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# Hydrogenation of $\alpha,\beta$-Unsaturated Aldehydes over Pt–Sn/Nylon

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Hydrogenation of $\alpha,\beta$-unsaturated aldehydes has been carried out over supported Pt and Pt–Sn/ catalysts. Over platinum there is preferential formation of saturated adehydes due to the lower energy of the C=C double bond with respect to the C=O bond. Addition of tin to Pt/Nylon causes a drastic change in the product distribution. On the Pt–Sn samples the reaction proceeds mainly through the hydrogenation of the C=O bond with formation of $\alpha,\beta$-unsaturated alcohols. The rate of reaction has been found to increase with the addition of small amounts of tin. However, catalysts having a Sn/Pt ratio higher than 1.2–1.3 are inactive. It is suggested that the effect of tin ions is related to their acid properties which enhance the reactivity of the C=O bond. At higher tin contents the platinum active sites are unable to activate hydrogen molecules.

## INTRODUCTION

A recent investigation on the reactivity of Pt/Nylon catalysts has shown that the interaction between platinum and Nylon leads to a decrease in the rate of C=C double bond hydrogenation. An even more drastic effect on the rate of reaction is caused by addition of tin. Pt–Sn/Nylon samples having Sn/Pt ratios higher than one are practically inactive in the hydrogenation of propene (*1*). It has been suggested that the platinum–support and the platinum–tin interaction lead to a weaker chemisorption bond of the olefin on the platinum active sites and therefore to a lower reactivity. This is in agreement with the experimental findings which show that the order of reaction with respect to the olefin is higher on the less active samples.

In order to find an application of our Pt–Sn/Nylon catalysts to reactions of industrial interest, we have tested their catalytic performance in the hydrogenation of several organic molecules. Results on the selective hydrogenation of $\alpha,\beta$-unsaturated aldehydes have recently been reported (*2*). It has shown that addition of Sn to Pt favors the formation of unsaturated alcohols which can reach yields higher than 70%. As selective catalysts for the hydrogenation of $\alpha,\beta$-unsaturated aldehydes to the corresponding unsaturated alcohols, noble metal catalysts (*3–8*) and several supported and unsupported Ag–Cd and Ag–Zn–Cd alloys (*9*) have been reported. However, to our knowledge, no paper has been published on this hydrogenation over Pt–Sn as catalyst, even though it has been reported that addition of tin to platinum increases the rate of hydrogenation of saturated aldehydes to alcohols (*10*).

In recent years the Pt–Sn system has been the subject of several investigations due to its performance as a reforming catalyst (*11–13*). It has been reported that addition of Sn to Pt/$Al_2O_3$ leads to a catalytic system which shows a better selectivity and, above all, a higher stability under reforming conditions. In spite of the large number of investigations, the role of tin is still unclear.

In this paper we report a detailed catalytic study on the effect of tin on the selective hydrogenation of unhindered $\alpha,\beta$-unsaturated aldehydes (namely, acrolein and

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TABLE 1

Chemical Composition of Pt–Sn/Nylon Preparations

| Sample code | Pt (wt%) | Sn (wt%) | $[Pt/(Pt + Sn)]^a \cdot 100$ |
|---|---|---|---|
| RP100 | 1.17 | — | 100 |
| RP90 | 0.90 | 0.062 | 90.0 |
| RP82 | 1.20 | 0.16 | 82.0 |
| RP70 | 1.03 | 0.26 | 70.7 |
| RP65 | 1.55 | 0.51 | 64.9 |
| RP55 | 1.06 | 0.53 | 54.9 |
| RP50 | 1.54 | 0.87 | 51.4 |
| RP40 | 1.20 | 1.11 | 39.1 |
| RP22 | 1.06 | 2.34 | 21.6 |
| RP00 | — | 2.0 | 0 |

[a] Atomic ratios.

cinnamaldehyde) which are known to be difficult to hydrogenate to the corresponding unsaturated alcohols.

## EXPERIMENTAL

*Materials.* Nylon 66 powder, used as support, was obtained by grinding pellets of commercial Nylon 66 (SNIAMID) at liquid-nitrogen temperature. The surface area of the powder was <1 $m^2/g$.

