Selective Hydrogenation of α,β-Unsaturated Aldehydes to give Unsaturated Alcohols over Platinum–Germanium Catalysts

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On Pt–Ge catalysts cinnamaldehyde is hydrogenated to cinnamyl alcohol with a selectivity of 90—95% at conversions higher than 90%.

Catalytic hydrogenation of α,β-unsaturated aldehydes to give saturated aldehydes is readily achieved by most platinum metal catalysts under mild conditions.[1] The selective reduction to give unsaturated alcohols instead is difficult to obtain.

Recently we have reported[2,3] that addition of tin chloride to Pt/Nylon or Pt/C leads to a large increase in the overall rate of hydrogenation of α,β-unsaturated aldehydes and to a high (~75%) selectivity towards the formation of the corresponding unsaturated alcohol. It has been suggested that the promoting action of tin may be attributed to the presence of tin ions and is related to their acidic properties which enhance the reactivity of the C=O group.[2—6]

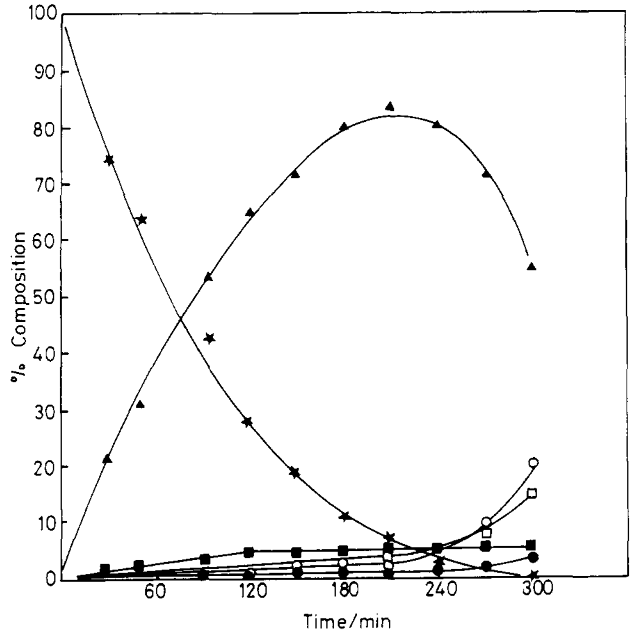

Figure 1. Hydrogenation of cinnamaldehyde over Pt–Ge/Nylon (3% Ge); T = 333 K; solvent = ethanol; ★, cinnamaldehyde; ▲, cinnamyl alcohol; ■, hydrocinnamaldehyde: ○, phenylpropanol; ●, β-methylstyrene; □, phenylpropane.

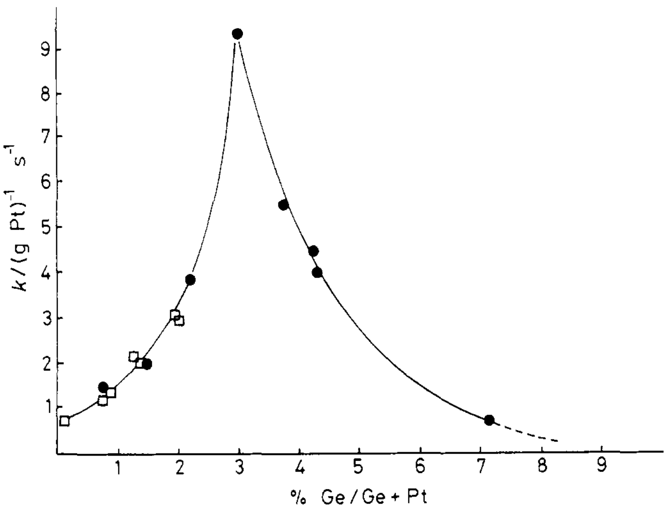

Figure 2. Influence of Ge content on the rate constant of cinnamaldehyde hydrogenation. T = 333 K; solvent = ethanol; ●, series A; □, series B.

