particles. A more detailed discussion about such a difference cannot be fulfilled under the light of the present results.

3.3. Crotonaldehyde hydrogenation in gas and in liquid phases

The catalytic results corresponding to Au/CeO_2 tested under gas phase conditions are shown in Fig. 5. In the first 20 min of reaction time a strong adsorption of the crotonaldehyde by the solid was detected. This phenomenon would be related to the large area of the support (240 m^2/g) since it was also observed when the catalytic run was carried out over the bare support. Mainly ethanol (EOH) and butanol (BOL) were detected in this period, showing that reactions consuming a large amount of hydrogen were favored. Regarding ethanol formation, ceria sites would be active for this reaction. Since ethanol was the main detected product it could be supposed that this period is governed by support active sites (redox and acid–base ones). In addition, other secondary products were detected: hydrocarbons (HYC) and condensation products (CP).

At 20 min of reaction time the conversion was approximately 45% and the main product was crotyl alcohol (UOL) with a selectivity value of nearly 70%. The selectivity to butanal (BAL) was extremely low (5%) indicating that the catalyst is highly selective. In the following 30 min the conversion decreased from 45 to 15%. At 60 min of time on

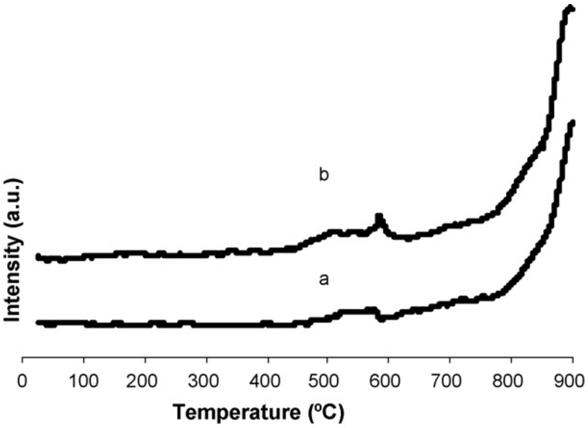

Fig. 4. TPR profiles: (a) Nb_2O_5 and (b) Au/Nb_2O_5.

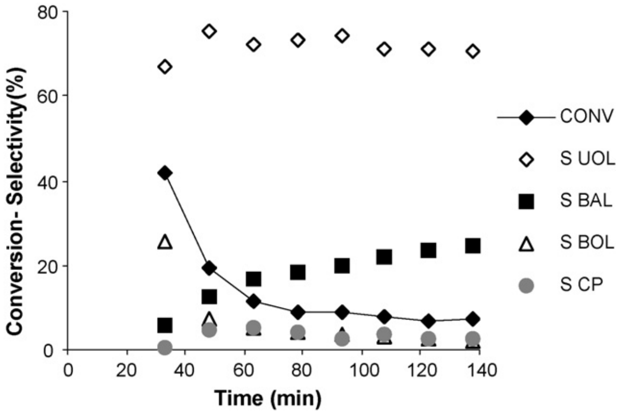

Fig. 5. Crotonaldehyde hydrogenation in gas phase at 120 °C over Au/CeO_2. Conversion and selectivities as functions of time on stream.

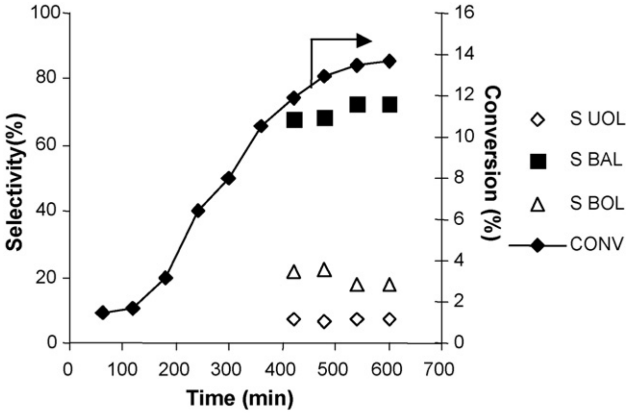

Fig. 6. Crotonaldehyde hydrogenation in liquid phase at 60 °C over Au/CeO_2. Conversion and selectivities as functions of time.

stream, a quasi-steady-state regime was attained, with a conversion level of approximately 8%. In this period the amount of ethanol and other secondary products (hydrocarbons and condensation products) was extremely low and the main product were the primary hydrogenation ones formed on the gold surface. The Au/CeO_2 catalyst was selective towards crotyl alcohol (selectivity equal to 78%) in the steady-state regime. It is important to note that selectivity to unsaturated alcohol measured in a large variety of catalysts is typically in the 10–40% range [3a,21–23]. Besides, the C=O/C=C ratio is quite high (2.73). Thus, Au/CeO_2 should be considered as highly selective.

The results corresponding to Au/CeO_2 tested in liquid phase are shown in Fig. 6 and in Table 1. For the first 7 h of reaction time, the conversion attained was low, turning difficult the correct quantification of products.

At 10 h of reaction time, the conversion was nearly 15%. The selectivity towards crotyl alcohol was low (<10%), while the main product was butanal, with a selectivity value of nearly 70%. The value of C=O/C=C was 0.9, being much lower than the one observed for the reaction performed in gas phase. In liquid phase condition, polymerization of crotyl alcohol takes place and would be the reason for the low selectivity towards crotyl alcohol. This secondary reaction was also observed for Pt/ZnO catalyst tested under the same experimental conditions [12,24]. In an additional experiment the catalysts were tested under the same experimental conditions, using crotyl alcohol as the reactant. For this experiment, at 24 h of reaction time, mainly butanol and an unidentified polymer were detected.

