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Selective Hydrogenation of Cinnamaldehyde over Salt-Promoted Pd-Based Catalysts

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Abstract

The effect of salt additives ($AlCl_3$, $SnCl_2$, $FeCl_3$) on the catalytic behavior of $Pd_{3\%}/Al_2O_3$ catalyst in the selective liquid-phase hydrogenation of cinnamaldehyde in i-propanol was investigated at 25ºC and 4 bar H_2 for salt concentrations in the range 4.5×10^{-5}-5.0×10^{-3} M. The effect of added metal salts on the catalytic behavior of Pd/Al_2O_3 is rather complex. In the case of $AlCl_3$, a significant enhancement of the C=O bond hydrogenation could be achieved, accompanied by a strong suppression of the C=C bond hydrogenation. The selectivity towards cinnamyl alcohol formation could be raised from 26% to 70% by introducing small concentrations of $AlCl_3$ (~2.0×10^{-3} M) into the reaction mixture. Selectivity improvement was also observed upon the addition of $SnCl_2$ (up to 67%) and $FeCl_3$ (up to 70%), however, at the expense of activity which is believed to be due to poisoning of the Pd surface by metallic Fe and Sn. The mechanisms of the additives effects on the catalytic behavior of Pd/Al_2O_3 are discussed.

Keywords*:* Selective Hydrogenation; Cinnamaldehyde; Pd; Salt effect; Selectivity improvement.

Introduction

The selective hydrogenation of α,β-unsaturated aldehydes has been the subject of extensive research due to the wide industrial applications of their corresponding hydrogenation products [1,2]. An important representative of α,β-unsaturated aldehydes is cinnamaldehyde which is the main component of cassia oil (~90%) and Ceylon cinnamon bark oil (~75%), and is present in smaller quantities in many other essential oils. In addition to its application in perfume and flavor industries, cinnamaldehyde is used as a starting material to produce the more valuable unsaturated alcohol, cinnamyl alcohol. Cinnamyl alcohol has many applications; it is very much valued in perfumery, both for its odor characteristics and its fixative properties. Moreover, cinnamyl alcohol

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is an important building block in organic syntheses [3]. It is also an intermediate in the synthesis of pharmaceuticals, such as the antibiotic chloromycetin [1].

However, the production of cinnamyl alcohol via selective hydrogenation is a difficult task. This is because the formation of the saturated aldehyde is, from a thermodynamic point of view, favored over that of the unsaturated alcohol [4]. It is also well known that it is, in general, more easy to hydrogenate the unsubstituted isolated C=C double bond than to hydrogenate the isolated C=O aldehydic or ketonic group [5]. On technical scale, cinnamyl alcohol is prepared conventionally by the reduction of cinnamaldehyde either with alkali borohydrides [6] or with isopropanol or benzyl alcohol in presence of the corresponding aluminum alcoholate according to the Meerwein-Ponndorf reduction [1]. To a much lesser extent, cinnamaldehyde is also industrially prepared by the selective hydrogenation over osmium-on-carbon catalyst [7].

Compared with the traditional methods, the catalytic selective hydrogenation method is superior in saving resources, reducing waste disposal and protecting the environment [8,9]. This is the reason why catalytic research is being performed to optimize the heterogeneously catalyzed hydrogenation process. Thereby, the addition of promoters (salts, electropositive metals) to the hydrogenation-active catalyst (noble metals) was found to play an important role in enhancing the selectivity of the catalyst towards the industrially desired unsaturated alcohol [10-13].

Already in the twenties of last century, metal ion additives were used to improve the selectivity of platinum catalysts to unsaturated alcohols [14-15]. Both the rate of hydrogenation and the selectivity to cinnamyl alcohol were increased on platinum black or platinum oxide catalysts in the presence of iron chloride and zinc acetate [15]. These salts were also found to increase the yields of geraniol from citral [14]. The effect of cobalt, iron, tin and germanium chlorides on the Pt-catalyzed hydrogenation of cinnamaldehyde was investigated by Galvagno *et al*. [16]. A large increase in the rate of hydrogenation and in the selectivity to cinnamyl alcohol was observed and was attributed to a polarization of the C=O bond by the cations acting as Lewis acids. Yu *et al*. reported a remarkable increase in both the activity and selectivity of polymer-stabilized platinum colloid in the liquid-phase hydrogenation of cinnamaldehyde and crotonaldehyde upon modification with a series of metal cations [17, 18]. In the case of non-noble metals, the activity and selectivity of Co-B/SiO_2 amorphous catalyst in the hydrogenation of cinnamaldehyde could be enhanced by La-additives [19]. The promoting effect of La-dopant was attributed, among other reasons, to the presence of La^{2+} and La^{3+} species.

Aim of this study is to investigate the effect of salt additives on the catalytic behavior of Pd in the selective liquid-phase hydrogenation of cinnamaldehyde under mild conditions. Despite its inferior selectivity towards cinnamyl alcohol formation, Pd was chosen for two reasons: Our previous studies [20, 21] have shown that using Pd under mild reaction conditions simplifies significantly the reaction scheme and thus the kinetic treatment. In addition, the inferior selectivity of Pd appeared advantageous in selectivity promotion studies, since the slightest selectivity improvements could be easily recognized.

Experimental

Catalyst preparation

$Pd_{3\%}/Al_2O_3$ catalyst was prepared by impregnating γ-Al_2O_3 (Merck, BET surface area = 130 m^2/g [22]) with an acidified solution of $PdCl_2$ (Ferax Laboratories). The catalyst precursor was dried overnight at 120ºC, calcined for one hour under oxygen (Arab Gas Co.) at 350ºC followed by reduction with H_2 for 4 h at 400ºC. The Pd-particle size was estimated from the X-ray diffraction line of Pd to be ~120 nm.

