Selective hydrogenation of cinnamaldehyde over Pd/SiO$_2$ catalysts: selectivity promotion by alloyed Sn

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Abstract

The effect of added Sn on the catalytic behavior of Pd/SiO$_2$ sol-gel catalysts in the liquid-phase hydrogenation of cinnamaldehyde at 25 °C and 3 atm H$_2$ pressure was studied for Sn-loadings ranging from 0 to 3%. Sn–Pd alloying could be confirmed by means of X-ray diffraction (XRD)-measurements. Although no significant amounts of cinnamyl alcohol could be detected, added Sn was found to have a positive effect on selectivity by increasing the rate constant ratio (k_2/k_1) of the hydrogenation route to cinnamyl alcohol to that producing phenylpropanal. Produced cinnamyl alcohol reacts, however, consecutively and very rapidly to phenylpropanol. The observed promotion of selectivity (however, at the expense of activity) is discussed and attributed to both geometric and electronic effects of alloying Pd with Sn, resulting in a strong suppression of the rate of forming the saturated aldehyde rather than enhancing the rate of forming cinnamyl alcohol.
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1. Introduction

The selective hydrogenation of α,β-unsaturated aldehydes has been the subject of great interest, manifested in the large numbers of articles published on this issue ([1] and references therein). This is due to the important role this reaction plays in the production of fine chemicals for perfume and pharmaceutical industries [2–4], as well as due to the importance of the semi-hydrogenated products such as cinnamyl alcohol as a building block in organic synthesis [2]. From a thermodynamic point of view, the formation of saturated aldehyde and/or saturated alcohol is favored over that of unsaturated alcohol. It is also well known that it is, in general, more easy to hydrogenate the unsubstituted isolated C=C double bond than the isolated C=O aldehydic or ketonic group [5]. It is, however, possible to increase the selectivity towards the industrially more desired unsaturated alcohol by manipulating the catalyst properties, e.g. by adding promoters [1,6–8].

Due to the good results it showed, Sn has been widely investigated as a selectivity promoter [1,9–21]. For example, Poltarzewski et al. [12] have studied the hydrogenation of cinnamaldehyde and acrolein on nylon supported bimetallic Pt-Sn catalysts. The authors reported an increase in selectivity from 0 to 75% in the case of cinnamaldehyde and from 30 to 60% in the case of acrolein as 15 at.% Sn is loaded. In the hydrogenation of citral, intermediate loadings of Sn were also reported to produce a fivefold increase in the catalytic activity of Pt catalyst, accompanied by an increase in the selectivity to unsaturated alcohols

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from 65 to 90% [13]. Most of these studies are concerned with Pt as a hydrogenation active catalyst, and to a much lesser extent with Rh, Ru and Cu. To our knowledge, no attempt has been made to promote the selectivity towards cinnamyl alcohol by adding Sn to Pd catalysts. This is probably due to the fact that Pd has an extremely poor selectivity in this reaction, compared to Pt, Ir and Os ([1] and references therein). On the other hand, Sn-promoted Pd catalysts could be successfully used in the selective hydrogenation of dienes to olefins and were shown to have improved selectivities over the unpromoted Pd catalysts [22,23].

In this work, we aim at investigating the enhancement effect of Sn on the catalytic behavior of Pd in the liquid-phase hydrogenation of cinnamaldehyde under mild conditions.

2. Experimental

$Pd_{3\%}Sn_x/SiO_2$ catalysts ($x = 0$, 0.15, 0.3, 0.45, 0.75, 1 and 3%) were prepared by the sol-gel method. Pd and Sn were obtained as $PdCl_2$ (Ferax Laboral) and $SnCl_2 \cdot 2H_2O$ (BDH), respectively. Cinnamaldehyde (97%, Merck) and toluene (Acros) were used without further purification. The SiO_2 sol-gel support was prepared from tetraethoxysilane (Fluka). Helium and hydrogen gases (Arab Gas Co.) were purified from water vapor and oxygen gas by using proper O_2 and H_2O traps.

