Hydrogenation of cinnamaldehyde over sol–gel Pd/SiO$_2$ catalysts: kinetic aspects and modification of catalytic properties by Sn, Ir and Cu additives

S. Mahmoud [a,*], A. Hammoudeh [a], S. Gharaibeh [b], J. Melsheimer [c]

[a] *Chemistry Department, Yarmouk University, Irbid, Jordan*
[b] *Department of Earth Sciences and Environment, Yarmouk University, Irbid, Jordan*
[c] *4–6 Faradayweg, FHI der. Max-Planck Institute, Berlin 14195, Germany*

Abstract

When 1% v/v solution of cinnamaldehyde/toluene was hydrogenated at 25 °C and 47 psi hydrogen pressure over sol–gel Pd/SiO$_2$ catalysts, a modification effect was observed. Sn and Ir were found to noticeably enhance the selectivity of Pd catalysts with respect to the hydrogenation of the C=O bond relative to the favored hydrogenation of the C=C bond. The produced cinnamyl alcohol, however, converts readily to phenylpropanol. On the other hand, Cu has caused a decrease in activity without any significant improvement on selectivity under the above conditions. The reaction kinetics were studied for the unmodified Pd catalysts, and the orders were determined to be first with respect to hydrogen, and zero with respect to cinnamaldehyde. The apparent activation energy was calculated and found to have a value of 30.1 kJ/mol. Also, the effects of metal loading and catalyst mass were studied. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogenation; Sol–gel; Cinnamaldehyde; Kinetics; Palladium

1. Introduction

Hydrogenation of α,β-unsaturated aldehydes into the corresponding unsaturated alcohols is highly desirable from an industrial point of view [1]. On the other hand, the production of the saturated aldehydes from the unsaturated ones has some industrial and biological applications [2]. It is also thermodynamically preferred and can be achieved easily compared to the former one [1,3,4].

The selectivity of a hydrogenation catalyst towards the production of unsaturated alcohols rather than the saturated aldehydes may be improved by using additives, such as transition metal salts, promoters, different supports, different solvents, or alloying the base metal of the catalyst with another one. This modifies its electronic and chemisorption properties towards a better adsorption of C=O bond rather than C=C bond, while preserving the hydrogenation activity of the catalyst [1,3–8]. For example, Pd catalysts are very active in many hydrogenation reactions, but are poorly selective towards the production of unsaturated alcohols from their unsaturated aldehyde counterparts [1,2,9]. In contrast, Sn and Ir have a relatively low activity, but are highly selective in this respect [1,3,6, 10,11].

In this paper, we have studied the catalytic properties of some Pd and Pd-based catalysts in the hydrogenation of cinnamaldehyde. Sn, Cu, or Ir were

* Corresponding author. Fax: +962-2-727-4725.
E-mail address: smahmoud@yu.edu.jo (S. Mahmoud).

incorporated to the Pd catalysts during the preparation process, where the sol–gel method was used in an acidic medium for the preparation of Pd/SiO$_2$ catalysts of different metal loadings and Pd/M ratios. The purpose of using the sol–gel technique was to produce highly dispersed catalysts with a large BET surface area, and a better distribution and interaction of the metal surface atoms with the support. The Pd metal was chosen as the base metal, even though it is known to have poor selectivity, because of its known high hydrogenation activity. On the other hand, Sn, Ir and to some extent Cu, have been shown to have good modifying effects on many metals in the hydrogenation of unsaturated aldehydes [1,5,8,11–13]. For instance, alloying the base metal with a more electropositive one such as Ir, Sn or Cu may result in an improvement of the selectivity of the base metal due to the electron donation from the electropositive metal which leads to a better chemisorption of C=O group, and thus, its activation for hydrogenation [1]. Sn, Ir and Cu have a good modifying effect on the catalytic properties of other noble metals such as Pt in some hydrogenation reactions [1,4–6,8,11,14–17]. For example, Sn has significantly improved the selectivity of platinum in the hydrogenation of acrolein [5], crotonaldehyde [11], citral [6] and cinnamaldehyde [4]. Therefore, for the reasons that Sn, Ir and Cu have modification effects, Pd has good hydrogenation activity, and sol–gel catalysts have large surface area and may have better catalytic properties than impregnation catalysts [18,19], a series of Pd-M/SiO$_2$ (M = Sn, Ir, Cu) sol–gel catalysts were prepared and tested in the hydrogenation of cinnamaldehyde.