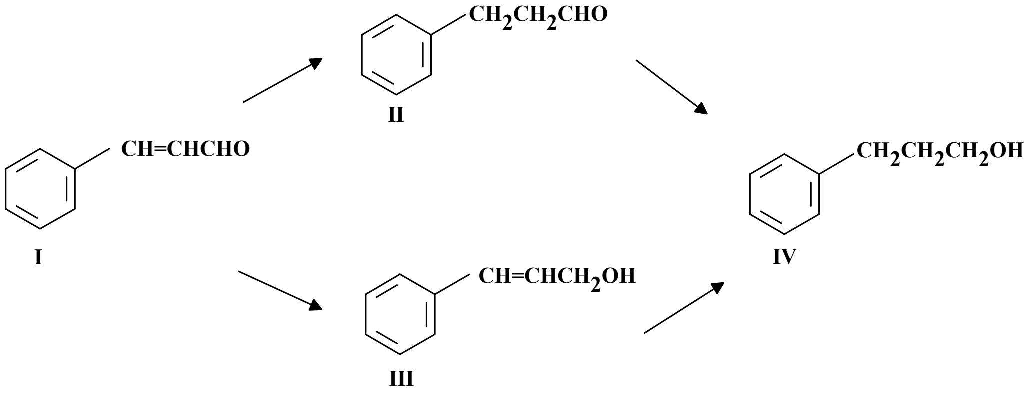
Liquid-phase hydrogenation of cinnamaldehyde

The hydrogenation reaction was carried out in a stainless steel hydrogenator (Parr-4842) with a Waltow-945 controller. Before reaction, the catalyst (0.100 g) was activated in the Parr-hydrogenator by heating in alternated cycles under hydrogen atmosphere and vacuum for one hour at 150ºC. After cooling to room temperature, 100 mL of 1% v/v (0.078 M) cinnamaldehyde in i-propanol were added into the reaction vessel. The reaction was then performed under constant hydrogen pressure of 4 bar. The reaction progress was monitored by taking ~ 0.50 mL samples at different time intervals for GC analysis (for details see [20]). The reaction products were analyzed by GC/MS (VG Analytical Instruments, VG 7070 E) for structure confirmation and product identification.

The effect of salt additives was investigated using the following salts: $FeCl_3.6H_2O$ (Panreac Quimica SA), $AlCl_3.6H_2O$ (Fluka) and $SnCl_2.4H_2O$ (Merck). The concentrations of these salts in the reaction mixture were in the range of 1×10^{-6} M to 1×10^{-2} M.

Results

Control experiments



Scheme 1

(Scheme 1) shows the general reaction pathways in the hydrogenation of cinnamaldehyde. Route 1 leads to the formation of the undesired product, phenylpropanal (II). Cinnamyl alcohol (III) is formed in Route 2 via the hydrogenation of the C=O double bond. Both cinnamyl alcohol (III) and phenylpropanal (II) can in principle be further hydrogenated to the corresponding saturated alcohol, phenylpropanol (IV). Control experiments have, however, shown that the hydrogenation of phenylpropanal to phenylpropanol (II→IV) does not take place under the mild reaction conditions applied in this study (25ºC and 4 bar H_2, 1 vol-% i-propanolic solution). This is in agreement with previous results obtained using Pd/SiO_2 catalysts in toluene as a solvent [20, 21]. Similar results were reported by Li *et al.* for the selective hydrogenation of cinnamaldehyde over Co-B amorphous alloy catalysts [4]. The reaction was, thereby, carried out in ethanol at 110ºC and 10 bar H_2 [4]. Indirect evidence for the low hydrogenation activity of the carbonyl group of phenylpropanal was reported by Cairns *et al.* in their investigation of the cinnamaldehyde hydrogenation on standard Pd/SiO_2 catalysts in decalin at 110ºC [23]. All these results indicate that it is more difficult to hydrogenate the isolated C=O (that in phenylpropanal) than the conjugated one (that in cinnamaldehyde).

In addition to the above mentioned hydrogenation products, two further products were obtained in minor quantities when i-propanol was used as a solvent. These products were identified by means of GC-MS as i-propyl and di(i-propyl) acetal of phenylpropanal. These acetal products can be formed, on the one hand, by the reaction of phenylpropanal (II) with i-propanol and/or by the reaction of cinnamaldehyde with i-propanol followed by the hydrogenation of the C=C double bond. To check the second possibility, control experiments were performed without catalyst or hydrogen aiming at elucidating the reactivities of cinnamaldehyde (I) and phenylpropanal (II) towards i-propanol. No reaction of cinnamaldehyde with i-propanol could be detected, indicationg that the obtained acetal and semi-acetal come only from the reaction of phenylpropanal with i-propanol. Phenylpropanal diethyl acetal was reported to form in the selective hydrogenation of cinnamaldehyde in ethanol at 308 K using Pt-based catalysts [24]. The reaction scheme proposed by Li *et al.* (Co catalyst in ethanol) suggests also that the acetal is formed directly from phenylpropanal [4], supporting, thus, our results.

