Liquid-Phase Hydrogenation of Crotonaldehyde over Platinum- and Palladium-Based Catalysts

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The selective hydrogenation of crotonaldehyde in liquid phase, at a temperature of 353 K and a H_2 pressure of 400 kPa, is studied over different palladium- and platinum-based catalysts (Pd–Pb/α-Al_2O_3, Pd–Zn/α-Al_2O_3, Pd/ZnO, and two Pt/ZnO samples, prepared from $Pt(NH_3)_4(NO_3)_2$ and H_2PtCl_6, respectively). The intrinsic selectivity of palladium cannot be modified by alloying or following a promotion with a second metal, and the selectivity to crotyl alcohol measured over palladium-based samples is nil or extremely low. The selectivity corresponding to the Pt/ZnO catalysts increases with the time-on-stream reaching high levels. The formation of a Pt–Zn alloy is the origin of the enhanced selectivity toward crotyl alcohol; this effect is more pronounced for the sample that has been prepared from H_2PtCl_6.

Introduction

The most important product of the hydrogenation of α,β-aldehydes is the corresponding unsaturated alcohol, which is a reactant in the synthesis of cosmetic, pharmaceutical, and specialty chemical products. In industrial processes, metal hydrides are used to perform this reaction;[1,2] however, heterogeneous catalysts should be preferred to conventional methods, mainly because of environmental concerns, but also for technical and economical considerations.

Thermodynamic favors hydrogenation of C=C over C=O.[3] Thus, the design of active and selective catalysts for the hydrogenation of α,β-unsaturated compounds is of great significance. Traditionally, supported noble-metal catalysts have been used for the hydrogenation of α,β-aldehydes and the effect of promoters such as tin[4–6] and zinc[7,8] on the selectivity were studied. Besides, the effect of the porosity of the support[9] and its reducibility[10,11] on the catalytic performance were analyzed. For liquid-phase conditions, the influence of the nature of the solvent on the activity and selectivity of the catalysts was studied.[12] Acrolein, crotonaldehyde, cinnamaldehyde, and citral were the most studied substrates. An enhancement of the selectivity to the desired unsaturated alcohol due to the steric effect was clearly shown: the bigger the substituent at the C=C group, the better the selectivity toward the reduction of the carbonyl bond.

Liquid-phase hydrogenation is an attempt to evaluate catalysts under conditions similar to the industrial ones; thus, a solvent is needed for diminishing thermal effects, dissolving solid reactants, and controlling the high reaction rate, as well as cleaning the catalytic surface. Crotonaldehyde boils at 374 K; thus, the hydrogenation of this molecule could be performed without complication both in liquid and gas phases. The number of articles regarding the hydrogenation of crotonaldehyde in gas phase is ∼5 times greater than the corresponding to the same reaction under liquid-phase conditions. The reason would be that alcohols are used as the preferred solvents because they activate the C=O bond. However an undesirable secondary effect arises: the formation of acetals and hemiacetals.[13,14] For

the liquid-phase hydrogenation of crotonaldehyde, this fact, joined to the low steric protection of the olefinic bond, are detrimental to selectivity. As a consequence, a catalyst that exhibits high selectivity in the gas phase could lose this property under liquid-phase conditions. The liquid-phase hydrogenation of crotonaldehyde then is still a big challenge for researchers.

The present work is focused on the hydrogenation of crotonaldehyde in the liquid phase over platinum- and palladium-based catalysts. The following catalysts are studied: Pd/ZnO, Pt/ZnO, Pt-$ZnCl_2$/SiO_2, Pd–Pb/α-Al_2O_3 and Pd–Zn/α-Al_2O_3. For all these systems, previous studies have demonstrated that an alloy between the noble metal and the support or the promoter was formed.[15–18] The objective of the present study is to determine if alloying or promotion with a second metal species improves the intrinsic chemoselectivity of platinum and palladium for the hydrogenation of crotonaldehyde in the liquid phase. Note that the Pt/ZnO catalysts have been tested for the hydrogenation of crotonaldehyde in the gas phase,[15,18] showing high selectivity levels toward crotyl alcohol (90%).