2. Experimental

Pd and Pd-based catalysts of different metal loadings on SiO$_2$ were prepared by the sol–gel method (Table 1). Pd, Ir, Sn and Cu were obtained as PdCl$_2$ and IrCl$_4$ (Ferax Laboral), SnCl$_2$·2H$_2$O (BDH) and Cu(II) acetate (Fluka), 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$_2$O traps.

Table 1

Catalytic selectivity and activity of sol–gel Pd/SiO$_2$ and Pd-M/SiO$_2$ catalysts in the hydrogenation of cinnamaldehyde at different conditions (M = Ir, Sn or Cu)

Catalyst	Selectivity (%)[a]	Activity[b]
0.1% Pd	70–78	0.13
0.5% Pd	70–75	1.01
1% Pd	70–73	2.24
2% Pd	74–77	3.98
3% Pd	74–78	8.42
5% Pd	72–78	11.82
Pd 3%-Sn 0.15%	72–76	7.20
Pd 3%-Sn 0.5%	50–58	6.40
Pd 3%-Cu 0.45%	–	–
Pd 3%-Cu 0.15	70–78	4.0
Pd 2.8%-Ir 2.2%	75	10.8
Pd 1.3%-Ir 3.7%	59–62	10.0

[a] Selectivity is constant at all conversions with slight fluctuations in the above indicated ranges.

[b] Activity is expressed as %conversion/min g catalyst.

2.1. Catalyst preparation

Samples of the sol–gel catalysts ($\sim$5 g each) were prepared by mixing aqueous solutions of proper concentrations of PdCl$_2$ (in HCl/H$_2$O), and IrCl$_4$, SnCl$_2$ or Cu(II) acetate with absolute ethanol and tetraethoxysilane following procedures in [20]. At the end of this preparation process, sol–gel catalysts with high surface area were produced (Table 1). 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 [21].

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. A total of 100 ml 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 and 343 K) and hydrogen pressure (15, 30, 47 and 60 psi), 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.

2.3. Analysis of the reaction mixture

A gas chromatograph (HP 5890) with TCD connected to an electronic integrator (HP 3395) was used for analyzing samples of the reaction mixtures. The separation of the mixtures was performed on a 10 m long × 530 μm o.d. capillary column, coated with a 2.65 μm film of phenylmethylsiloxane (HP-5). Helium carrier gas was passed at a flow rate of 12 ml/min, with the injector and detector temperatures of 200 and 220 °C, respectively. Column temperature was programmed at 70 °C (initial), 130 °C (final, with 12 min hold) and a 15 °C/min heating rate. Samples of the reaction mixture were also analyzed by GC/MS (VG Analytical Instruments, VG 7070 E) for structure confirmation.

3. Results and discussion

The Pd and Pd-based bimetallic catalysts of different atomic ratios of Pd/M (M = Ir, Sn or Cu) were prepared on silica support with a BET surface area of ∼450 m^2/g by the sol–gel method (Table 1). All Pd-based catalysts, except those containing Cu, were of high activity (Table 1), and their reaction products were only phenylpropanal and phenylpropanol (Fig. 1). Cu-containing catalysts were of much lower activity.
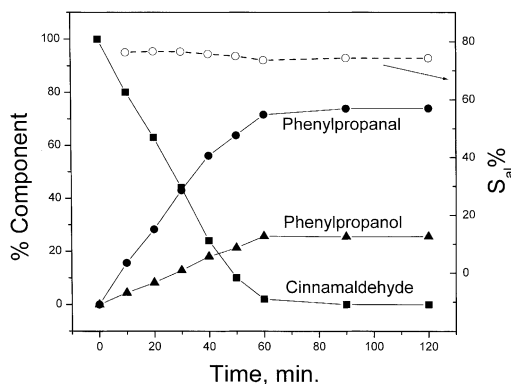

Fig. 1. Conversion of 1% v/v cinnamaldehyde/toluene over 0.50 g of 2% Pd/SiO$_2$ at 25 °C and 47 psi H$_2$ pressure.