Pt/Nylon and Pt–Sn/Nylon samples were prepared by impregnation of Nylon powder, under $N_2$, with a $C_2H_5OH$ solution of $H_2PtCl_6$ or $H_2PtCl_6$ and $SnCl_2$ having the appropriate concentration of the metals. After filtering, the remaining solvent was removed at room temperature by evaporation under $N_2$ flow and by drying under vacuum at 343 K.

Before catalytic activity measurements, the samples were reduced *in situ* at 343 K by flowing $H_2$. The complete reduction to metallic platinum was verified by XPS analysis (*14*). Chemical analysis of the catalysts, obtained by atomic absorption, is reported in Table 1.

For comparison commercial samples of platinum on carbon were also tested.

Acrolein was distilled under nitrogen before use. Cinnamaldehyde was distilled under vacuum. Solvent (analytical grade) materials were used without further purification.

*Procedure.* Hydrogenations were carried out in a 100-ml four-necked flask, fitted with reflux condenser, thermocouple, and dropping funnel. The catalyst was added to the required amount of solvent (95% ethanol, unless otherwise specified), then reduced at 343 K for 1 h under $H_2$ flow. After cooling to reaction temperature the organic reactant was injected through one arm of the flask. The reaction mixture was stirred with a stirrer head with permanent magnetic coupling (Medimex) at a rate of 500 rpm and the reaction was carried out at constant temperature and atmospheric pressure under $H_2$ flow. Acrolein hydrogenation was carried out at 318 K, whereas cinnamaldehyde was hydrogenated at 333 K.

The progress of the reaction was followed by analyzing a sufficient number of microsamples withdrawn from the reaction mixture.

Chemical analysis was performed with a gas chromatograph (C. Erba, Model 4200). In the acrolein hydrogenation, reaction products were separated by a column (3 m × 1 mm) of 10% FFAP on Chromosorb W operating at 343 K. The gas chromatographic column used for analyzing the products during cinnamaldehyde hydrogenation was a 10% GP over SP2100 (3 m × 3 mm) operating at 423 K. Quantitative analysis was carried out by calculating the area of the chromatographic peaks by an electronic integrator (Spectra Physics, Model SP4000).

Preliminary runs carried out with different amounts of catalyst and different stirring rates showed the absence of external diffusional limitations.

## RESULTS

The results of the hydrogenation of cinnamaldehyde over a commercial 10% Pt/C sample are reported in Fig. 1. Under our reaction conditions ($T$ = 333 K, solvent = ethanol) the reaction products are mainly hydrocinnamaldehyde ($C_6H_5—CH_2—CH_2$

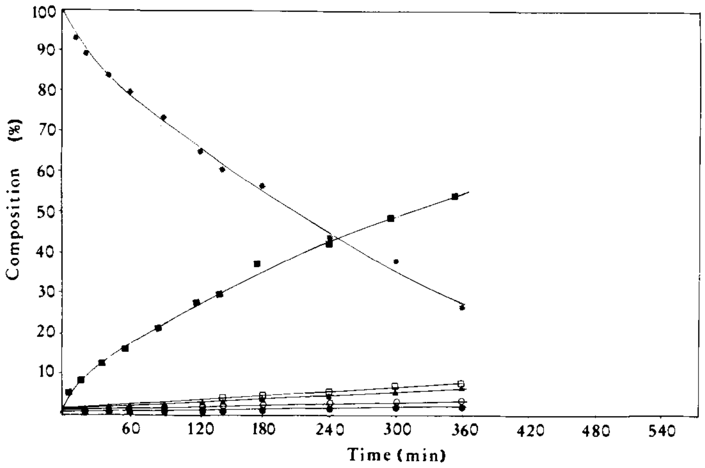

FIG. 1. Hydrogenation of cinnamaldehyde over 10% Pt/C; $T = 333$ K; solvent = ethanol; *, cinnamaldehyde; ■, hydrocinnamaldehyde + diethylacetal; □, phenylpropane; ▲, cinnamyl alcohol; O, phenylpropanol; ●, β-methylstyrene.