2.1. Catalyst preparation

Samples of the sol-gel catalysts (~5 g each) were prepared by mixing aqueous solutions of proper concentrations of $PdCl_2$ (in HCl/H_2O), and $SnCl_2$ with absolute ethanol and tetraethoxysilane following procedure in [24]. At the end of this preparation process, sol-gel catalysts with high surface area were produced (~450 m^2/g). The BET surface area of the obtained sol-gel catalysts was measured using a specially built, modified and calibrated N_2 adsorption single-point glass apparatus [25].

2.2. Liquid-phase hydrogenation of cinnamaldehyde

Catalysts were activated before use by heating at 450 °C under hydrogen atmosphere for 1 h, and then

cooling to room temperature. One hundred-milliliter samples of 1% (v/v) (0.0770 M) cinnamaldehyde in toluene were added with a 0.50 g catalyst sample of each catalyst into the reaction vessel of a Parr-hydrogenator. These reactions were performed under various conditions of temperature (298, 313, 323, 323, 343 and 353 K) and 3 atm hydrogen pressure, in a 100 ml s.s. Parr-hydrogenator (Parr-4842) with a Watlow-945 controller. The reaction progress was monitored by taking ~0.50 ml samples at different time intervals for GC analysis according to procedure in [26]. The reaction products were also analyzed by GC/MS (VG Analytical Instruments, VG 7070 E) for structure confirmation.
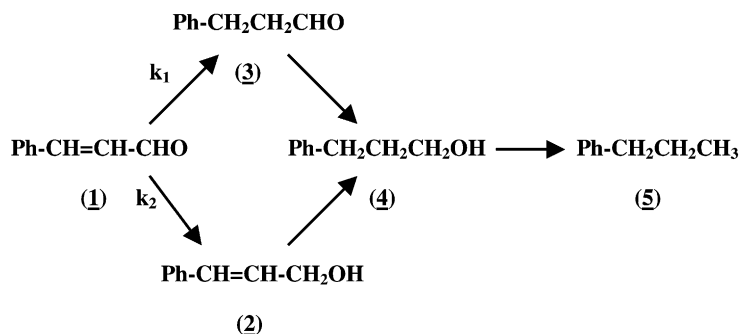
2.3. XRD

X-ray diffraction (XRD)-measurements were performed for the catalyst samples on a Phillips-PW 1729 generator, connected to a computer, using Cu Kα-tube ($\lambda = 1.5418$ Å) in the range of $2\theta = 30$–$90°$ with a scanning rate of 0.5°/min.

3. Results

3.1. General remarks

Scheme 1 represents the general routes of the hydrogenation of cinnamaldehyde (1) over noble metal catalysts. The 1,2-addition gives the unsaturated alcohol (cinnamyl alcohol (2)), the 3,4-addition gives the saturated aldehyde (phenylpropanal (3)) and the 1,4-addition gives the enol product that isomerizes into phenylpropanal (3). Further hydrogenation leads to the formation of phenylpropanol (4), that can also be hydrogenated to propylbenzene (5).

In the hydrogenation of cinnamaldehyde over Pd and Sn-modified Pd-catalysts under 3 atm H_2 and 25 °C, mainly phenylpropanal (3) and phenylpropanol (4) were obtained as major reaction products. In the cases of higher Sn-loadings (larger than 0.5%), minor quantities of cinnamyl alcohol (2) were also detected, but no traces of propylbenzene (5) could in any experiment be observed. The product distribution for the hydrogenation of cinnamaldehyde over $Pd_{3\%}Sn_{1\%}$ under 3 atm H_2 at 25 °C is shown as an example in Fig. 1.

Ph-CH₂CH₂CHO

k_1 (3)

Ph-CH=CH-CHO → Ph-CH₂CH₂CH₂OH ⟶ Ph-CH₂CH₂CH₃

(1) k_2 (4)   (5)

Ph-CH=CH-CH₂OH

(2)

Scheme 1.