In most cases, the formation of acetal by-products can be neglected. It must be noted, however, that when metal salts are added to the reaction solution, acetal formation was largely enhanced and can, therefore, be no more neglected (figure 1). This enhancement of acetal formation due to added metal salts is not surprising, since the added metal salts ($FeCl_3$, $SnCl_2$, $AlCl_3$) are acidic. Acetal formation is known to be an acid catalyzed reaction. The extent of acetal formation was found to depend on the type of added metal salt (figure 1). Whereas in the case of 0.005 M $FeCl_3$ acetal formation did not exceed 2% after 200 min of the reaction of phenylpropanal with i-propanol (without catalyst or hydrogen), acetal by-products were in the case of 0.0050 M $AlCl_3$ observed to reach 9% in 250 min. With 0.0050 M $SnCl_2$, intermediate values were obtained (figure 1).

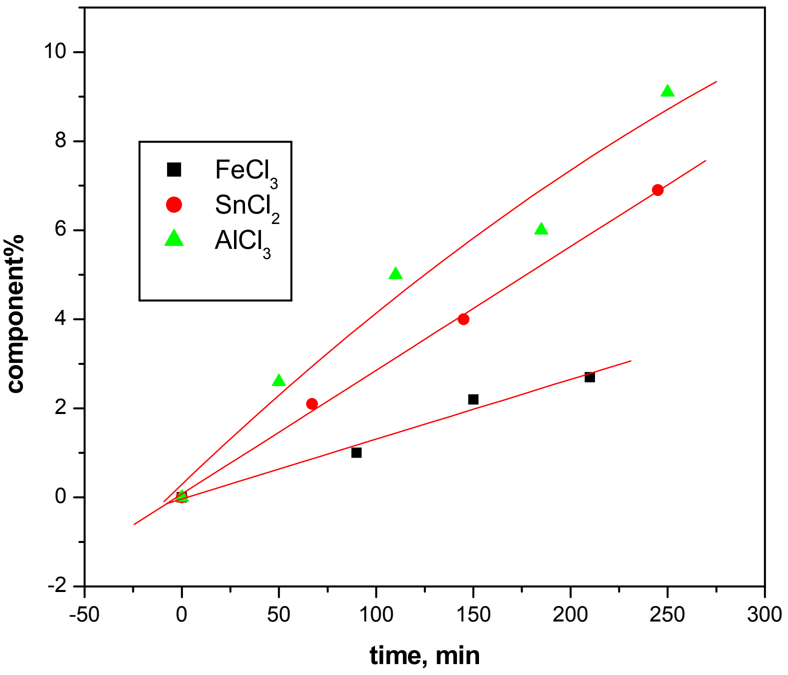
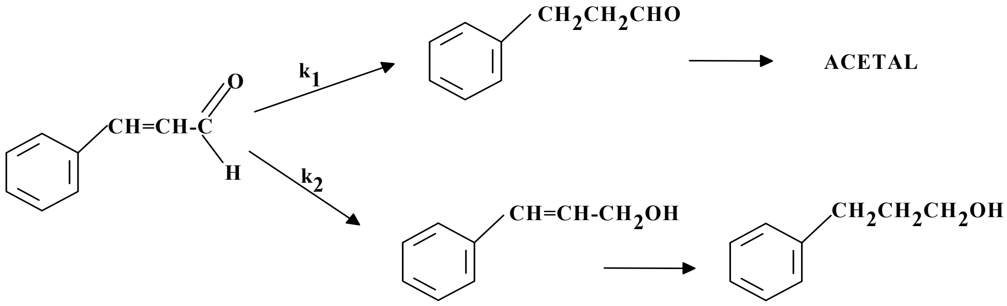


Figure 1. Effect of metal salts (0.0050 M) on Reaction of 1-vol% phenylpropanal with i-propanol at 25°C. Reaction performed without a catalyst and without hydrogen.

Based on these results, the general reaction scheme (Scheme 1) can be modified for the reaction conditions applied in this study (room temperature, 4 bar H_2 and Pd-based catalyst in i-propanol) as shown in (Scheme 2).



Scheme 2

With help of scheme 2, we can define now the selectivity towards cinnamyl alcohol formation, S_{ol}, as follows:

$$S_{ol}\% = \frac{k_2}{k_1 + k_2}.100\%$$

where, k_1 is the rate constant for route **1** and k_2 is the rate constant for route **2**. k_1+k_2 is set equal to k, the total rate constant of cinnamaldehyde hydrogenation. k corresponds, thereby, to the catalytic activity. If k_2 was substituted by the concentrations of the hydrogenation products formed via route **2**, and $k_1+k_2=k$ was substituted by the sum of the concentrations of all hydrogenation products and acetal by-products (which corresponds to the conversion), then the expression for selectivity, S_{ol}, would read as follows:

$$S_{ol}\% = \frac{[cinnamylalcohol]\% + [phenylpropanol]\%}{conversion\%} \cdot 100\%$$

An example of the results obtained in our experiments is depicted in (figure 2) for cinnamaldehyde hydrogenation at 25ºC and 4 bar in i-propanol with 4.5×10^{-5} M $AlCl_3$ as promoter. The initial rate of reaction, $rate_0$, is used in this study as a measure for the catalytic activity. It can be extracted from the decline in the cinnamaldehyde concentration in the initial range of reaction. Thus,

$$rate_0 = [CALD]_0 \frac{x}{t}$$

with $[CALD]_0$ being the initial concentration of cinnamaldehyde and x is the conversion in time t.