Experimental Section

Preparation and Characterization of the Catalysts. Two platinum catalysts supported on ZnO were prepared by impregnation of the support (zinc oxide from Asturienne des Mines, surface area of 42 m^2/g) with aqueous solutions of $Pt(NH_3)_4(NO_3)_2$ (Strem Chemicals, 99%) and H_2PtCl_6·$6H_2O$ (Strem Chemicals, 99%), respectively. After water evaporation, samples were calcined in air at 673 K and subsequently reduced at the same temperature. The catalyst prepared with the first precursor is called Pt/ZnO ex-nit, whereas the other one is called Pt/ZnO ex-chl. For further details, see ref 19.

To perform a comparison, a platinum catalyst supported on an inert carrier was also prepared. A Pt/γ-Al_2O_3 catalyst was obtained by impregnation of γ-Al_2O_3 (Rhône Poulenc, surface area of 146 m^2/g) with an aqueous solution of H_2PtCl_6.

A monometallic palladium supported catalyst was prepared via wet impregnation on α-Al_2O_3 (Rhône Poulenc, 13 m^2/g) with a toluene (Sigma–Aldrich, anhydrous, 99.8%) solution of *bis*-acetylacetonate-palladium ($Pd(C_5H_7O_2)_2$) (Aldrich, 99%) for 24 h. Afterward, the solid was washed with fresh solvent, filtered, calcined at 673 K, and then reduced at 573 K. To prepare the bimetallic Pd–Zn/α-Al_2O_3 sample, the base mono-

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metallic palladium catalyst was placed in contact with solutions of diethylzinc in *n*-heptane. Further details are found in ref 17.

From the Pd/α-Al$_2$O$_3$ sample, a binary Pd−Pb/α-Al$_2$O$_3$ catalyst was prepared by contacting the base catalyst with a solution in *n*-heptane of tetra-*n*-butyl lead (Ventron, purity of 98.89%).[16]

The palladium particle size was studied by means of transmission electron microscopy (TEM) in a JEOL Model 100CX2 (Tokyo, Japan). Approximately 100 metal particles were measured to perform the particle size distribution. The average diameter of the crystals in the different catalysts was calculated from the following formula:

$$d = \frac{\sum n_i d_i}{n_i}$$

The method of the double isotherm[20] was used to determine the amount of irreversible adsorbed hydrogen over palladium-based catalysts. Hydrogen sorption and backsorption isotherms were measured at 298 K in a homemade glass volumetric apparatus. To calculate the metal dispersion, it was assumed that the adsorption stoichiometry is one H atom per one surface Pd atom.

A ZnO-supported palladium catalyst (Pd/ZnO) was prepared by impregnation of the same support, corresponding to Pt/ZnO with a solution of PdCl$_2$ (Merck, 99.999%), with a target palladium concentration of 1%.

A CHNSO elemental analyzer (Perkin−Elmer, Model Serie II) was used to perform a microanalysis of the carbon and hydrogen of the spent catalyts. The carbon and hydrogen concentrations (expressed as percentages) in the catalysts after evaluation for the hydrogenation of crotonaldehyde in the liquid phase were measured.

Catalytic Test. Hydrogenation experiments were conducted in a Parr Instruments system, with a volume of 50 mL, operated in batch mode. The magnetic stirring was set at 800 rpm. The reactive mixture was a 0.07 M solution of crotonaldehyde (Carlo Erba, 99.9%) in isopropanol (Sigma−Aldrich, anhydrous, 99.5%) and the catalyst mass was 100−200 mg. In a typical experiment, the catalyst was reduced ex situ and introduced in the reaction media under H$_2$ (Air Liquide, 99.99%) flow at room temperature. Subsequently, the reactor was purged with H$_2$ and the temperature was raised to 353 K. Finally, it was pressurized at 400 KPa. Aliquots of the reactive media at different reaction times were analyzed by gas chromatography with a ZB wax semicapillary column.