In a previous study [26], the authors showed that all phenylpropanol produced during the hydrogenation of cinnamaldehyde over Pd-based catalysts at 25 °C does entirely come through the second route, i.e. through the consecutive hydrogenation of the formed cinnamyl alcohol. Control experiments have shown that the hydrogenation of phenylpropanal over Pd/SiO₂ catalysts does not occur significantly at 25 °C. Whereas, the hydrogenation of cinnamyl alcohol proceeds very fast, 30 times faster than the hydrogenation of cinnamaldehyde to cinnamyl alcohol [26]. Based on these facts, a selectivity measure, S_{ol}, is now introduced and is defined as,

$$S_{ol} = \frac{\text{phenylpropanol\% + cinnamyl alcohol\%}}{\text{conversion\%}}$$

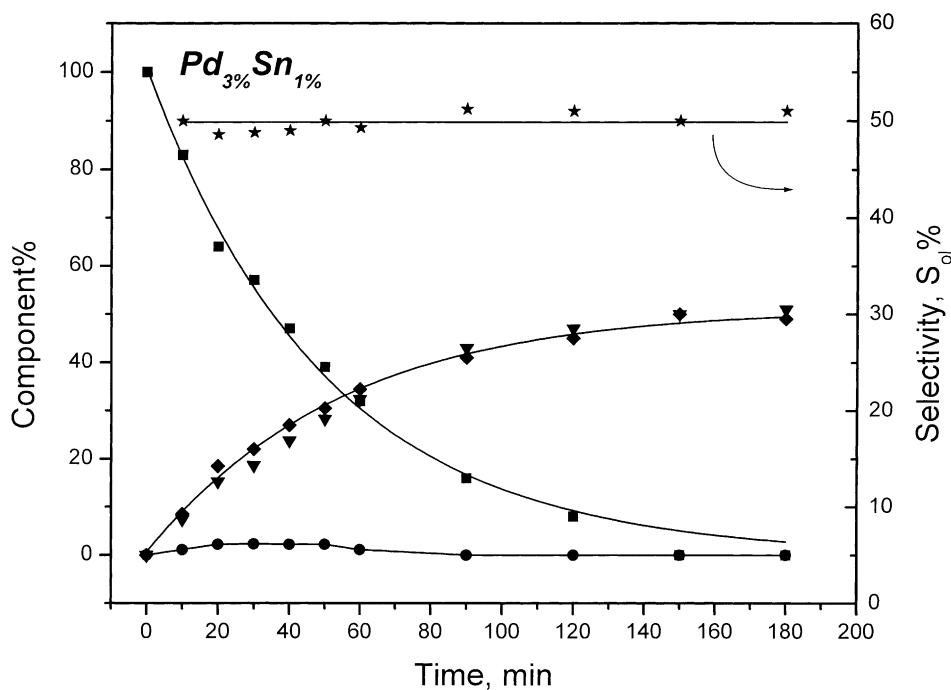Fig. 1. Conversion of 1% (v/v) cinnamaldehyde/toluene over 0.5 g of $Pd_{3\%}Sn_{1\%}/SiO_2$ catalyst at 25 °C and 3 atm H_2 pressure. (■) Cinnamaldehyde; (●) cinnamyl alcohol; (◆) phenylpropanal; (▼) phenylpropanol; (★) selectivity.

S_{ol} describes accordingly the fraction of cinnamaldehyde converted via the second hydrogenation route (i.e. $\underline{1} \rightarrow \underline{2} \rightarrow \underline{4}$) with respect to the total conversion. In other words, S_{ol} reflects the preference of cinnamaldehyde to undergo hydrogenation through the route of forming cinnamyl alcohol. S_{ol} corresponds thereby to $k_2/(k_1 + k_2)$, where k_1 and k_2 are the rate constants of the two reduction routes represented in Scheme 1. (To avoid any possible confusion, it is important to remember, that practically no cinnamyl alcohol was produced because it was consecutively hydrogenated very rapidly to phenylpropanol.) As seen in Fig. 1, S_{ol} does not change with reaction time. This constancy in the S_{ol}-value (observed also for all other catalysts investigated in this study) is consistent with the low reactivity of phenylpropanal under the above conditions, as mentioned previously.