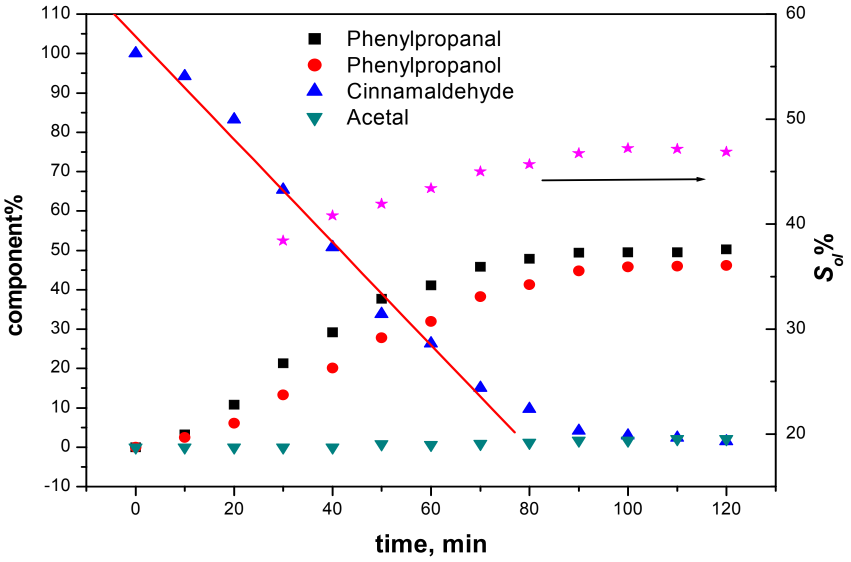


Figure 2: Conversion and product distribution in the hydrogenation of cinnamaldeyde over $Pd_{3\%}/Al_2O_3$ in i-propanol with 4.5×10^{-5} M $AlCl_3$ at 25°C and 4 bar H_2.

In a previous study [20], the kinetics of cinnamaldehyde hydrogenation over Pd was investigated under mild conditions in detail. The reaction was found to be zero-order with respect to cinnamaldehyde concentration. Accordingly, the reaction rate must be equal to the rate constant, hence $\boldsymbol{rate_0 = k}$.

From (figure 2), it is obvious that the selectivity, $S_{ol}\%$, is almost constant, especially at the end of the linear range. This constancy in the $S_{ol}\%$-value is an indication for the fact that phenylpropanal is not hydrogenated under reaction conditions. Otherwise, the amount of phenylpropanol would increase at the expense of phenylpropanal leading to a continuous increase in $S_{ol}\%$.

It is also important to notice that no appreciable amounts of cinnamyl alcohol were formed during the reaction. The reason behind this behavior is the fact that the hydrogenation of cinnamyl alcohol to phenylpropanol is, as could be determined in a previous study [20], about 30 times faster than the hydrogenation of cinnamaldehyde to cinnamyl alcohol. Consequently, any produced cinnamyl alcohol is simply transformed readily into phenylpropanol. These results indicate the easiness of the hydrogenation of isolated C=C double bond (that in cinnamyl alcohol) compared to that of isolated C=O (that in phenylpropanal), in agreement with kinetic expectations [5].

Effect of $FeCl_3$

The effect of $FeCl_3$ on the selective hydrogenation of cinnamaldehyde in i-propanol was investigated for $FeCl_3$ concentrations in the range 4.5×10^{-5}-3.6×10^{-3} M. Figure 3 summarizes the effect of added $FeCl_3$ on the catalytic activity (k) and on the selectivity (S_{ol}%) of the used $Pd_{3\%}/Al_2O_3$ catalyst at 25°C and 4 bar H_2. The S_{ol}%-values presented in (figure 3) are average values of the S_{ol}%-time series obtained in each experiment corresponding to a specific $FeCl_3$ concentration. In all experiments, the selectivity, S_{ol}%, fluctuates in a range between 5-10%. With help of the experimentally obtained values for the catalytic activity ($k=k_1+k_2$) and the average value of selectivity ($S_{ol}\%=100\%*k_2/(k_1+k_2)$), it is possible to determine k_1 and k_2. Their values are represented in (figure 3) as a function of the concentration of $FeCl_3$ in the reaction mixture.

Two concentration regions can be recognized in (figure 3): one for $FeCl_3$ concentrations below 5×10^{-4} M and one for $FeCl_3$ concentrations higher than 5×10^{-4} M. In the low concentration region, the total catalytic activity (k) is almost not affected by added $FeCl_3$. Thereby, k_1 is only slightly suppressed by increased $FeCl_3$ concentration and attains about 75% of its unmodified value (i.e., without $FeCl_3$) when the $FeCl_3$ concentration reaches 5×10^{-4} M. On the other hand, k_2 is slightly enhanced (by about 35%), leading to a slight improvement in selectivity (from 25% to 40%) in this concentration region. At $FeCl_3$ concentrations higher than 5×10^{-4} M, a strong abrupt deactivation of the catalyst takes place. Both k_1 and k_2 are, thereby suppressed. k_1 (i.e., the C=C hydrogenation) is, however, much more strongly suppressed than k_2 (C=O hydrogenation). Consequently, an improvement in selectivity is observed and selectivity values as high as 70% could be obtained.