Results

Catalysts Characterization. The list of the catalysts, their metal contents, and the corresponding particle size are listed in Table 1. A low amount of palladium was fixed on α-Al$_2$O$_3$, because of the meager concentration of reactive OH responsible for the anchoring of palladium precursor (Pd(C$_5$H$_7$O$_2$)$_2$). The metal dispersion of the monometallic sample was quite high (see the last column in Table 1) and corresponds to a palladium particle size of 2 nm. Upon the addition of the promoter, the palladium dispersion notably diminishes, because a dilution of the palladium surface due to the presence of lead occurs, as previously postulated for both Pd−Zn/α-Al$_2$O$_3$ and Pd−Pb/α-Al$_2$O$_3$.[16,17]

In profile b in Figure 1, the TPR profile of the lead-modified sample is shown. For the sake of comparison, the results of the corresponding unmodified sample (Pd/α-Al$_2$O$_3$) is also reported (profile a in Figure 1). It could be clearly observed that the

Table 1. Main Catalyst Properties (Metal Weight (%), TEM Average Particle Size, and Metal Dispersion) for the Hydrogenation of Crotonaldehyde in the Liquid Phase

	Metal Content (wt %)		TEM particle size (nm)	Pd or Pt dispersion[a]
catalyst	Pt	Pd		
Pt/ZnO ex-nit	1.0		4.0	0.32
Pt/ZnO ex-cl	1.0		4.2	0.31
Pt/γ-Al$_2$O$_3$	2.1		2.1	0.42
Pd/α-Al$_2$O$_3$		0.20	2.4	0.52
Pd−Pb/α-Al$_2$O$_3$		0.2 (0.3)	2.7	0.07
Pd−Zn/α-Al$_2$O$_3$		0.2 (1.0)	3.2	0.12
Pd/ZnO		1.2	4.6	0.33

[a] Calculated from the chemisorption data for palladium-based catalysts and from TEM results for the platinum-based catalysts (the mean particle diameter and assuming cubo-octahedrally shaped metal particles).
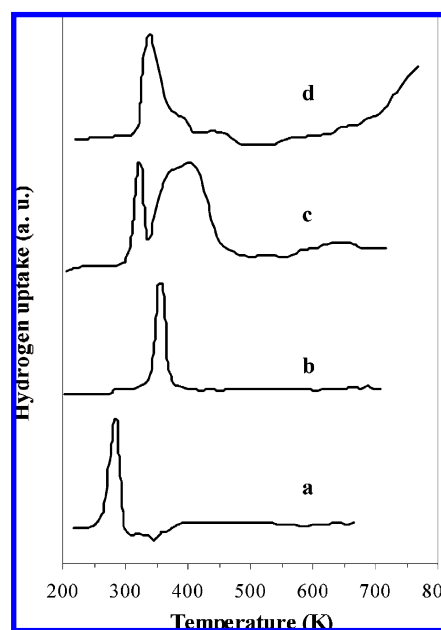

Figure 1. Temperature-programmed reduction (TPR) profile for (a) Pd/α-Al$_2$O$_3$, (b) Pd−Pb/α-Al$_2$O$_3$, (c) Pd−Zn/α-Al$_2$O$_3$, and (d) Pd/ZnO.

properties of noble-metal particles are strongly modified upon the introduction of lead. The monometallic sample present two main features: a consumption peak centered at 293 K and a release peak at 358 K. The first one is attributed to the reduction of PdO, whereas the second one is attributed to palladium hydride decomposition. The addition of lead provokes a shift of the reduction to a higher temperature (373 K). We attribute the strong modification of the reducibility of the noble metal to the formation of a palladim-lead alloy. Besides, the formation of such an alloy for Pd−Pb/α-Al$_2$O$_3$ was previously postulated from a combined XPS and FTIR study.[16]

Profile c in Figure 1 corresponds to the other bimetallic sample, Pd−Zn/α-Al$_2$O$_3$. For this catalyst, a shift to higher reduction temperatures is also observed, from 293 K to 323 K in the monometallic and bimetallic samples, respectively. A broad peak is observed between 323 K and 473 K; it is assigned to the reduction of zinc oxidic species in close contact with palladium. The TPR result corresponding to the Pd/ZnO catalyst is shown in profile d in Figure 1. Compared with palladium supported on inert α-Al$_2$O$_3$ (profile a in Figure 1), the reducibility of the noble metal is strongly affected by the reducible support. The reduction of PdO occurs at relatively high temperature. Besides, a consumption is detected in the range of 353−473 K, which is assigned to the reduction of zinc species
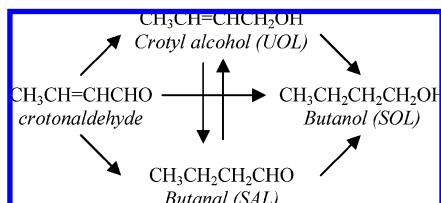
Figure 2. Hydrogenation of crotonaldehyde.