The rate of consumption of cinnamaldehyde in the initial range, R_0, is used in this work as an activity measure,

$$R_0 = [CALD]_0 \frac{x}{t}$$

where $[CALD]_0$ is the initial concentration of cinnamaldehyde and x the conversion in time, t. Since $[CALD]_0$ was constant in all performed experiments (0.077 M), only x/t was taken into consideration to describe the catalytic activity of the investigated catalysts.

3.2. XRD-measurements

XRD-measurements were carried out on the following catalysts in the reduced form: $Pd_{3\%}$, $Pd_{3\%}Sn_{1\%}$ and $Pd_{3\%}Sn_{3\%}$ (Fig. 2). Obviously, Pd–Sn alloying takes place and the Pd_2Sn intermetallic compound could unambiguously be identified. The presence of small amounts of other Pd–Sn intermetallic compounds such as Pd_3Sn and/or PdSn cannot be ruled out due to eventual overlapping with the Pd and Pd_2Sn XRD-peaks. Fig. 2 also shows that metallic palladium phases are still present on the catalyst surface. In the case of the $Pd_{3\%}Sn_{1\%}$ catalyst, there are significant amounts of metallic palladium with clear characteristic diffraction peaks at 40.3 and 46.7°. On the other hand, only very small amounts of metallic
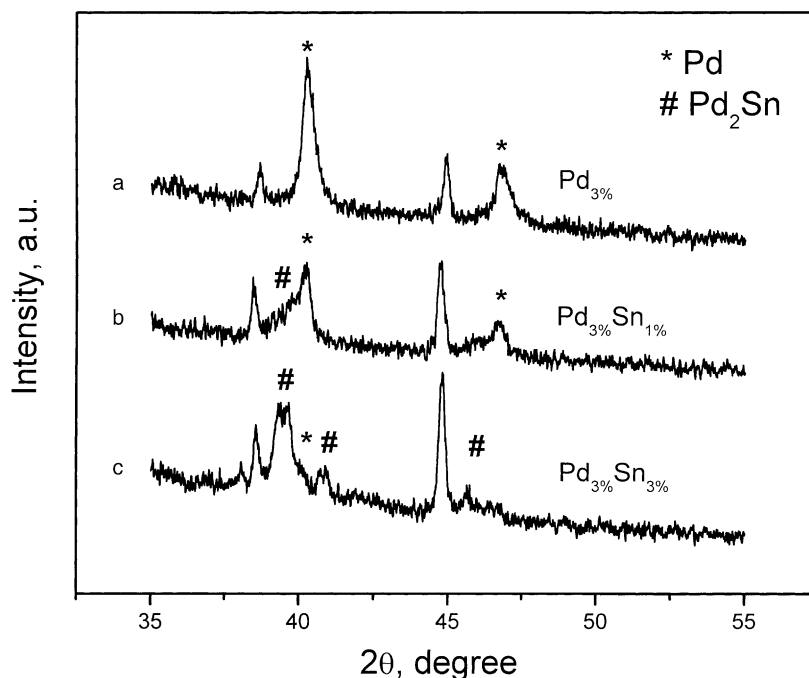

Fig. 2. X-ray diffraction patterns of SiO_2-supported $Pd_{3\%}$, $Pd_{3\%}Sn_{1\%}$ and $Pd_{3\%}Sn_{3\%}$ sol-gel catalysts.

palladium are recognizable in the $Pd_{3\%}Sn_{3\%}$ catalyst as indicated by the small shoulder at 40.3°. These Pd phases are, however, expected to contain some dissolved Sn, since Pd and Sn are known to form solid solutions with various compositions [27], whereby place exchange and diffusion of Sn into Pd had been reported to proceed efficiently at temperatures above 523 K [28], which is a much lower temperature than that used in this work in the reduction stage of preparation (see Section 2). In the related system of alumina supported Pd-Sn catalysts, prepared by diffusion impregnation followed by calcination and reduction up to 773 K, the presence of such Pd-Sn solid solutions with Sn < 16% could be identified (in addition to the Pd_3Sn and Pd_2Sn intermetallic compounds) by means of Mössbauer spectroscopy [29].