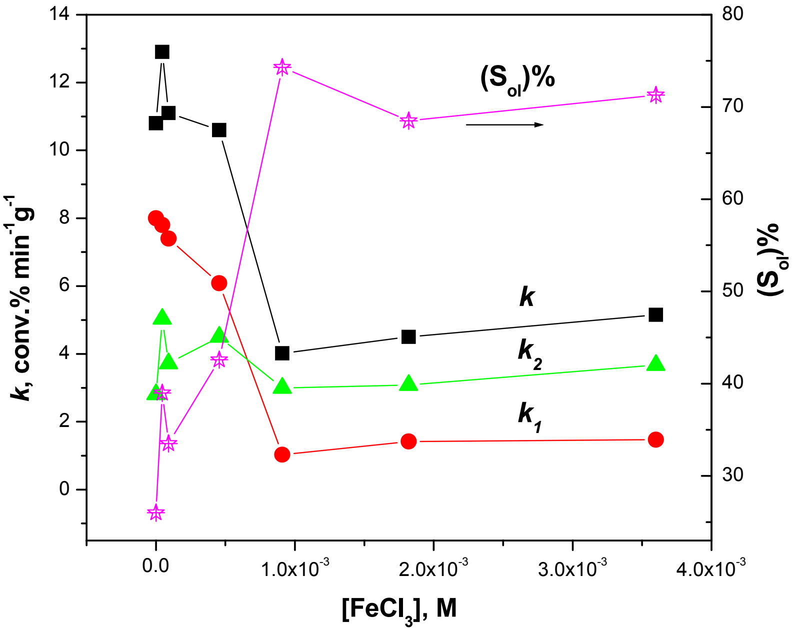


Figure 3. Effect of added $FeCl_3$ on activity and selectivity of $Pd_{3\%}/Al_2O_3$ in cinnamaldehyde hydrogenation in i-propanol at 25°C and 4 bar H_2.

Effect of $SnCl_2$

The effect of $SnCl_2$ on the selective hydrogenation of cinnamaldehyde in i-propanol was investigated in the concentration range 9.1×10^{-5}-1.0×10^{-2} M. At $SnCl_2$ concentrations > 1.0×10^{-3} M, indications of catalyst poisoning are observed. For example, at $SnCl_2$ concentration of 0.01 M , only 20% conversion could be achieved within the first 50 minutes of reaction. Beyond this point, no change in the conversion was observed. Also at $SnCl_2$ concentrations of 4.5×10^{-3} M and 6.8×10^{-3} M, a plateau in the cinnamaldehyde concentration was observed to get established after about 80 min of reaction, an indication of complete activity loss at that stage.

In all experiments with $SnCl_2$ additives, acetal formation was found to take place yielding appreciable amounts that cannot be neglected. At $SnCl_2$ concentration of 4.5×10^{-4} M and 9.1×10^{-4} M, the fraction of acetal reaches about 10%. It is, however, remarkable that the amount of acetal formed does not correlate with the concentration of $SnCl_2$. With the highest $SnCl_2$ concentration used in this work (0.010 M), the acetal formation did not exceed 2%. Also with 6.8×10^{-3} M, only 2-3% acetal could maximally be observed. Instead, a correlation can be recognized between acetal formation and the catalyst activity. The acetal formation was highest when the catalytic activity was highest. One possible explanation of this behavior is that acetal formation depends on the concentration of phenylpropanal. The latter is formed during the reaction and its concentration is maximum, the higher the catalytic activity.

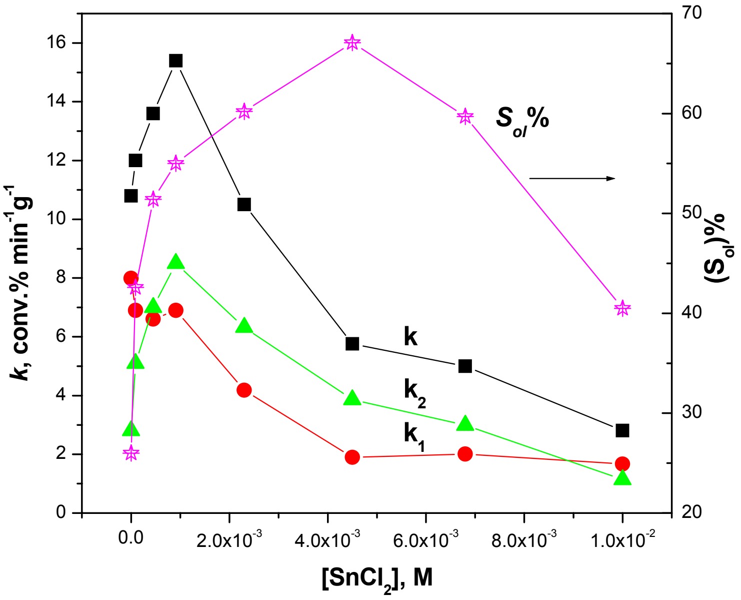


Figure 4. Effect of added $SnCl_2$ on activity and selectivity of $Pd_{3\%}/Al_2O_3$ in cinnamaldehyde hydrogenation in i-propanol at 25°C and 3 bar H_2.

Figure 4 summarizes the effect of added $SnCl_2$ on the catalytic activity (k) and selectivity (S_{ol}%) of the used $Pd_{3\%}/Al_2O_3$ catalyst at 25°C and 4 bar H_2. A significant increase in the catalytic activity from 10.8 to 15.4 conv.% $min^{-1}g^{-1}$ (i.e., by ~50%) is observed as the concentration of $SnCl_2$ is increased from zero to 9.1×10^{-4} M. This increase in activity corresponds mainly to an increase in the k_2-value. k_1 is initially slightly suppressed then remains unchanged until 9.1×10^{-4} M. Accordingly, S_{ol}% increases from 26% to 55% at 9.1×10^{-4} M, as evident in (figure 4).