The low selectivity attained for Au/CeO_2 indicates that this sample should be considered as an unselective catalyst for the hydrogenation of crotonaldehyde in liquid phase.

Let us compare the present results, corresponding to Au/CeO_2 with those obtained for a selective Pt/ZnO [24]. Pt/ZnO catalyst prepared from H_2PtCl_6 and previously reduced at 400 °C, was tested in gas and liquid phases under similar conditions as for Au/CeO_2. Conversion levels attained by Au/CeO_2 catalysts are much lower than those of Pt-based samples. This difference would be due to the fact that gold is much less active than traditional hydrogenation catalysts (based on Pd, Pt or Ni), due to its low ability to dissociate H_2 [25]. While for gas phase the catalyst presented a selectivity to crotyl alcohol equal to 83%, for liquid phase this selectivity was relatively low: 35%. The reason of the low selectivity towards the desired product in liquid phase was assigned to occurrence of crotyl alcohol polymerization reaction. Thus, similar trends were observed for Au/CeO_2 and for Pt/ZnO catalysts.

Regarding Au/Nb_2O_5 the catalytic results for the gas phase hydrogenation reaction are reported in Fig. 7. Adsorption of crotonaldehyde was not observed in this case. In addition, the formation of secondary products (hydrocarbons, ethanol, condensation products) was negligible.

The conversion of the niobia-supported sample was lower than the corresponding to Au/CeO_2. The selectivity towards crotyl alcohol of the Au/Nb_2O_5 was extremely low, indicating that this sample is unselective for the title reaction. Taking into account that gold is well dispersed on niobia (particles lower than 5 nm according to XRD results) it is difficult to explain why gold lost its intrinsic selectivity when supporting on niobia. Claus and coworkers [3a] pointed that only the edges of single crystallites are the active sites for the preferred C=O hydrogenation in gold particles surface. Moreover, the nature of the support strongly influences the morphology of gold particles [3a,21]. If these arguments are considered, one could argue that niobia favors the presence of gold crystallites with low concentration of edges, and consequently the catalysts being unselective. Summing up, niobia is an unfavorable support for gold, when this metal is used as a catalyst for selective hydrogenation reactions, since it suppress the intrinsic selectivity of gold.

The catalytic results of Au/Nb_2O_5 in liquid phase are shown in Table 1. As in the case of the ceria-supported catalyst, the attained conversion level was low. Furthermore, the conversion at any reaction time was lower than that measured on Au/CeO_2. The selectivity towards crotyl alcohol was extremely low. These results showed that the Au/Nb_2O_5 catalyst should be considered as an unselective one for the title reaction.

In a previous work, a Pt/Nb_2O_5 catalyst was tested under the same experimental conditions in liquid phase [24]. The

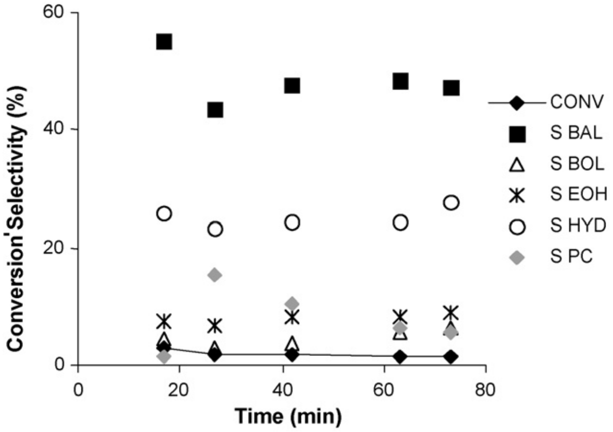

Fig. 7. Crotonaldehyde hydrogenation in gas phase at 120 °C over Au/Nb_2O_5. Conversion and selectivities as functions of time.

conversion of this sample, measured at 2 h of reaction time was approximately 50%. The comparison between Pt/Nb_2O_5 and Au/Nb_2O_5 indicates that platinum is much more active than gold, as was already reported. For both catalysts, the formation of secondary products was quite low, while the selectivity towards crotyl alcohol, measured at similar conversion level (approximately 25%) was quite similar (20% approximately). Thus, gold is not much more selective towards the hydrogenation of C=O bond than platinum, as could be expected. This would be due to a negative influence of niobia on the intrinsic selectivity of gold particles. Therefore the high selectivity of Au towards the hydrogenation of C=C bonds depends mainly on the support material used.

The Pt/Nb_2O_5 catalyst was also tested for the gas phase hydrogenation of crotonaldehyde (unpublished results). It was observed that the conversion was quite high, while the desired selectivity was 19%. On the other hand, $Au/Nb_2\ O_5$ was unselective.

4. Conclusion

Au/CeO_2 is highly selective for the gas phase hydrogenation of crotonaldehyde. The selectivity value is among the highest reported in the literature. However, the catalyst is unselective when the same reaction is performed in liquid phase, mainly due to secondary reactions.

Au/Nb_2O_5 is an unselective catalysts for the hydrogenation of C=O bond. This would be due to a negative influence of the support on the morphological features of gold particles. As postulated by Claus and coworkers, the morphology of gold crystallites strongly influence the selectivity towards C=O hydrogenation [21,22], thus it is supposed that niobia give rise to unselective gold particles.

The comparison of the present results with those corresponding to Pt-based catalysts, corroborates that Au is markedly less active than Pt.

Au/CeO_2 is highly selective for the hydrogenation of crotonaldehyde to crotyl alcohol in gas phase. However, the selectivity is lost for liquid phase conditions due to overreaction of crotyl alcohol.

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