3.1. Kinetic aspects

3.1.1. Reaction mechanism and definitions

Scheme 1 represents the general routes of the hydrogenation of cinnamaldehyde (**I**), over noble metal catalysts. The 1,2-addition gives the unsaturated alcohol (cinnamyl alcohol (**II**)), the 3,4-addition gives the saturated aldehyde (phenylpropanal (**III**)) and the 1,4-addition gives the enol that isomerizes into phenylpropanal. Further hydrogenation leads to the formation of phenylpropanol (**IV**), which can be also hydrogenated to propylbenzene (**V**). It is widely accepted that the hydrogenation of α,β-unsaturated aldehydes on metal surfaces occurs via the Horiuti–Polayni mechanism involving either di-$\sigma_{C=O}\eta^2$, di-$\sigma_{C=C}\eta^2$, or di-$\pi\eta^2(\eta^4)$ adsorbed states as described in Scheme 1 [1,5,22]. The overall rate of reduction of cinnamaldehyde (CALD) can be given by the following equation:

$$\text{Rate} = \frac{-\text{d}[\text{CALD}]}{\text{d}t} = k[\text{CALD}]^n P_{\text{H}_2}^m \qquad (1)$$

where k is the overall rate constant, n the order with respect to cinnamaldehyde and m the order with respect to hydrogen. Substituting the relation between the concentration of cinnamaldehyde and its conversion, X,

$$[\text{CALD}] = [\text{CALD}]_0(1 - X) \qquad (2)$$

where $[\text{CALD}]_0$ is the initial concentration of cinnamaldehyde, in Eq. (1), the rate can be expressed as

$$\text{Rate} = [\text{CALD}]_0 \frac{\text{d}x}{\text{d}t} \qquad (3)$$

$$or, \text{Rate} = [\text{CALD}]_0 \frac{x}{t} \qquad (4)$$

in the initial range. The latter was used in this study as a measure of catalytic activity. S_{al}, the selectivity with respect to phenylpropanal, is defined as

$$S_{\text{al}} = \frac{\text{phenypropanal}\%}{\text{conversion}\%} \times 100\% \qquad (5)$$

3.1.2. Kinetic parameters

A detailed kinetic study was carried out only for the unmodified Pd-catalysts. In order to be able to determine kinetic parameters, it is necessary first of all to ensure that the reaction is in the kinetic regime, i.e. the data collected correspond to the true reaction kinetics and are not controlled by any of the diffusion
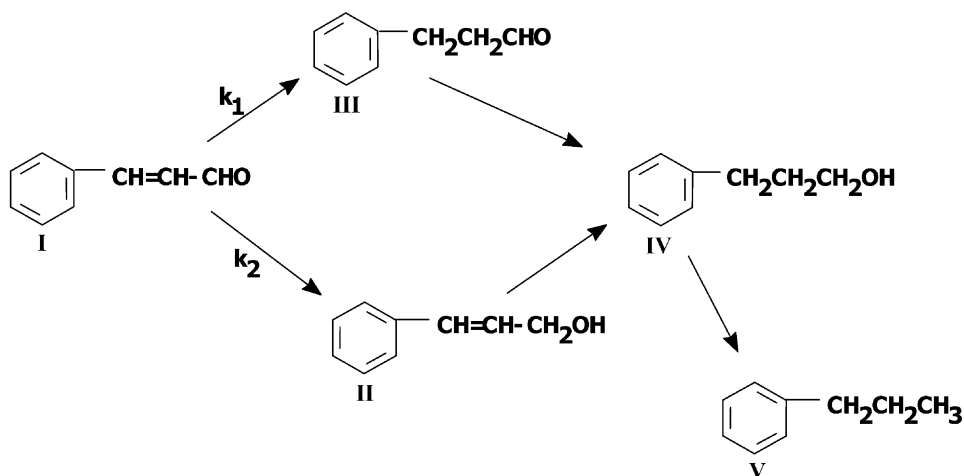
Scheme 1.

processes that take place in such rather complicated systems. This is especially important in the above system, since three phases are encountered (gaseous, liquid and solid).