in strong contact with the noble metal (probably an alloy). Up to 673 K, the reduction of the support begins.

A high platinum loading was achieved in the Pt/ZnO catalysts (1%) and the dispersion of the noble metal (as calculated from TEM particle size measurements, assuming a cubooctahedral shape for Pt crystals) was ~30% for both samples, prepared from $Pt(NH_3)_4(NO_3)_2$ and H_2PtCl_6, respectively.

In a previous work,[19] the characterization of both Pt/ZnO ex-nit and Pt/ZnO ex-chl was performed using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and TPR. The results showed that the noble metal formed an alloy with zinc after a reduction treatment. Chlorine has a promoter effect in the formation of such an alloy. For this reason, the reduction temperature necessary to form the alloy was 573 K for the sample prepared from $Pt(NH_3)_4(NO_3)_2$, whereas, for the catalyst prepared from H_2PtCl_6, the Pt−Zn alloy is formed at lower reduction temperatures.

Hydrogenation of Crotonaldehyde over Palladium-Based Catalysts (Pd/α-Al$_2$O$_3$, Pd−Zn/α-Al$_2$O$_3$, Pd−Pb/α-Al$_2$O$_3$, and Pd/ZnO). Figure 2 shows the scheme of the reaction of hydrogenation of crotonaldehyde .

The importance of transport limitations involved in the reaction of interest was evaluated by the Madon−Boudart test.[21] In pursuing this, two Pd/α-Al$_2$O$_3$ catalysts were used, with metal loadings of 0.20 and 0.88 wt % and dispersion values, as measured by hydrogen chemisorption, of 52% and 28%, respectively. The plot of ln(activity) versus ln(concentration of Pd surface atoms) for this reaction over Pd/α-Al$_2$O$_3$ shows a slope of less than unity, which indicates that internal (pore) mass-transfer limitations should not be neglected in this case. Since palladium-based catalysts are unselective toward crotyl alcohol (as will be discussed later in this work), no attempt to remove diffusion limitations was attempted.

The variation of conversion with time was measured for the palladium-based catalysts. A monotonic increase in conversion was observed and no sign of deactivation was detected. The conversion level attained after 5 h of reaction time, as well as the activity and the selectivity to crotyl alcohol of the samples, are reported in Table 2. The activity was calculated as the number of moles of crotonaldehyde converted per mole of surface palladium per second. The comparison between the different catalysts shows that the conversions of the bimetallic Pd−Zn and Pd−Pb samples were lower than that corresponding to the unmodified catalyst. This difference is due to the depleted concentration of surface palladium in the bimetallic samples, compared to the monometallic one. This result clearly indicates that the addition of the modifier originates a dilution of the noble-metal surface, as concluded from chemisorption results (see Table 1). On the other hand, the specific activity was similar for all cases (monometallic and bimetallic samples), indicating that only Pd atoms are reactive toward crotonaldehyde.

Regarding the selectivity, Pd/α-Al$_2$O$_3$ only produced butanal. For the binary Pd−Pb/α-Al$_2$O$_3$, butanal was the main product, while a minor amount of crotylalcohol, corresponding to a selectivity value of 4%, was measured for all of the reaction