At $SnCl_2$ concentrations > 9.1×10^{-4} M, a sharp significant decrease in the catalytic activity occurs. Both k_1 and k_2 are suppressed, but k_1 is more affected than k_2. Consequently, the S_{ol}%-value increases further to 67%. At 4.5×10^{-3} M $SnCl_2$, k_1 reaches its smallest value and remains at higher concentrations unchanged. In the same concentration range (> 4.5×10^{-3} M), k_2 keeps decreasing. This leads to a decrease in S_{ol}%. The strong deactivation at concentrations higher than 9.1×10^{-4} M is probably due to catalyst poisoning by adsorbed or reduced Sn-species on the Pd surface, as will be discussed further in section 4.1.

Effect of $AlCl_3$

The effect of $AlCl_3$ on the selective hydrogenation of cinnamaldehyde in i-propanol was investigated in the concentration range 9.1×10^{-5}-1.0×10^{-2} M. No indications of catalyst poisoning were observed at any used $AlCl_3$ concentration.

In all experiments with $AlCl_3$ additives, acetal formation was found to take place yielding appreciable amounts that cannot be neglected. At $AlCl_3$ concentration of 4.5×10^{-4} M, 9.1×10^{-4} M and 2.3×10^{-3} M, the fraction of acetal reaches ~10-12%.

Figure 5 summarizes the effect of added $AlCl_3$ on the catalytic activity (k) and selectivity (S_{ol}%) of the used $Pd_{3\%}/Al_2O_3$ catalyst at 25°C and 4 bar H_2. In the concentration range < 4.5×10^{-4} M $AlCl_3$, k_1 experiences a sharp drop losing about 40% of its initial value (i.e., when no $AlCl_3$ was added). At the same time, k_2 increases significantly by 2.5 times the initial value without $AlCl_3$, corresponding to 250% increase. As a result of the increase in k_2 and the decrease in k_1, S_{ol}% increases and reaches ~55% at 4.5×10^{-4} M $AlCl_3$. At higher $AlCl_3$ concentrations, k_1 remains unchanged while k_2 keeps growing but with a slower rate reaching a plateau at ~10 conv.% $min^{-1}g^{-1}$. Consequently, a plateau in S_{ol}% is observed at ~70%.

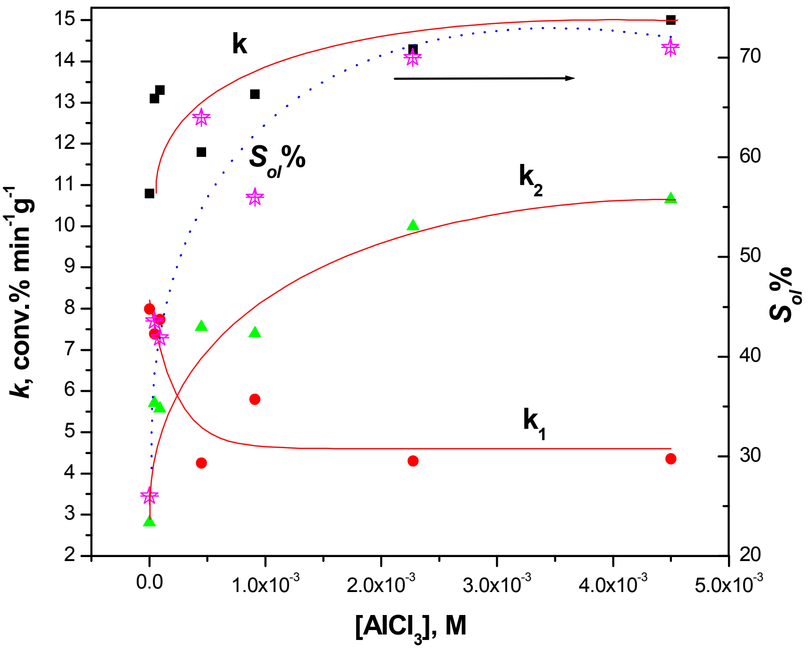


Figure 5. Effect of added $AlCl_3$ on activity and selectivity of $Pd_{3\%}/Al_2O_3$ in cinnamaldehyde hydrogenation in i-propanol at 25°C and 4 bar H_2.

Disscussion

Do metal cations undergo reduction by hydrogen?

Unfortunately, reduction potentials of metal cations in i-propanol are not available to answer the above question. However, the standard reduction potentials in water, E^0, appear to be helpful regarding this issue. From the reported values of the reduction potential in concern ($E^0_{Al^{3+}/Al} = -1.66\ V$, $E^0_{Sn^{2+}/Sn} = -0.14\ V$, $E^0_{Fe^{3+}/Fe} = -0.036\ V$), we may conclude that the reduction of Al^{3+} is far improbable, even when the hydrogen pressure is 4 bar. The high reduction potential for the reduction of Fe^{3+} to metallic iron (-0.036 V) implies that such a reduction may, in principle, be possible under above conditions. In a control experiment, a solution of 5.0×10^{-4} M $FeCl_3$ in i-propanol was hydrogenated with 4 bar H_2 over 0.100 g $Pd_{3\%}/Al_2O_3$. The concentration of $FeCl_3$ was followed spectroscopically with time and was found to decrease exponentially. Such a decrease in $FeCl_3$ concentration in solution is caused by the adsorption of $FeCl_3$ on the catalyst surface, where Fe^{3+} reduction may eventually take place. Reduction to Fe^{2+} is also possible ($E^0_{Fe^{3+}/Fe^{2+}} = +0.77\,V$). UV-Vis spectroscopy indicates, however, that the solution is Fe^{2+} free. On the other hand, this does not exclude its presence on the catalyst surface.