3.3. Catalytic behavior

The effect of Sn on the catalytic activity and selectivity of $Pd_{3\%}/SiO_2$ sol-gel catalysts is summarized in Fig. 3 for Sn-loadings ranging from 0 to 1%. It is apparent that the catalytic activity drops linearly with increasing Sn-loading, losing about 67% of its initial value (i.e. that of unmodified Pd) when the Sn-loading reaches 1%. This behavior is similar to those reported for Ru/C [10] and Rh/SiO$_2$ [11] modified by Sn to increase their selectivity in the hydrogenation of citral (an α,β-unsaturated aldehyde) to the corresponding saturated alcohols, but is different from that observed for Sn-Pt/nylon, where a maximum in the catalytic activity was obtained at intermediate Sn/Pt ratios [12]. The decrease in catalytic activity shown in Fig. 3 is, however, accompanied by an increase in the S_{ol}-value from 25 to 50%, corresponding to an improvement in the k_2/k_1 ratio from 0.33 to 1. Using the experimentally obtained values for the catalytic activity (corresponding to $k_1 + k_2$) and the measured S_{ol}-value, k_1 and k_2 were calculated and are represented in Fig. 3 as a function of the Sn-loading. While the first hydrogenation route to phenylpropanal suffers a strong exponential suppression with increased Sn-loading, the second hydrogenation route ($\underline{1} \rightarrow \underline{2} \rightarrow \underline{4}$) remains almost unaffected
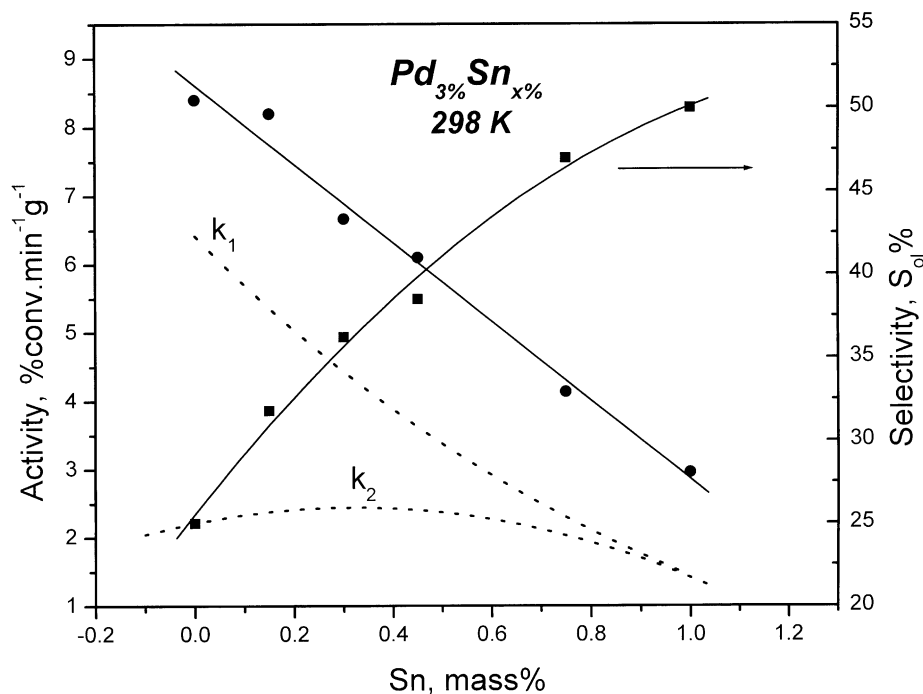

Fig. 3. Catalytic activity (●) and selectivity (■) of Sn-promoted 3% Pd/SiO$_2$ sol-gel catalysts as a function of the Sn-loading. k_1 and k_2 are the rate constants of the two parallel hydrogenation routes as depicted in Scheme 1.

with Sn-loading of up to 0.6%, before it afterwards slightly drops.