—CHO) and hydrocinnamaldehyde diethylacetal ($C_6H_5$—$CH_2$—$CH_2$—CH—$(OC_2H_5)_2$) with smaller amounts of phenylpropane ($C_6H_5$—$CH_2$—$CH_2$—$CH_3$), cinnamyl alcohol ($C_6H_5$—CH=CH—$CH_2OH$), phenylpropanol ($C_6H_5$—$CH_2$—$CH_2$—$CH_2OH$), and β-methylstyrene ($C_6H_5$—CH=CH—$CH_3$). In order to make the figures simpler, the amount of hydrocinnamaldehyde and hydrocinnamaldehyde diethylacetal are reported together. Formation of hydrocinnamaldehyde diethylacetal occurs readily through the reaction between hydrocinnamaldehyde (formed by hydrogenation of cinnamaldehyde) and ethanol used as solvent. Acetals of cinnamaldehyde were not detected under the same conditions.

Hydrogenation of acrolein at 318 K on the same 10% Pt/C produced the corresponding saturated aldehyde with a selectivity >94%. Similar results were obtained on Pt/C with different (1-5%) platinum loading.

On the platinum/Nylon catalyst a significant increase in selectivity toward allyl alcohol was observed in the hydrogenation of acrolein. Yields to allyl alcohol of about 30% were obtained under experimental conditions identical to those used for Pt/C.

In the hydrogenation of cinnamaldehyde the catalytic activity of Pt/Nylon was slightly lower than that of Pt/C and the product distribution was very similar.

Addition of tin to Pt/Nylon causes an increase in selectivity towards the unsaturated alcohol both in the case of acrolein and cinnamaldehyde. Typical results obtained in the hydrogenation of cinnamaldehyde on a Pt–Sn/Nylon sample (RP70) are reported in Fig. 2. Cinnamyl alcohol, hydrocinnamaldehyde (with the corresponding diethylacetal) and phenylpropanol were the main products. Phenylpropane and β-methylstyrene were obtained in smaller amounts.

In contrast to Pt/C, the Pt–Sn system produced mainly cinnamyl alcohol. The selectivity values as a function of time, for the same Pt–Sn/Nylon sample, are reported in Fig. 3. Selectivities were calculated by the expression $S_i = C_i/\Sigma C_p$ where $C_i$ is the concentration of the product $i$ and $\Sigma C_p$ is the total concentration of the products. It can be noted that in the first 2 h the selectivity to cinnamyl alcohol remains almost constant (deviations are due to the experimental error in measuring small amounts of byproducts) regardless of the conversion levels of cinnamaldehyde. After the unsatu-

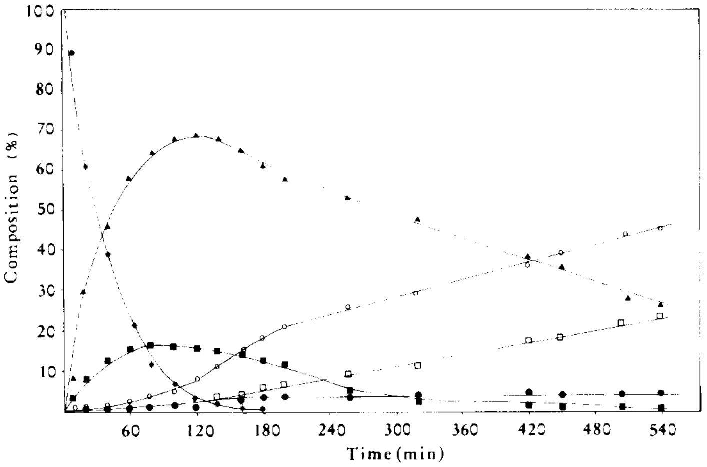

FIG. 2. Hydrogenation of cinnamaldehyde over Pt–Sn/Nylon (RP70); $T$ = 333 K; solvent = ethanol. For key to symbols, see Fig. 1.

rated aldehyde has almost disappeared from the reaction vessel, cinnamyl alcohol is further hydrogenated to phenylpropanol. This indicated that in the initial stages hydrogenation of the C=C double bond and C=O group occurs through parallel reactions. The presence of cinnamaldehyde inhibits the formation of phenylpropanol.