Table 2. Catalytic Properties of Pd- and Pt-Based Catalysts. Hydrogenation of Crotonaldehyde in Liquid Phase at 353 K

sample	conversion, X (%)[a]	turnover number, TON ($\times 10^3$)[b]	Selectivity to Crotyl Alcohol (%)	
			S_{uol}^{i} [c]	S_{uol}^{f} [d]
Pd/α-Al$_2$O$_3$	15	15.0	0	0
Pd−Zn/α-Al$_2$O$_3$	6	13.7	1	1
Pd−Pb/α-Al$_2$O$_3$	3	14.7	4	4
Pd/ZnO	10		3	3
Pt/γ-Al$_2$O$_3$	60	8.2	1	2
Pt/ZnO ex-cl	19	2.2	45	60
Pt/ZnO ex-nit	18	2.1	26	32

[a] Percent of conversion measured after 5 h of reaction time. [b] Number of molecules converted per surface Pt/Pd atom after 5 h of reaction. [c] Selectivity to crotyl alcohol measured after 5 h. [d] Selectivity to crotyl alcohol measured after 16 h.
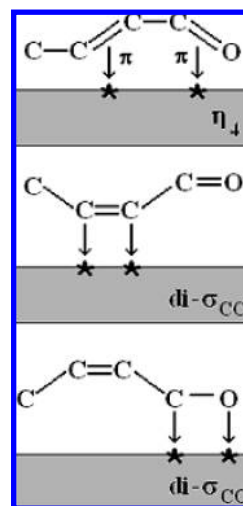

Figure 3. Possible adsorbed structures of crotonaldehyde on the surfaces of metal particles.

times. The selectivity measurements performed over Pd−Pb/α-Al$_2$O$_3$ indicate that alloying does not notably modify the intrinsic nil selectivity of palladium toward the hydrogenation of the carbonyl group.

Low selectivity to crotyl alcohol was also measured over the other bimetallic catalyst tested for the reaction of interest, Pd−Zn/α-Al$_2$O$_3$. Despite the strong modifications of palladium due to the modifier, the selectivity toward crotyl alcohol is not increased in a noticeable way (only 2% of selectivity to the unsaturated alcohol was attained over the bimetallic catalysts).

The Pd/ZnO catalyst was also practically unselective toward the hydrogenation of the carbonyl bond of crotonaldehyde (see Table 2).

The whole of the catalytic results obtained over monometallic and bimetallic palladium-based samples for the hydrogenation of crotonaldehyde in the liquid phase indicates that the adsorbed form of crotonaldehyde on the palladium surface would be di σ_{C-C} (see Figure 3). Thus, the undesired hydrogenation of the olefinic bond is obtained. This adsorption method could not be altered by electronic modification of the noble metal arising from alloying with a second metal (lead or zinc). At this point, it interesting to comment on the results corresponding to the selective hydrogenation of the triple bond in the presence of double bond over palladium bimetallic catalysts. It had been suggested that the improvement in the selectivity of palladium upon the addition of a second metal, is originated by a dilution of the noble metal surface and not to an electronic modification of palladium.[22−24]

Although the palladium-based catalysts are practically unselective, the low production of crotyl alcohol measured over Pd−Pb/α-Al$_2$O$_3$ and Pd−Zn/α-Al$_2$O$_3$ should be explained. Mainly from previous XPS analysis,[16] it was determined that lead oxidic species in close contact with palladium particles are present in the Pd−Pb/α-Al$_2$O$_3$ catalyst. Also, for the Pd−Zn/α-Al$_2$O$_3$ sample, zinc oxide was detected by XPS. It could be expected that Pb^{n+} and Zn^{n+} (acid sites) could activate the C=O group (basic site) of crotonaldehyde, increasing the desired selectivity. Given the catalytic evaluation of Pd−Pb/α-Al$_2$O$_3$, it could be concluded that the intrinsic nil selectivity of palladium for hydrogenating the carbonyl group is slightly altered by the modification with lead.

It could be postulated that the oxidic species of the second metal (acid sites) would attract the lone pair of the carbonyl bond, weakening the C=O bond and favoring hydrogenation toward crotyl alcohol. Aramedia et al.[13] reported that the promotion of palladium with iron oxidic species increases the selectivity to the unsaturated alcohol for the hydrogenation of citral. Although the increase in the selectivity due to promotion with iron species was much higher than that for the catalysts of the present study, they also determined that the presence of Lewis acid additives induces an electronic modification of palladium and concomitantly favors adsorption via C=O group. Finally, it is interesting to comment on the results corresponding to the determination of the total carbon content over the spent palladium-based catalysts. For all of the cases, the amount of carbon on the used catalysts could not be measured by the elemental analyzer. This result is consistent with the fact that no deactivation process was observed for the samples under the reaction conditions.