The $Pd_{3\%}Sn_{3\%}$ catalyst (not included in Fig. 3 for clarity purposes) showed a rather low activity of 0.36%/(min g). The higher Sn-loading has also no noticeable improvement on the selectivity beyond that obtained in the case of $Pd_{3\%}Sn_{1\%}$. The low catalytic activity of this catalyst may be attributed to the very small amounts of the metallic Pd phase as identified in the XRD-measurements. It is worth noticing that the XRD-peak corresponding to this phase is much larger in the case of the $Pd_{3\%}Sn_{1\%}$ catalyst, which exhibits a much higher activity. A correlation between the catalytic activity and the amount of metallic Pd phase seems to exist. This, on the other hand, suggests that the pure Pd_2Sn intermetallic compound itself is not active at room temperature and that the observed enhancement in selectivity at room temperature is due to the dissolved Sn in the metallic Pd phase. In agreement with this conclusion, Sales et al. [22] measured in the selective hydrogenation of hexadienes only poor catalytic performance of the Sn-rich Pd-Sn

catalysts containing Pd_2Sn phases, compared to the Sn-poorer ones containing only Pd_3Sn phases and dissolved Sn. The activity of Pd_2Sn is the subject of further investigations.

The reduction of cinnamaldehyde over Pd/SiO_2 sol-gel catalyst was previously investigated at $25\,^\circ C$ and 3 atm H_2 [26]. The reaction was found to be zero-order with respect to the cinnamaldehyde concentration, in agreement with the results of other groups, obtained however, under different conditions [30,31]. For the Sn-modified Pd catalysts investigated in this work, zero-order kinetics was also observed for Sn-loadings of <0.45%. The reaction order was found to change and become one at higher Sn-loadings (Sn $\geq$ 0.45%), indicating that the adsorption of cinnamaldehyde on Pd has been suppressed. Alloying Sn with Pd [28,29] and Ni [32] had been reported to suppress the CO chemisorption on these noble metals, where both electronic and geometric arguments were drawn to explain the observed weakening of the CO adsorption. The suppression of cinnamaldehyde adsorption is discussed in detail in Section 4.
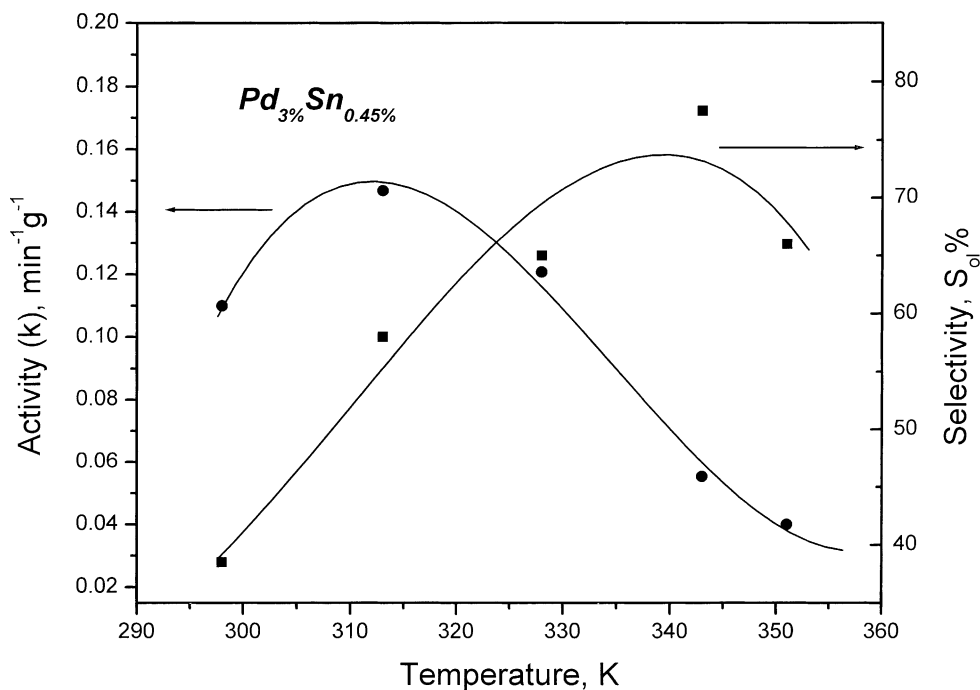

Fig. 4. Effect of temperature on the catalytic activity (●) and selectivity (■) of the $Pd_{3\%}Sn_{0.45\%}$ catalyst. The rate constant of the first-order hydrogenation of cinnamaldehyde is taken as a measure of activity.