The influence of addition of tin on the selectivity to unsaturated alcohol is reported in Fig. 4 for the hydrogenation of cinnamaldehyde and in Fig. 5 for the hydrogenation of acrolein. The selectivity values reported in Figs. 4 and 5 refer to the first stage of the reaction, before the primary products are further hydrogenated. In both cases addition of a small amount of tin drastically increases the selectivity to unsaturated alcohol which remains constant for Sn contents greater than 15%. When the amount of tin was larger than 50–60% the catalysts were practically inactive and therefore a selectivity value could not be measured. The higher selectivity to unsaturated alcohol is mainly the result of a large increase in the rate of hydrogenation of the C=O group.

The kinetic analysis of the disappearance

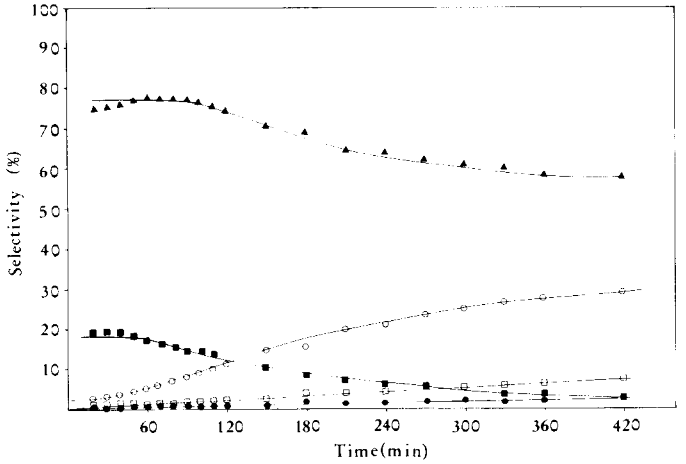

FIG. 3. Product selectivities during cinnamaldehyde hydrogenation over Pt–Sn/Nylon (RP70); $T$ = 333 K; solvent = ethanol. For key to symbols, see Fig. 1.

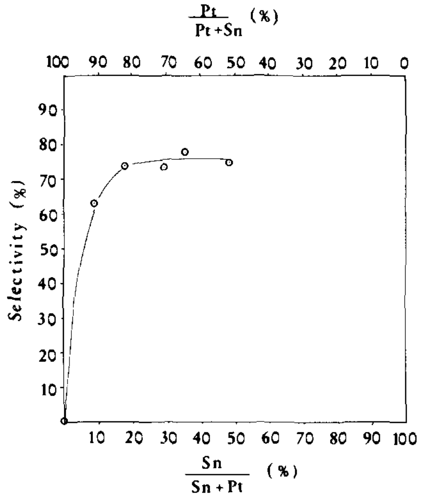

FIG. 4. Influence of the Sn/Pt ratio on the selectivity to cinnamyl alcohol; $T$ = 333 K; solvent = ethanol.

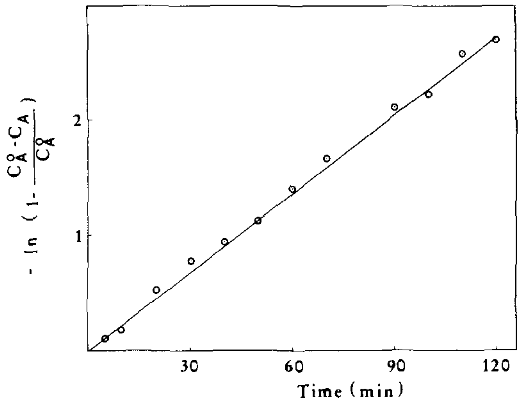

FIG. 6. Kinetic analysis of the disappearance of cinnamaldehyde over Pt–Sn/Nylon; $T$ = 333 K; solvent = ethanol.

of cinnamaldehyde shows that on all Pt and Pt–Sn samples the experimental data can be fitted with a kinetic law of first order with respect to the organic reactant (Fig. 6). The rate constants (calculated from plots similar to that of Fig. 6) as a function of tin content are reported in Fig. 7. On Pt/Nylon a rate constant of $0.8 \times 10^{-4}$ g $Pt^{-1}$ $s^{-1}$ was measured. An increase in the reaction rate up to three orders of magnitude is observed on the bimetallic samples having Sn contents between 15 and 60%.