Consideration of the effect of $AlCl_3$ concentrations on the catalytic behavior of $Pd_{3\%}/Al_2O_3$ (figure 5) delivers important hints that are useful in answering the above question, whether reduction of Fe^{3+} and Sn^{2+} did take place or not. No indications of catalyst deactivation were observed in the case of $AlCl_3$ (figure 5). Instead, a slight increase in the total activity has been recorded. Now, there is no reason to believe that the adsorption of $FeCl_3$ or $SnCl_2$ is stronger than that of $AlCl_3$. Catalyst poisoning due to $FeCl_3$ and $SnCl_2$ adsorption is, therefore, not more probable than that due to $AlCl_3$. Yet, deactivation occurs in the case of $FeCl_3$ and $SnCl_2$ but not in the case of $AlCl_3$. By comparing (figures 3-5), it is also obvious that deactivation in presence of $FeCl_3$ occurs at lower concentrations than in presence of $SnCl_2$, whereas in presence of $AlCl_3$ no deactivation occurs at all. This order in deactivation easiness is the same order of the corresponding redox pairs in the activity series in aqueous solutions.

These observations suggest, thus, that the reduction of Fe^{3+} and Sn^{2+} did actually take place under reaction conditions. Experimental findings from other groups support this conclusion, although the reduction conditions in these studies are more severe than those applied in this work. Richard *et al*. investigated the effect of $FeCl_2$ additives to Pt catalysts on cinnamaldehyde hydrogenation in i-propanol at 100°C and 60 bar H_2 [13]. Both the initial rates and the initial selectivities were improved with increased [$FeCl_2$] added to the Pt/C containing slurry. A volcano-type behavior was observed with a maximum in activity and selectivity at Fe-to-Pt ratio of 0.3. After reaction, the catalyst grains were cut into thin sections and analyzed by energy-dispersive x-ray spectrometry with a 1.5-nm spatial resolution. Richard *et al*. found that almost all Fe^{2+} were reduced on Pt and that iron adatoms deposited on the surface of Pt. Also, Jung *et al*. investigated the hydrogenation of maleic anhydride over Pd-Sn/SiO_2 catalysts in the liquid phase [25]. The bimetallic catalysts were prepared by co-impregnating SiO_2 with acidified aqueous solutions of $PdCl_2$ and $SnCl_2$, followed by reduction with H_2 at 200°C. XPS analysis of the prepared catalyst showed that under above conditions, 16% of all tin was reduced to the zero-valent state [25].

General mechanisms of selectivity promotion in the selective hydrogenation of α,β-unsaturated aldehydes

Most of the reports concerning selectivity promotion in the selective hydrogenation of α,β-unsaturated aldehydes were devoted to catalytic systems where activity and selectivity of platinum group metals were modified with a more electropositive metal [10, and references therein]. The mechanisms invoked to explain the observed enhancement in selectivity to the unsaturated alcohol are presented below:

Mechanism 1*: Electrophilic activation of the C=O bond.*

The added electropositive metal or the added oxidized metal species present on the hydrogenation active metal or in its closest vicinity acts as an electrophilic site or as a Lewis site on which the adsorption through the C=O bond is enhanced as a result of the interaction of the oxygen lone electron pair with the proposed electrophilic or Lewis sites. Thus, the C=O bond hydrogenation probability is increased.

According to this mechanism, selectivity promotion is attributed to the enhancement in the C=O hydrogenation (i.e., to an increase in k_2, Scheme 2). The hydrogenation of the C=C bond (k_1, Scheme 2) shouldn't be affected by the presence of such electrophilic or Lewis sites. This mechanism is the most frequently invoked one to explain the selectivity promotion by electropositive species [e.g., 16, 26-30].

Mechanism 2: *Suppression of C=C adsorption.*

The presence of an electropositive metal on or in closest vicinity to the hydrogenation active metal leads to an increase in the electron density of the latter. This results in a greater repulsion between the d-orbital electrons of the hydrogenation active metal with the C=C bond electrons, disfavoring, thus, the adsorption through the C=C bond. The electron transfer from the electropositive metal to the hydrogenation active metal was experimentally identified in the case of Fe/Pt system by means of x-ray absorption edge spectroscopy [31]. Such an electron transfer from Fe to Pt was predicted in the theoretical study of Delbecq and Sautet of this mechanism [32].

According to this mechanism, the C=C adsorption is inhibited. k_1 should, therefore, decrease. Only small enhancement of the C=O bond adsorption would be expected due to increased backdonation into π^*_{CO} (only small increase in k_2, if any).

Mechanism 3: *Geometric dilution effect.*

Adsorption of α,β-unsaturated aldehydes in the η^4-(C-C-C-O) mode occurs on ensembles with multi-adsorption sites. It requires at least two atoms of the hydrogenation active metal in proper distance to each other to take place. By incorporation of hydrogenation inactive atoms in and/or above such ensembles, the metal atoms become rather isolated from each other, the ensemble is simply destroyed and multi-sites adsorption will be inhibited. On Pd(111), the η^4 adsorption mode is the most favorable one [33].This adsorption mode is, however, nonselective because it is a precursor for the 1,4-addition, the product of which is enol that isomerizes into the corresponding saturated aldehyde. In the case of Pd, the inhibition of this mode will decrease k_1, and thus increase the selectivity to unsaturated alcohol. In the same manner, destruction of active ensembles to further extents leads to the inhibition of the di-σ_{CC} and di-σ_{CO} modes, making thus the η^1-on top mode (adsorption through oxygen atom of the carbonyl group) the only possible adsorption mode. The latter is a precursor for C=O bond hydrogenation and the selectivity to unsaturated alcohols is increased (see e.g., [21, 34]).