The effect of temperature on the catalytic activity and selectivity of the $Pd_{3\%}Sn_{0.45\%}$ catalyst is shown in Fig. 4. The catalytic activity goes through a maximum at about 313 K. After that, it drops continuously with increasing temperature. This behavior seems to support the above findings of weakened cinnamaldehyde adsorption. On unmodified Pd/SiO_2 catalysts, the reaction rate increased monotonically with increased temperature according to the Arrhenius relationship [26]. In the presence of Sn, the weakened adsorption of cinnamaldehyde leads eventually to decreased amounts of adsorbed cinnamaldehyde, and thus to decreased activities at higher temperatures.

Raising the temperature results also in an increase in the S_{ol}-value. This is attributed to the increase in the reduction rate of phenylpropanal at higher temperatures, leading to an increase in the phenylpropanol concentration at the expense of that of phenylpropanal. This observation is in agreement with the results of hydrogenating cinnamaldehyde in decalin at 95 °C, where at these rather high temperatures the selectivity to phenylpropanal was found to decrease significantly with increased conversion [33]. At $T > 343$ K, S_{ol} drops slightly, a behavior that may be explained by a possible suppression of phenylpropanal adsorption, decreasing thus its further reduction to phenylpropanol.

4. Discussion

Sn has been widely used to improve the selectivity of various transition metal catalysts (e.g. Cu, Pt, Ru, Rh) in the hydrogenation of α,β-unsaturated aldehydes [1,10–21]. Different explanations were drawn to explain the observed promotion of selectivity towards unsaturated alcohols and these can be summarized as follows:

(i) The presence of Sn^{n+}-species acting as Lewis acid sites at or near the hydrogenation active metal particles favors the adsorption of the reacting aldehyde through its carbonyl group as a result of the larger interaction of these Lewis sites with the lone electron pair of the oxygen atom, increasing thus the hydrogenation probability of the C=O double bond.

(ii) Formation of Sn–metal alloys leads to increased electron densities on the metal atoms, suppressing thus the probability of C=C double bond adsorption.

(iii) Isolation of the active metal atoms by Sn-species hinders the adsorption of α,β-unsaturated aldehyde as a flat molecule, decreasing the probability of forming the saturated aldehyde.

Generally, all these factors may be expected to contribute simultaneously to the observed enhancement in selectivity. However, depending on preparation procedure and metal nature, one or more of the above mechanisms may dominate as discussed below for our Pd-Sn catalysts.

Although no SnO_2 phases were detected in the XRD-measurements, the presence of oxidic noncrystalline Sn-species cannot be ruled out. Indeed, the Mössbauer spectroscopy measurements of Sales et al. [29] to several Pd-Sn catalysts (with no XRD-peaks corresponding to SnO_2) indicate clearly the presence of SnO_2, reaching in some cases 35% of all Sn-loading on the catalyst surface. We observe, however, no increase in the hydrogenation rate of the carbonyl group as a function of the Sn-loading, as expected for selectivity promotion by Lewis sites. From Fig. 3, it is evident that the rate constant of hydrogenating the carbonyl group (k_2) remains constant up to Sn = 0.6%, before it afterwards slightly drops. In fact, in almost all cases, where selectivity improvement have been attributed to ionic Sn-species, an enhancement in the reaction rate due to Sn-additives was observed, at least at intermediate loadings [1,12–17]. Promotion of catalytic activity and selectivity due to metal salt additives were also reported [34,35], supporting our conclusion that ionic Sn-species acting as Lewis sites should have a positive effect on the catalytic activity of the catalysts. (This is true at least for low and intermediate loadings. High Sn-loadings can lead to blocking off the metal atoms resulting in a decrease in the catalytic activity.) Since no increase in the reduction rate of C=O group is observed, we believe that the enhancement in selectivity due to Sn in this work cannot be related to the presence of Lewis acidic Sn-species at or near the Pd atoms. All Sn^{n+}-species on or in the closest vicinity to the Pd particles seem to have been reduced to zero-valent Sn under preparation conditions mentioned in Section 2.

