

Selective Hydrogenation of α,β -Unsaturated Aldehydes to Unsaturated Alcohols over Mixed Ruthenium–Tin Boride Catalysts

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On Ru–Sn boride catalysts, cinnamaldehyde is hydrogenated to cinnamyl alcohol with 65% selectivity at 73% conversion.

Hydrogenation of α,β -unsaturated aldehydes to give unsaturated alcohols selectively has been a tough task to achieve for catalytic chemists. Platinum group metals generally exhibit very good activity and selectivity for the formation of saturated aldehydes and/or alcohols.¹ In fact, in the case of palladium catalysts, the reaction is known to stop spontaneously, once the saturated aldehyde is formed.

Galvagno *et al.*² have reported the use of Pt–Sn/Nylon catalysts for selective formation of cinnamyl alcohol from cinnamaldehyde, and there were a number of earlier reports^{3–5} on the high catalytic activity of nickel and cobalt boride. We have recently studied various hydrogenation reactions using metal borides as catalysts. We now report the high activity and selectivity shown by the mixed metal boride catalyst Ru–Sn–B for the hydrogenation of cinnamaldehyde to

cinnamyl alcohol. We also show that in addition to tin as an important component in our catalyst system, the method of reduction using sodium borohydride and the incorporation of boron also play important roles in influencing the activity and selectivity in this reaction.

The catalyst Ru–Sn boride was prepared as follows. Appropriate quantities of aqueous ruthenium chloride (Fluka, Switzerland) and tin(II) chloride (B.D.H., India) were mixed, and aqueous sodium borohydride was then added in drops at room temperature until the reduction was complete. The solids were washed free of sodium using water and then absolute ethanol, and finally air dried before use. The metals were also supported on γ -alumina (Harshaw-Chemie, B.V. Netherlands, surface area 200 m²/g). Preparation of the supported catalysts followed the same sequence, with the

Table 1. Activity and selectivity data (%) for hydrogenation of cinnamaldehyde^a

Entry	Catalyst ^d	Conversion	PhCH=CHCH ₂ OH	PhCH ₂ CH ₂ CHO	PhCH ₂ CH ₂ CH ₂ OH	Other products ^c	Selectivity for PhCH=CHCH ₂ O ^b
1	Ru–Sn–B	73.4	47.3	5.3	14.4	6.4	64.5
2	Ru–Sn–B/Al ₂ O ₃	65.2	29.4	14.6	19.5	1.7	45.1
3	Ru–B	98.7	—	98.4	—	—	—
4	Ru/Al ₂ O ₃	24.6	6.1	4.5	—	14.0	24.8
5	Ru–Sn/Al ₂ O ₃	17.9	0.9	0.6	—	16.3	—

^a Reaction at 100 °C, *P* 100 lb in⁻²; 0.5 ml of cinnamaldehyde, in 4.5 ml of ethyl acetate; 20 h reaction. ^b Selectivity for cinnamyl alcohol = % cinnamyl alcohol/% conversion. ^c Other products are mostly unidentified low molecular weight compounds. About 70% of these products is the decarbonylated product, styrene. ^d Ruthenium content is 2% by weight on all supported catalysts and in all bimetallic catalysts the atomic ratio of Ru to Sn is 1 : 1.

following difference. Before the reduction step, the alumina support was soaked in the mixed-metal salt solution for about 16 h. Chemical analysis showed that all the catalysts contained boron. Ru-Sn catalysts supported on alumina which do not contain boron were also prepared by a conventional impregnation technique,⁶ and reduced in flowing H₂. Hydrogenations were carried out in a 300 ml capacity Parr autoclave (Model 4561, Parr Instrument Company, Illinois), with ethyl acetate as solvent. The products were analysed by gas chromatography using Carbowax 400 M on Chromosorb.

Table 1 lists the data on hydrogenation reactions on the various catalysts studied. The unsupported Ru-Sn-B catalyst shows the highest activity and selectivity for cinnamyl alcohol formation (entry 1, conversion 73.4%, selectivity 64.5%), followed in activity and selectivity by Ru-Sn-B supported on alumina (entry 2). It is interesting that unsupported Ru-B (without any tin) shows 98.6% conversion, but the only product is the saturated aldehyde; Ru-B/Al₂O₃ behaved similarly. The catalysts prepared by conventional methods are also highly non-selective for cinnamyl alcohol formation (entries 4 and 5). Similar, but less pronounced, effects were observed for the hydrogenation of crotonaldehyde. Addition of tin and boron to ruthenium resulted in a dramatic increase in the selectivity for crotyl alcohol formation under similar conditions.

Two types of sites are suggested to be responsible for the selective hydrogenation of the carbonyl group. (i) Tin could be present as Sn²⁺ and interacting with ruthenium metal. Sn²⁺, a Lewis acid, could then polarise the carbonyl bond and facilitate attack by hydride formed on an adjacent ruthenium atom. (ii) Sn⁰ might form an alloy with ruthenium and enrich

the electron density on Ru⁰. This might facilitate the activation of hydrogen in a more hydridic form and favour selective attack on C=O. There is some evidence for both these types of sites, based on our spectroscopic characterisation of the catalysts.⁷

The role of boron probably lies in changing the electron charge distribution around ruthenium, thereby enhancing its intrinsic catalytic activity. Such a correlation was suggested earlier in the case of nickel boride catalysts by Swartz *et al.*⁵ based on X-ray photoelectron spectroscopic studies. Levy and Boudart⁸ also suggested a similar correlation based on their studies on the catalytic activity of tungsten carbide.

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