To check the above requirement, the catalyst mass in 100 ml reaction solution was varied from 0.0625 to 0.5 g (corresponding to a variation of the catalyst loading from 0.0625% (w/v) to 0.5% (w/v)) and the agitation rate was varied from 1000 to 1200 rpm. No dependency of the reaction rate on the agitation rate could be observed. The reaction rate was also found to vary linearly with the catalyst mass (catalyst loading) (Fig. 2), thus, excluding any important role of external diffusion as a controlling step. On the other hand,
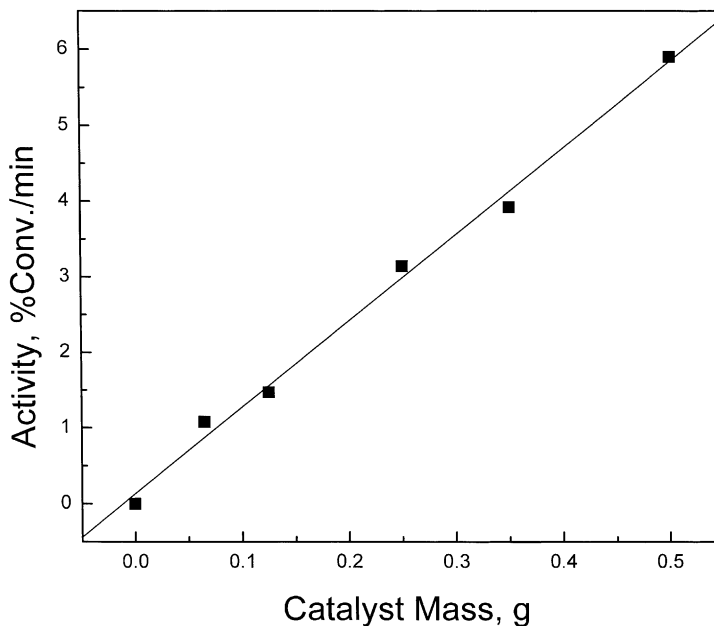

Fig. 2. The catalytic activity of 5% Pd/SiO$_2$ as a function of catalyst mass, at 25 °C and 47 psi H$_2$ pressure.

based on the value obtained for the activation energy (see below) and for the size of the catalyst used, the role of internal diffusion is estimated to be insignificant and the data obtained, therefore, represent the true kinetics of the process.

The dependence of the reduction rate on cinnamaldehyde concentration and hydrogen pressure was studied for cinnamaldehyde concentrations varied from 0.25 to 1.0 vol.% (0.019–0.077 M) and hydrogen pressure varied from 15 to 60 psi. The reaction order with respect to cinnamaldehyde (n) and with respect to hydrogen (m) was determined by double logarithmic plots of the reduction rate of cinnamaldehyde and $[CALD]_0$ or P_{H_2}, respectively. Under the above conditions (temperature $= 25\,°C$) it was found that this reaction is zero-order with respect to cinnamaldehyde and first-order with respect to hydrogen. This is in agreement with the results of Satagopan and Chandali [23], obtained, however, for cinnamaldehyde concentrations ranging from 0.79 to 1.586 M and hydrogen pressure ranging from 10 to 50 bar. At this point, it is noteworthy that on other noble metals such as Pt and Ir this reaction was first-order with respect to cinnamaldehyde under the same conditions as for Pd in this study [24], indicating a stronger adsorption of cinnamaldehyde on Pd surfaces than on Pt and Ir. At higher cinnamaldehyde concentrations (0.79–1.586 M) and hydrogen pressures (10–50 bar), Satagopan and Chandalia [25] reported a reaction order of zero with respect to cinnamaldehyde on Pt/C catalysts.