Hydrogenation of Crotonaldehyde over Pt/ZnO Based Catalysts. The possible existence of transport limitations was evaluated by the Madon−Boudart test.[21] Two Pt/ZnO ex-nit catalysts were used, with metal loadings of 1 and 2.2 wt % and dispersion values, as calculated from particle size measured by transmission electron microscopy (TEM), of 33% and 10%, respectively. The plot of ln(activity) versus ln(concentration of surface Pt) for the hydrogenation showed a value of unity for the slope, showing that internal (pore) mass-transfer limitations can be neglected in this case. The lack of external diffusion limitation was confirmed by measuring constant activity values for varying the rate of stirring in the 300−1000 rpm range.

The variation of conversion of crotonaldehyde, measured as a function of the time-on-stream, was measured for the Pt/ZnO ex-chl sample (see Figure 4). A deactivation process was observed, and the maximum level of conversion (27%) was attained after 12 h. Afterward, the catalyst was inactive. The deactivation of platinum catalysts in the hydrogenation of crotonaldehyde in the liquid phase was also observed by Lercher et al.,[25] Bartok et al.,[26] and Vannice and Dandekar.[11] The loss of the activity of the samples could be related with a poisoning with CO, which originates from decarbonylation reactions.[25,27] For the Pt/ZnO ex-chl catalyst tested in the present work, the occurrence of decarbonylation reaction could be neglected based on various facts: (i) the catalytic properties over the spent catalyst could not be restored after the reaction mixture was flushed with an inert gas, or with air (to displace adsorbed CO), (ii) no C$_3$ hydrocarbons were detected, (iii) the loss of CO was reported to occur for a higher reaction temperature (>313 K), with the crotonaldehyde being quite stable under the present reaction conditions. Another origin of the deactivation could be related to the formation of coke or other side carbonaceous products. This last interpretation is supported by the relatively
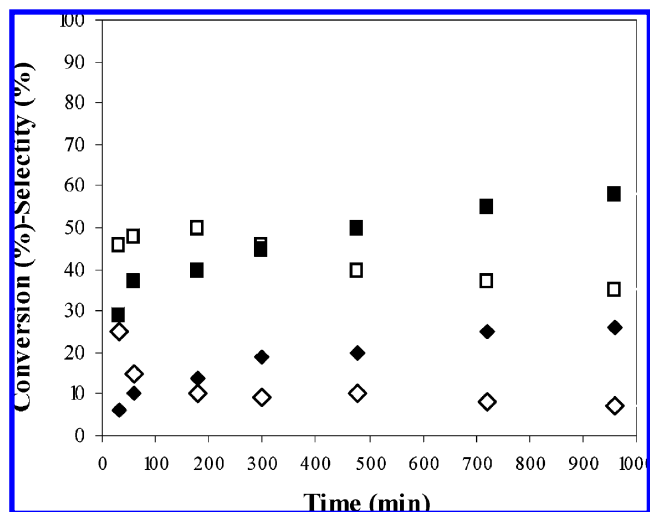

Figure 4. Variation of (◆) conversion and the selectivity to (■) crotylalcohol, (◇) butanol, and (■) butanal with time for the hydrogenation of crotonaldehyde in the liquid phase over Pt/ZnO ex-chl (353 K, 400 kPa, 100 mg of catalyst).

high amount of carbon (measured as elemental carbon) present in the spent Pt/ZnO sample. The C/H ratio was ∼0.7, which suggests that the carbonaceous species responsible for the deactivation of the catalyst would be not graphitic or carbonaceous polyaromatic carbon (for which the C/H atomic ratio is a high value), but rather a polymerization or condensation product. These species would be the responsible for the deactivation of the catalyst during the time-on-stream.

From the conversion data, the activity of the Pt/ZnO ex-chl sample was calculated as the integral turnover number (TON) for the first 5 h of reaction time (see Table 2).