In order to improve selectivities to give unsaturated alcohols, a study has been undertaken on the effect of the nature of the second component added to platinum catalysts. In this communication we report the unique role of germanium which when added to platinum catalysts leads to selectivities of about 95%.

Catalysts were prepared by a conventional impregnation method. Nylon 66 (SNIAMID, 50—100 mesh, Brunauer–Emmett–Teller surface area <1 m^2/g) was impregnated with H_2PtCl_6 or with H_2PtCl_6 and $GeCl_4$ from EtOH solutions for 5 h at room temperature. After removal of solvent by filtering and drying, the impregnated catalysts were subsequently reduced by bubbling H_2 for 1 h in a slurry of catalyst in EtOH. The amount of platinum in the catalysts was in the range 1.2—2.0%. Hydrogenations were carried out in a 100 ml four-necked flask fitted with a hydrogen reservoir, dropping funnel, thermocouple, and a stirrer head with permanent magnetic coupling. The progress of the reaction was followed by analysing a sufficient number of microsamples. Details of the experimental apparatus and gas-chromatographic analysis are reported elsewhere.[3]

Two series of experiments were carried out. In the first series (series A) a 2.0% Pt/Nylon catalyst was always used, and a different amount of $GeCl_4$ was added to the reaction mixture before the hydrogenation of the aldehyde was started. In the second series (series B) Pt–Ge/Nylon catalysts obtained by co-impregnation of Pt and Ge salts were used instead. Catalysts having different Pt : Ge ratios were obtained by changing the relative salt concentration of the impregnating solutions.

The presence of germanium drastically changed the catalytic hydrogenation of the α,β-unsaturated aldehydes. Over Pt–Ge the main reaction product was cinnamyl alcohol, in contrast with the formation of hydrocinnamaldehyde over the monometallic Pt sample. Typical results obtained over the Pt–Ge system are reported in Figure 1. Hydrocinnamaldehyde, β-methylstyrene, phenylpropanol, and phenylpropane were obtained in very small amounts. The concentration of the two latter compounds increases after almost all the cinnamaldehyde has disappeared from the reaction vessel as a result of a further hydrogenation of the unsaturated alcohol. Preliminary runs carried out over carbon supported samples showed a higher rate of reaction (probably due to a higher platinum dispersion) but a very similar product distribution.

The rate of cinnamaldehyde disappearance was found to be first order with respect to the aldehyde concentration regardless of the Pt : Ge ratio. The effect of the relative amount of Ge on the overall rate of reaction is reported in Figure 2. The presence of Ge also changes drastically the reaction selectivity. While on the monometallic Pt sample cinnamyl alcohol is practically not formed (S < 2%), addition of only 0.2 atomic %Ge (Ge/Ge + Pt) leads to a selectivity of 64%. Values of about 90 ± 5% have been obtained for Ge contents of 1 to 7 atomic %. At Ge contents higher than 7—10% the catalytic activity was very low and no selectivity values could be measured. It is noteworthy that both series of experiments (series A and B) carried out with similar Pt : Ge ratios gave similar results.

An examination of the rate constants as a function of the Ge content (Figure 2) shows that the higher selectivity is mainly due to an activation of the C=O group over the Pt–Ge system. As we have previously suggested[3,5] the electronegative element (Ge) has two main effects. At low concentration it contributes to accelerate the rate of reaction by activating the C=O bond through an enhancement of the positive charge on the carbon atom. At higher concentration however the adsorbed Ge ions deactivate the platinum sites responsible for hydrogen activation. The higher selectivity found on Pt–Ge with respect to the previously studied Pt–Sn system is probably related to the higher electronegativity of Ge and a study to verify this hypothesis is in progress.

The differences found between the previously studied Pt–Sn system[3] and the results reported here suggest that the presence of chlorine traces is not responsible for the observed catalytic behaviour. This was confirmed with blank runs carried out on the monometallic Pt/Nylon by adding an equivalent amount of HCl or NaCl to the reaction mixture.

On the basis of the results reported in this communication it can be concluded that the use of small amounts of Ge together with platinum provides a composite catalyst which can be successfully used for the selective synthesis of α,β-unsaturated alcohols under mild conditions.

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