The effect of temperature on the hydrogenation of cinnamaldehyde was studied in the temperature range from 25 to 70 °C. From an Arrhenius plot of the obtained data, the apparent activation energy was found to be 30.1 kJ/mol. Such a relatively high value suggests that internal mass transfer is unlikely to play an important role under the above conditions, since activation energies are halved under internal diffusion controlled regimes [26]. Fig. 3 shows the reduction rate of cinnamaldehyde as a function of Pd-loading in the catalyst. In all points, the mass of the catalyst was 0.50 g and the Pd-loading was varied from 0.1 to 5%. A linear relationship was obtained indicating that there is no significant change in the specific surface area of the Pd particles in this Pd-loading range as prepared by the sol–gel method described in the experimental part (Section 2.1).
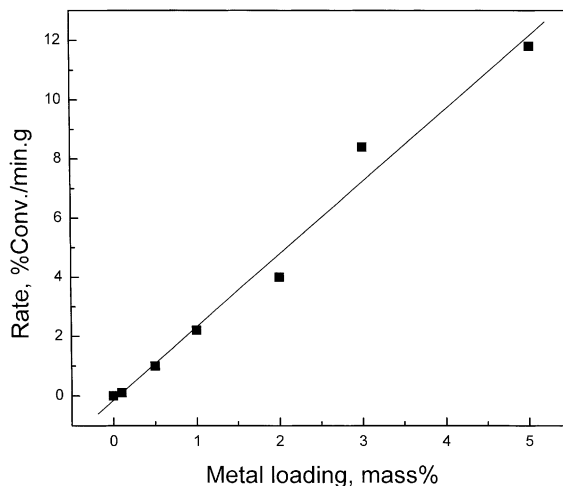

Fig. 3. The catalytic activity of 5% Pd/SiO$_2$ as a function of metal loading, in the hydrogenation of 1% v/v cinnamaldehyde/toluene solution at 25 °C and 47 psi H$_2$ pressure.

3.1.3. Catalytic activity of modified Pd-catalysts

The activities of different Cu, Sn and Ir-modified Pd catalysts are listed in Table 1. Obviously Cu and Sn additives depress the reactivity of the 3% Pd catalyst, whereby the deactivation effect of Cu is larger than that of Sn. Both Cu and Sn are inactive in hydrogenating cinnamaldehyde under the above described conditions. This depression of reactivity is, thus, attributed to the geometric and electronic modification properties of Pd-clusters due to their direct contact with Cu or Sn, where alloying can also probably take place. It is still not clear why the effect of Cu is much large than that of Sn. In the case of Ir-modified catalysts, the situation is more complicated because Ir is an active hydrogenation catalyst under the above described conditions. This is the subject of a detailed study, which is being carried out at present in our laboratory.

3.2. Selectivity

No significant amounts of products other than phenylpropanal and phenylpropanol could be detected, indicating that under the above conditions the further reduction of phenylpropanol to propylbenzene is negligible and that the selectivity towards cinnamyl alcohol is practically zero for all catalysts under investigation in this study. The selectivity to phenylpropanal, S_{al}, was constant (e.g. ~70–78% for

the unmodified Pd catalysts) at all conversions (Fig. 1) and independent of the catalyst mass or metal loading (Table 1). Moreover, S_{al} remains constant, even several hours after the 100% conversion was reached. This leads to the conclusion that under the above reaction conditions (25 °C, $P_{H_2} = 47$ psi) the reduction of phenylpropanal to phenylpropanol does not take place. Otherwise, one would expect S_{al} to decrease with time due to the decrease in the concentration of phenylpropanal as a result of its reduction to phenylpropanol. Control experiments have proved that the reduction of phenylpropanal in solution at 25 °C and 3 atm H_2 on 0.5 g of 2 and 3% Pd/SiO$_2$ catalysts does not yield any detectable amount of phenylpropanol. This result is very important, since it indicates that all phenylpropanol obtained in the reduction of cinnamaldehyde under the above conditions does actually completely come through the formation of cinnamyl alcohol as an initial step in this reaction. The absence of cinnamyl alcohol as a product does not, on the other hand, contradict the above conclusion and can be easily explained by the very fast reduction of cinnamyl alcohol at 25 °C and 47 psi H_2. This could be shown experimentally for 0.0625 g of 5% Pd/SiO$_2$, where the rate constant of the reduction of cinnamyl alcohol (0.076 M solution in toluene) was determined to be 7.7×10^{-5} mol/l/s. This value of k is about seven times higher than that for the total reduction of cinnamaldehyde under the same conditions (compare with Fig. 2) or about 30 times higher than that for the reduction pathway of cinnamaldehyde to cinnamyl alcohol only (see the discussion below). A similar behavior was reported by Cairns et al. for Pd catalysts produced by the H_2 reduction of [Pd$_2$Br$_4$(PR3)$_2$] supported on silica [8]. These catalysts were found to readily convert cinnamyl alcohol to phenylpropanol in decalin at 135 °C, whereas they were unable to reduce phenylpropanal to phenylpropanol at the same conditions. The above catalysts do not, however, produce in the hydrogenation of cinnamaldehyde any phenylpropanol, indicating the complete inhibition of cinnamaldehyde hydrogenation to cinnamyl alcohol over these catalysts. On standard Pd/SiO$_2$ catalysts, Cairns et al. [8] have also recognized that the rate of production of phenylpropanol in the hydrogenation of cinnamaldehyde in decalin at 95 °C was greater than that from the hydrogenation of phenylpropanal, in agreement with our observations.