Selectivity promotion by salt additives

It is plausible to invoke mechanism 1 to explain the selectivity promotion effect of salts. Metal cations are Lewis acids. They are, therefore, expected to interact strongly with the oxygen atom of the carbonyl group making, thus, the adsorption via this group over Pd more preferable. Mechanism 1, however, doesn't predict any effect on k_1. The strong dependence of k_1 on the salt concentration, as presented in (figures 3 – 5), indicates that the situation is more complex to be explained simply by mechanism 1 alone. Mechanism 2 and/or mechanism 3 must be invoked to explain the observed suppression in k_1 presented in (figures 3 – 5).

An XPS investigation of Sn-Pd surface alloys on Pd(111) provides evidence to strong Sn-induced perturbation of the electronic structure of Pd upon alloying, consistent with charge transfer from Sn → Pd [35]. The same result was reported for an XPS investigation of Pd-Sn/SiO_2 catalysts prepared by co-impregnation [25]. Such a charge transfer will increase the electron density on Pd, increasing thus the four-electron Pauli repulsion with the π_{CC} electrons. The adsorption through the C=C bond is, therewith, inhibited and k_1 decreases. An electron donating effect from Sn → Pt was also drawn to explain the selectivity promoting effect of tin, where the selectivity to unsaturated alcohol increased from 0% to 75% in the case of cinnamaldehyde hydrogenation and from 30% to 60% in the case of acrolein hydrogenation as 15 atom% of tin was loaded in the Pt catalyst [36]. In agreement with the above picture, the cyclohexane hydrogenation rate was found to decrease upon modification of Pt-based catalysts with Sn [34].

No reference is available at the moment that confirms experimentally the charge transfer from Fe → Pd. It was however confirmed in the related Fe-Pt system [31]. The electronic effect of Fe would be hence similar to that of Sn mentioned above.

Mechanism 3 cannot be neglected. Once formed, Sn and Fe atoms are strongly bound to the surface. Their presence on the surface would prevent the adsorption in the η^4 mode that requires multi-adsorption sites. The fact that k_1 is more affected than k_2 in the catalyst deactivation at high $FeCl_3$ and $SnCl_2$ concentrations (Figures 3 and 4) confirms that mechanism 3 plays an important role with respect the selectivity promoting effects of salt additives. Such a geometric effect of dilution was proposed to explain the inhibition of the double bond isomerization ability of Pd upon Sn addition in the liquid phase hydrogenation of 1,5- and 1,3-hexadienes over Pd [37], a reaction that is known to require multi-adsorption sites.

Mechanism 3 is also necessary to explain the decrease in k_1 observed in the case of $AlCl_3$, where no reduction of Al^{3+} into zero-valent Al is expected to take place.

However, the interaction of $AlCl_3$ with the Pd surface under reaction conditions seems to be rather weak, and the number of adsorbed cationic species is, therefore, limited. This can be concluded from the fact that k_1 drops to ~56% of its initial value, which is a relatively high value, compared to that obtained in the case of $FeCl_3$ and $SnCl_2$. We observe also no negative effect on k_2, indicating that no poisoning of the catalyst took place. The concentration of Al-species adsorbed on Pd seems to be low and rather constant; it is not affected much by increasing the $AlCl_3$ concentration in solution. We believe that due to the weak interaction of $AlCl_3$ with Pd, adsorbed Al^{3+}-species is rather mobile. It can migrate to the Pd crystallite boundaries where it can interact more strongly with the oxide support. It is noteworthy that Al^{3+} at the boundaries of the Pd crystallite can still activate the C=O bond according to mechanism 1, but it has no geometric dilution effect. As these boundaries become completely occupied, no further enhancement of k_2 is induced corresponding to the experimentally observed plateau in k_2 and k (figure 5).

Conclusions

In this work, the selective hydrogenation of cinnamaldehyde in liquid phase was investigated under mild conditions (25°C and 4 bar H_2). Major point of interest was, thereby, to study the effect of salt additives on the catalytic behavior of alumina supported Pd catalysts, specially its selectivity to the hydrogenation of the carbonyl group.

The effect of added metal salts on the catalytic behavior of $Pd_{3\%}/Al_2O_3$ is rather complex. In the case of $AlCl_3$, A significant enhancement of the C=O bond hydrogenation could be achieved, accompanied by a strong suppression of the C=C bond hydrogenation. The selectivity towards the formation of cinnamyl alcohol could be raised from 26% to 70% by introducing small concentrations of $AlCl_3$ ($\sim 2.0\times10^{-3}$ M) into the reaction mixture.

In the case of $SnCl_2$ and $FeCl_3$, reduction of adsorbed Fe^{3+} and Sn^{2+} into the corresponding zero-valent state is believed to occur. The formation of adsorbed metallic Fe and Sn over the Pd surface has been drawn to explain the poisoning of the Pd catalyst when relatively high concentrations of these salts were used. At low $SnCl_2$ concentrations, a significant increase in the catalytic activity and selectivity (up to ~55%) was observed and found to correlate with an enhancement in the C=O bond hydrogenation. In the case of $FeCl_3$, selectivity was found to increase up to ~70%. At that stage, the Pd catalyst experiences, however, large loss of activity.

The rather complex effect of metal salts on the catalytic properties of $Pd_{3\%}/Al_2O_3$ can not be explained by a single mechanism. It is obviously the result of the cooperation of more than one of these three mechanisms.

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