Oxidic Sn-species far away from Pd are inactive and are not expected to promote the selectivity.

In this work, Sn–Pd alloying was found to take place (Section 3.2). An XPS-investigation of Sn–Pd surface alloys on Pd(1 1 1) provides evidence to strong Sn-induced perturbation of the electronic structure of Pd upon alloying, consistent with charge transfer from Sn $\rightarrow$ Pd. Such a charge transfer will increase the electron density on Pd, leading to a greater repulsion with the C=C double bond electrons, making its adsorption more difficult. This effect has been theoretically studied in details by Delbecq and Sautet on model surface $Pt_{80}Fe_{20}$(1 1 1) [36], where the Fe atoms were located in the second layer (i.e. not exposed to the reacting molecules). The Fe atoms were shown to act as electron-donating ligands and to increase the electron density on the surface Pt atoms, favoring the di-$\sigma_{C=O}$ adsorption mode. This electron transfer from Fe $\rightarrow$ Pt was experimentally evidenced by X-ray absorption edge spectroscopy [37]. Further examples for this effect can be found in the comprehensive review of Gallezot and Richard [1].

The geometric dilution effect of Pd atoms by alloyed Sn cannot be neglected. The theoretical study of Delbecq and Sautet [38], based on extended Hückel-calculations, shows that for Pd(1 1 1) the most stable adsorption mode is a planar (di-π η_2)-mode (also called η_4-mode), in which both unsaturated double bonds (C=C and C=O) are π-bonded to the surface. This is in agreement with the experimental results showing that acrolein adsorbs on Pd(1 1 1) preferentially in an η_4 (C, C, C, O)-mode [39]. With the η_4 (C, C, C, O)-mode, a poor selectivity to unsaturated alcohol is expected because the hydrogenation of C=C double bond will be favored for kinetic reasons and because the 1,4-addition of hydrogen leads to the formation of the corresponding enol product that isomerizes into the undesirable saturated aldehyde. Dividing the Pd ensembles by alloyed Sn into ensembles of smaller sizes would prevent the adsorption in the η_4-mode that requires multi-adsorption sites, and improves, thus, the selectivity. (This may explain the minor effect of the size of the ensembles of Pt catalysts on selectivity, as reported by Marinelli and Ponec [40], since the adsorption in the η_4-mode is not favored on closely packed Pt surfaces.) Such a geometric effect of dilution was also proposed to explain the inhibition of the double bond isomeriza-

tion ability of Pd upon Sn addition in the liquid-phase hydrogenation of 1,5- and 1,3-hexadienes over Pd [22], where such an isomerization reaction is known to require multi-adsorption sites. Strong dilution is also expected to increase the adsorption probability of the C=O group in the on-top mode, in which the carbonyl group interacts with the surface through the lone electron pair of the oxygen atom, favoring thus the formation of unsaturated alcohol. Based, however, on the fact that the reduction rate of the carbonyl group did not increase with increased Sn-loading, this possible explanation (i.e. strong dilution) for the enhancement in selectivity can be excluded.

Both alloying effects (electronic and geometric) do, as discussed above, inhibit the rate of formation of the saturated aldehyde by inhibiting the molecule from being adsorbed in such modes that lead to this product, rather than enhance the reduction rate of the carbonyl group.

5. Conclusions

In summary, the positive effect of added Sn on the selectivity of Pd in the hydrogenation of cinnamaldehyde at room temperature can be explained by both geometric and electronic alloying effects. The observed improvement in selectivity is attributed, however, mainly to a strong suppression of the adsorption/hydrogenation of the C=C double bond rather than to an enhancement in the hydrogenation of the carbonyl group.

Acknowledgements

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