Since all phenylpropanol come from the formed cinnamyl alcohol, the ratio k_1/k_2 of the rate constants of the two reduction pathways, as presented in Scheme 1, must be equal to the concentration ratio [phenylpropanal]/[phenylpropanol], which was found to remain constant at all conversions corresponding to the constant value of S_{al}. From the value of S_{al} it can be estimated that $k_1/k_2 \approx 3$. The effect of temperature and additives on the selectivity of Pd catalysts will be discussed in the following sections.

3.2.1. Effect of temperature

Raising the temperature to 40 and 55 °C was found to decrease the value of S_{al} to 28–37%, whereby a pattern of decreasing S_{al} (from 37 to 28%) with increased conversions could be distinguished. This decrease in the value of S_{al} corresponds to an increase in the concentration of phenylpropanol at the expense of phenylpropanal that can be attributed to the enhanced reduction of phenylpropanal to phenylpropanol at higher temperatures. This observation is in agreement with the results of hydrogenating cinnamaldehyde in decalin at 95 °C where at these relatively high temperatures the selectivity to phenylpropanal was found to decrease significantly with increased conversion [8]. The Cu and Sn modified Pd catalysts showed also a similar behavior. In the case of Pd 5%-Cu 0.15%, however, S_{al} drops only to 52–58%, which is consistent with the fact that Cu modified catalysts are much less active than the original Pd catalysts [17].

3.2.2. Effect of additives

3.2.2.1. Copper.
No change in the selectivity, S_{al}, could be observed as a result of modifying the Pd catalyst with Cu. The Pd 5%-Cu 0.15% catalyst shows a selectivity, $S_{al} \approx 70$–78% similar to that obtained by the unmodified Pd catalyst. Higher concentrations of Cu (0.45–1%) were experimentally found to turn the Pd catalyst almost inactive at 25 °C, making an investigation of the effect of these concentrations of Cu on the selectivity at 25 °C impossible.

3.2.2.2. Tin.
Small amounts of tin (0.15%) were found to produce no change in the selectivity S_{al} (72–76%) although a small drop in the activity was observed in comparison to the 3% Pd catalyst. Increasing the concentration of Sn up to 0.5% decreases

the value of S_{al} to 50–58%. This trend can be attributed to the enhanced formation of cinnamyl alcohol due to the presence of Sn, which leads to the formation of higher amounts of phenylpropanol relative to those of phenylpropanal. Such a promotion of the cinnamyl alcohol selectivity by tin is known from the related Pt–Sn system [3,5,11]. This is attributed to the possible presence of Sn^{4+} species on the catalyst surface causing an activation of the C=O bond in cinnamaldehyde and, thus, its ease of hydrogenation, which in turn have decreased the selectivity towards the production of phenylpropanal [12,27].