In the case of hydrogenation of acrolein the observed order of reaction was near zero. Addition of tin causes, also in this case, an increase in the reaction rate. However, the observed increase is much lower (Fig. 8) than that found in the cinnamaldehyde reduction.

All experiments reported in this paper have been carried out using ethanol as sol-

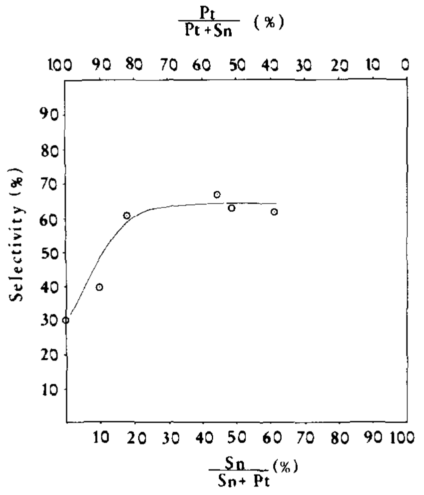

FIG. 5. Influence of the Sn/Pt ratio on the selectivity to allyl alcohol. $T$ = 318 K; solvent = ethanol.

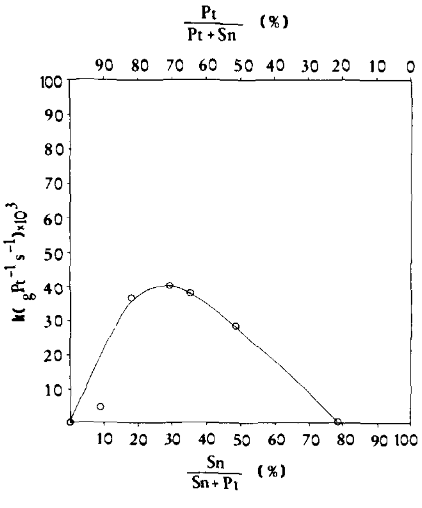

FIG. 7. Influence of the Sn/Pt ratio on the rate constant of cinnamaldehyde hydrogenation; $T$ = 333 K; solvent = ethanol.

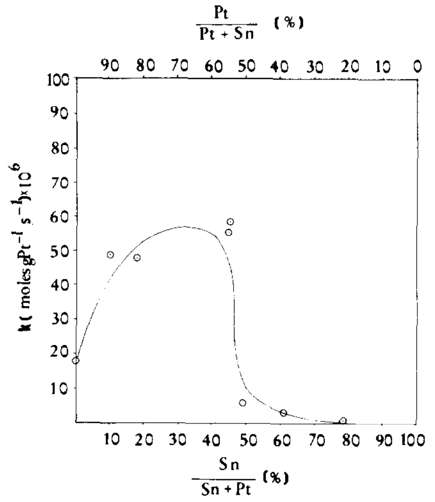

FIG. 8. Influence of the Sn/Pt ratio on the rate constant of acrolein hydrogenation; $T = 318$ K; solvent = ethanol.

vent. Preliminary runs performed using *n*-hexane and benzene as solvents showed that under these conditions it is not possible to hydrogenate the unsaturated aldehydes over the Nylon-supported samples.

## DISCUSSION

Addition of one molecule of hydrogen to $\alpha,\beta$-unsaturated aldehydes can occur in the first step through the following parallel reactions:

$$R{-}CH{=}CH{-}CHO + H_2 \rightarrow R{-}CH_2{-}CH_2{-}CHO \quad (1)$$

$$R{-}CH{=}CH{-}CHO + H_2 \rightarrow R{-}CH{=}CH{-}CH_2OH \quad (2)$$

The products of reactions (1) and (2) can be further hydrogenated to saturated alcohols and to the corresponding hydrocarbons. Under the conditions used in this work it has been found that in the case of hydrogenation of cinnamaldehyde, the diethylacetal of hydrocinnamaldehyde is also formed while no diethylacetal of cinnamaldehyde is observed. This is in contrast with previous results over supported palladium catalysts which show that, using methanol as solvent, the predominant initial product in the hydrogenation of cinnamaldehyde is cinnamaldehyde dimethylacetal which undergoes subsequent hydrogenations (*15*). As pointed out by Millman (*15*), the presence of hydrogen and moreover the nature of the catalyst play an important role in the acetal formation.