During the hydrogenation of crotonaldehyde over Pt/ZnO ex-chl, crotyl alcohol, butanal, and butanol were the only detected products. C$_4$ hydrocarbons (butanes, butadienes, butane) were not observed, showing that the catalysts has no dehydratation activity. Besides, the formation of diacetals (from carbonyl compounds and the alcoholic solvent), condensation of carbonyl compounds, and dehydratation of the alcohol were not detected. The distribution of the four hydrogenation products varied with reaction time, as depicted in Figure 4. For early reaction times, the main product was butanol; however, the selectivity to this secondary hydrogenation product decreased sharply with the time-on-stream. Moreover, the production of butanol over Pt/ZnO practically stopped after 30 min. Bartók et al.[26] obtained similar results during the hydrogenation of crotonaldehyde over platinum supported on clay mineral catalysts: the selectivity to butanol decreased sharply during the first hour of reaction, remaining afterward almost constant. If the possible forms of adsorption of crotonaldehyde (see Figure 3) are taken in mind, it could be postulated that the amount of the planar η^4 adsorption form on the platinum surface is relatively high at the beginning of the reaction. This specific sorption mode, which involves interaction with both double bonds, originates butanol. The planar form, following theoretical calculations,[28] is favored on Pt(100) and on highly uncoordinated metal sites (steps and kinks). However, along the reaction, these surface sites would be poisoned and the planar adsorption form would disappear.

On the other hand, the selectivity to crotyl alcohol increases with time, while the yield to this product is almost constant with the time-on-stream. Considering that the adsorption form of crotonaldehyde giving rise to crotyl alcohol is the di σ_{C-O} mode, it could be postulated that its concentration is constant

during the hydrogenation reaction. The selectivity to butanal, as well as the yield of this product, decrease smoothly with time. The specific sorption mode related with the production of butanal is the di σ_{C-C} mode. The concentration of the sites related to this specific form of adsorbed crotonaldehyde decreases with time, possibly because of irreversibly adsorbed molecules that are responsible for deactivation. In this manner, the catalyst becomes more selective to crotyl alcohol with time, under reaction conditions. The changes in selectivity are probably originated in this fact. This hypothesis would be consistent with the work of Maetz et al.,[29] who found that polymeric species being formed during the hydrogenation of butyne over platinum catalysts lead to high selectivity.

Finally, it is interesting to compare the catalytic pattern of Pt/ZnO ex-chl with that corresponding to a platinum catalyst obtained by supporting the metal on an inert carrier: Pt/Al$_2$O$_3$. The activity of this sample was higher than that measured over Pt/ZnO ex-chl (see Table 2), because of the fact that no deactivation process was observed over the alumina-supported sample. In contrast, the selectivity to crotyl alcohol was superior for Pt/ZnO than for Pt/Al$_2$O$_3$ (60% against 2%, for the former and for the latter catalysts respectively, measured under the same experimental conditions). The high selectivity to crotyl alcohol measured over the Pt/ZnO ex-chl catalysts would be due to the formation of a Pt−Zn alloy, which favors the adsorption of via the carbonyl bond (di σ_{C-O}). Still another interpretation is possible: a chlorine species, located at the Pt/ZnO interface, would promote the hydrogenation of C=O against that of C=C.

With this in mind, another pretreatment was performed over a Pt/ZnO ex-chlorine sample: a reduction under H$_2$ at 773 K instead of at 673 K. Based on the previous results,[19] it is speculated that the formation of the Pt−Zn alloy or the promotional effect of chlorine species would be highlighted at high temperature.

The activity for the Pt/ZnO ex-chl catalyst prereduced at 773 K was extremely low, and the level of conversion attained was <5 and it was not possible to measure the selectivities to the different products accurately. It is supposed that the more-intensive pretreatment notably decreases the concentration of active surface sites, because of sintering.

Turning the attention to the other platinum-based sample, the Pt/ZnO ex-nit catalyst, the dependence of conversion, and the selectivity to the different products, relative to time, is shown in Figure 5. The TON and some selectivity values are reported in Table 2.

The activity of this sample was slightly less than that corresponding to the Pt/ZnO ex-chl sample. Besides, Pt/ZnO ex-nit also showed a deactivation process.