3.2.2.3. Iridium. Although Ir is known to have high selectivity with respect to the formation of cinnamyl alcohol [1,10,13], 2.2% Ir in the Pd 2.8%-Ir 2.2% catalyst were not enough to change the selectivity, S_{al}, which was experimentally determined to be 74–75%, exactly the same as that for 3% Pd. This behavior can be explained by the large difference in activity between Pd and Ir. At 25 °C the reaction is apparently dominated by the presence of Pd. Higher Ir-contents (3.7%) lead to a drop in selectivity down to 60%. At this stage no cinnamyl alcohol was detected, however. The enhancement effects of Sn, Cu and Ir are the subject of an ongoing research study.

References

[1] P. Gallezot, D. Richard, Catal. Rev. Sci. Eng. 40 (1998) 81, and references therein.

[2] A.M.C. Castelijns, J.M.Hogeweg, S.P.J.Van Nispen, PCT Int. Appl. WO 9611898 Al, 25 April 1996, pp. 14.

[3] F. Delbecq, P. Sautet, J. Catal. 152 (1995) 217.

[4] T. Li, G. Li, Y. Xu, Cuihua Xuebao 20 (1999) 219.

[5] T. Marinelli, V. Ponec, J. Catal. 156 (1995) 51, and references therein.

[6] S. Recchia, C. Dossi, N. Poli, A. Fusi, L. Sordelli, R. Psaro, J. Catal. 184 (1999) 1.

[7] S. Recchia, C. Dossi, A. Fusi, R. Zanoni, J. Catal. 182 (1999) 186.

[8] G.R. Cairns, R.J. Cross, D. Stirling, J. Catal. 166 (1997) 89.

[9] H. Yamada, H. Urano, S. Goto, Chem. Eng. Sci. 54 (1999) 5231.

[10] A. Giroir-Fendler, D. Richard, P. Gallezot, Stud. Surf. Sci. Catal. 41 (1988) 171.

[11] J.L. Margitfalvi, A. Tompos, I. Kolosova, J. Valyon, J. Catal. 174 (1998) 246, and references therein.

[12] L. Sordelli, R. Psaro, G. Vlaic, A. Cepparo, S. Recchia, C. Dossi, A. Fusi, R. Zanoni, J. Catal. 182 (1999) 186.

[13] A.B. Anderson, R. Hoffmann, J. Chem. Phys. 60 (1974) 4271.

[14] E.A. Sales, M. de Jesus Mendes, F. Bozon-Verduraz, J. Catal. 195 (2000) 96, and references therein.

[15] A.B. Silva, E. Jordao, M.J. Mendes, P. Fouilloux, Appl. Catal. A 148 (1997) 253.

[16] B.K. Furlong, J.W. Hightower, T.Y.-L. Chan, A. Sarkany, L. Guczi, Appl. Catal. A Gen. 117 (1994) 41.

[17] S. Leviness, V. Nair, A.H. Weiss, J. Mol. Catal. 25 (1984) 131.

[18] R. Gomez, V. Bertin, T. Lopez, I. Schifter, G. Ferrat, J. Mol. Catal. A Chem. 109 (1996) 55.

[19] T. Lopez, M. Asomoza, P. Bosch, E. Garcia-Figueroa, R. Gomez, J. Catal. 138 (1992) 463.

[20] S. Mahmoud, I. Arafa, O. Sheikha, Asian J. Chem. 12 (2000) 1047.

[21] S. Mahmoud, S. Saleh, Clays Clay Min. 47 (1999) 481.

[22] B. Coq, P.S. Kumbhar, C. Moreau, P. Moreau, F. Figueras, J. Phys. Chem. 98 (1994) 10180.

[23] V. Satagopan, S.B. Chandalia, J. Chem. Tech. Biotechnol. 59 (1994) 257.

[24] A. Hammoudeh, S. Mahmoud, in preparation.

[25] V. Satagopan, S.B. Chandalia, J. Chem. Tech. Biotechnol. 60 (1994) 17.

[26] J.J. Carberry, in: J.R. Anderson, M. Boudart (Eds.), Catalytalis—Science and Technology, Vol. 8, Akademic-Verlag, Berlin, 1987, p. 152.

[27] J.L. Margitfalvi, G.Y. Vanko, I. Borbath, A. Tompos, A. Vertes, J. Catal. 190 (2000) 474, and references therein.