Reduction of $\alpha\beta$-unsaturated aldehydes to saturated aldehydes is readily achieved by most platinum metal catalysts under mild conditions, in various solvents, in batch or continuous processing and in liquid or vapor phase (*3*). Over palladium, for example, the reaction stops spontaneously when the saturated aldehyde is formed (*4*). The preferential formation of saturated aldehydes has been related to thermodynamic and kinetic factors. From a thermodynamic point of view it should be considered that the energy of the C=C double bond (615 kJ/mol) is smaller than that of the C=O bond (715 kJ/mol). From a kinetic point of view it is well known that hydrogenation of C=C double bonds occurs at a very fast rate even at low temperature over platinum metals. This preferential formation of saturated aldehydes on Pt/C is confirmed by the results reported in Fig. 1 which show, during the hydrogenation of cinnamaldehyde, the presence in the reaction products of large amounts of hydrocinnamaldehyde. Similar results were obtained in the hydrogenation of acrolein.

It is known that by dispersing platinum on a polyamide matrix its catalytic behavior is drastically altered, i.e., the reactivity towards a C=C double bond is strongly lowered (*1*). During the hydrogenation of acrolein this different behavior resulted in the appearance in the reaction products of a consistent amount of allyl alcohol. The higher selectivity toward allyl alcohol could be related to the observed lower tendency of Pt/Nylon to hydrogenate olefins. Formation of unsaturated alcohol was, however, not observed in the hydrogenation of cinnamaldehyde. This could result from a different reactivity of the C=O group in an aliphatic or in an aromatic aldehyde.

On the basis of these findings it seemed interesting to explore the possibility of producing $\alpha,\beta$-unsaturated alcohols from the corresponding aldehydes by employing Pt–Sn/Nylon samples which have been reported to have an even lower activity towards the hydrogenation of C=C bonds (*1*). In particular, it has been reported that addition of tin to Pt/Nylon causes: (a) a drastic decrease in the rate of hydrogenation of propene which is practically zero for a tin content greater than 50%, and (b) an increase in the order of reaction with respect to the olefin. This is in agreement with a weaker platinum–olefin bond resulting from a modification of the electronic properties of the noble metal.

In the present study, addition of tin to Pt/Nylon resulted in an increase in the selectivity to unsaturated alcohol both in the case of acrolein and in the case of cinnamaldehyde (Figs. 4 and 5). An examination of the rate constants as a function of Sn content (Figs. 7 and 8) shows, however, that the higher selectivity cannot be simply related to the lower reactivity of C=C bonds over Pt–Sn/Nylon samples. In fact, it can be observed that addition of tin leads to an increase in the rate of disappearance of the unsaturated aldehyde which is, in the case of cinnamaldehyde, and for a tin content of 20%, about three orders of magnitude higher than that observed on Pt/Nylon.

In order to try to understand the nature of the influence of tin on the catalytic properties of Pt/Nylon we have recently reported a detailed X-ray investigation on a series of Pt–Sn/Nylon samples having different Pt/Sn ratios (*16*). It has been found that after reduction platinum is in the metallic state, while no isolated metallic tin was detected. This was confirmed by XPS which shows that tin is present in an oxidized form (either Sn(II) and/or Sn(IV)) (*14*). The presence of tin influences the growth of platinum particles, which are smaller at the higher Sn contents. However, the increase in the number of active sites as a result of a larger platinum surface area cannot account for the higher activity of Pt–Sn/Nylon. The measured platinum surface areas varied from 50 $m^2/g$ on the Pt/Nylon samples up to 140 $m^2/g$ on Pt–Sn/Nylon having a Sn content of 60%. The observed increased in the catalytic activity by addition of Sn is instead up to three orders of magnitude. Moreover, the sample with 60% Sn (which showed the larger surface area) is practically inactive. This shows that no direct correlation exists between platinum surface area and catalytic activity. On the basis of the X-ray results it was also suggested that in the Pt–Sn/Nylon system two types of interaction exist: the first occurs via formation of a solid solution and the second through an interaction between platinum and tin ions. The presence of a solid solution was suggested on the basis of the platinum lattice parameters ($a_0$) measured on the mono- and bimetallic samples. On Pt/Nylon the calculated $a_0$ value (3.923 Å) was in close agreement with that of metallic platinum, whereas a systematic expansion up to 3.954 Å was observed on increasing the percentage of tin. Formation of Pt–Sn alloys (intermetallic compounds) was, however, not observed. This is in agreement with previous results on Pt–Sn/$Al_2O_3$ which show that Sn(IV) ions are mainly reduced to Sn(II) and only a small fraction of Sn(0) is formed. This fraction forms bimetallic aggregates with Pt (*12*). It has also been suggested that the reduction of tin at lower temperature (catalyzed by platinum) is caused by an intimate contact of Pt and Sn (*12*).