The product distribution corresponding to the sample prepared from the nitrate precursor was completely different from that of the catalyst prepared from the chlorine precursor. The most important difference is that the Pt/ZnO ex-nit catalyst was less selective to crotyl alcohol than the Pt/ZnO ex-chl for the entire reaction time. As in the case of Pt/ZnO ex-chl, the production of crotyl alcohol was almost constant, but the levels of production attained for the ex-nit sample were lower than those corresponding to the ex-chl catalyst. Butanal was the main product for all of the reaction times.

The difference in the selectivity to crotyl alcohol of ex-nit and ex-chl samples cannot be explained, based on morphological aspects, because both catalysts present similar platinum particle sizes. It seems as if, for the ex-nitrate sample, a very low activation of C=O is achieved and concomitantly, the selectivity to crotyl alcohol is much lower than that corresponding to the
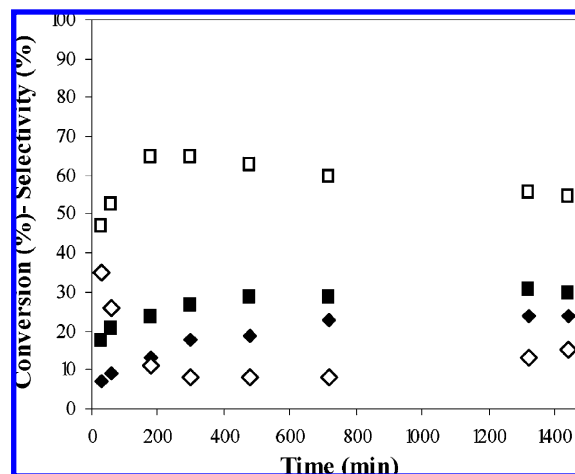

Figure 5. Variation of (◆) the conversion and the selectivity to (■) crotylalcohol, (◇) butanol, and (□) butanal with time for the hydrogenation of crotonaldehyde in the liquid phase over Pt/ZnO ex-nit (353 K, 400 kPa, 100 mg of catalyst).

ex-chlorine catalyst. The different selectivities toward crotyl alcohol between ex-nitrate and ex-chlorine samples would be related to the nature of the Pt−Zn alloy in each case. For the latter catalysts, the formation of the alloy between the noble metal and the promoter would be more extended than for the case of Pt/ZnO ex-nit, because of the presence of chlorine species. In this way, the same trends as those observed in the gas-phase hydrogenation of crotonaldehyde were observed.[19]

To clarify the role of chlorine species on the selectivity toward the hydrogenation of the carbonyl bond, the results obtained for the hydrogenation of crotonaldehyde over Pd/ZnO catalyst should be analyzed. For this sample, prepared from palladium chloride, the selectivity to crotyl alcohol (measured under the same experimental conditions as Pt/ZnO ex-nit and ex-chl) was almost nil. This result shows that the chlorine species supported on ZnO are not selective on its own right and that chlorine species acts as a promoter of platinum.

Conclusions

For the hydrogenation of crotonaldehyde in liquid-phase palladium catalysts supported on α,β-Al$_2$O$_3$ and ZnO, palladium catalysts modified with lead and zinc and Pt/ZnO catalysts were tested.

The selectivity to crotyl alcohol was nil for the monometallic palladium catalyst. For the promoted samples, the presence of oxidic species activates the carbonyl bond. However, the promotion effect is too low to consider practical employment of these catalysts. It is concluded that it is not possible to change the intrinsic selectivity of palladium toward the hydrogenation of molecules possessing both C=O and C=C bonds.

For the Pt/ZnO catalysts, an important enhancement of the selectivity to crotyl alcohol was observed, because of the formation of a Pt−Zn alloy. This effect is more marked on the sample prepared from H$_2$PtCl$_6$, probably because of a promotional effect of chlorine species. Both platinum catalysts prepared from the chlorine or the nitrate precursor become deactivated under reaction conditions. Polymerization or condensation products would be responsible for the deactivation of active platinum catalysts; however, at the same time, they improve the selectivity of platinum.

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