The two types of interaction which have been suggested between platinum and tin supported on Nylon would result in any case in a decrease in the rate of hydrogenation of the C=C double bond. The occurrence of a Pt–Sn solid solution would in fact decrease the rate of hydrogenation by decreasing the number of empty *d*-orbitals. A similar effect would also result from the interaction between Sn ions and Pt which would decrease the electronic density on platinum causing a lower degree of backdonation into the chemisorbed molecule and therefore a weaker chemisorption bond. This interpretation, however, does not explain the increase in the rate of hydrogenation of $\alpha,\beta$-unsaturated aldehydes observed at low tin content.

It has been reported in the literature that hydrogenation of ketones to alcohols is increased by the presence of electron-acceptor substituents (*17*). In particular, the rate of acetone hydrogenation to isopropanol over Raney nickel has been found to decrease by the introduction of an alkyl group into the ketone molecule. Similar results have also been published on copper chromite catalysts (*18*). Noller and Lin (*19, 20*) have recently reported that addition of small amounts of copper to Raney nickel increases its activity in the hydrogenation of crotonaldehyde and its selectivity for C=O bond hydrogenation. The effect of copper has been related to the increased electron donor properties of the chemisorbed hydrogen on the Ni–Cu system. It has been suggested that in the rate determining step, an electron donor species (probably $H^-$) attacks the C=O carbon atom. The higher the electron donor strength the stronger is its attack.

It can be suggested that in our case the effect of tin is related to the acidic properties of the Sn ions (Lewis acidity) which activate the carbonyl group by enhancing the positive charge on the C=O carbon atom. Another positive effect could also result from the formation of the Pt–Sn solid solution which, as in the case of Ni–Cu reported by Noller (*19, 20*), would increase the electron density on the platinum sites leading to chemisorbed hydrogen having a stronger negative charge.

The effect of acids on the hydrogenation of $\alpha,\beta$-unsaturated aldehydes can be found in many papers. Nagase *et al.* (*21*) have reported that addition of small amounts of $Fe^{3+}$ (which can be considered a Lewis acid) to Raney silver–zinc catalysts increases the selectivity to allyl alcohol. An increase in the selectivity to unsaturated alcohols by addition of $Fe^{3+}$ has been also reported in the early work of Tuley and Adams (*22*). The effect of an acidic modifier, such as acetic acid, $MnCl_2$ and $CoCl_2$, to Raney cobalt catalysts has been reported by Hotta and Kubomasu (*23*) for the hydrogenation of 2-methyl-2-pentenal. Addition of the acidic modifiers increases the selectivity to the unsaturated 2-methyl-2-pentenol.

At higher tin contents the catalytic activity of Pt–Sn/Nylon decreases drastically and samples having a Sn content >60% are practically inactive. An XPS investigation carried out on the same samples before and after reduction has shown no tin surface enrichment (*14*), ruling out the possibility that the low activity is related to a surface coverage of the active platinum sites by tin. It is therefore likely that on the Sn-rich samples the Pt–Sn interaction leads to platinum sites which are not able to activate the hydrogen atoms.

In conclusion, the results reported on the Pt–Sn/Nylon system show that addition of tin has a double effect on the hydrogenation of $\alpha,\beta$-unsaturated aldehydes over platinum catalysts. First, the acidic properties of Sn ions activate the carbonyl group which becomes more reactive than the C=C double bond. A second effect of tin is related to the electronic interaction with platinum which poisons the active metal sites responsible for hydrogen activation.

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