

Correlation between Hydrogenation Activity and Amount of Adsorbed Hydrogen Species on Rh–Sn Catalysts

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On Rh–Sn catalysts the most strongly adsorbed hydrogen species is found to be associated with tin and directly related to the catalytic activity in the hydrogenation of ethyl acetate.

It is now well established that the modification of a supported transition metal catalyst by an element belonging to groups 1B, 2B, 3A, or 4A can lead to drastic changes in its catalytic properties. For example Rh–Sn¹ and Pt–Sn² systems show a decrease in hydrocarbon hydrogenolysis compared to monometallic supported Rh or Pt catalysts. Though characterization of this kind of catalyst has been the subject of many studies, there is no clear correlation between their chemisorptive and catalytic properties. Nevertheless it has been shown^{1,2} that these catalysts exhibit a high temperature desorption peak for hydrogen which seems to be related to the presence of tin.

We present here some new results linking the amount of a strongly adsorbed hydrogen species to the activity of a Rh–Sn catalyst in the hydrogenation of ethyl acetate to ethanol.

Rhodium was impregnated on silica (Rhône-Poulenc, 365 m² g⁻¹, 1.21 cm³ g⁻¹) by cationic exchange of the chloropentammine–rhodium complex [RhCl(NH₃)₅]Cl₂. After calcination in dry air at 573 K and reduction in hydrogen at 573 K tin was added using SnBu₄. The reduction of this system leads to an active catalyst able to hydrogenate ethyl acetate to ethanol under medium pressure (5 MPa) and temperature (523 K).³

Thermodesorption of hydrogen in argon at 10 K min⁻¹ was carried out after reduction at 853 K in a flowing mixture H₂–Ar [*P*(H₂) 5 kPa] followed by: A, purge in Ar at 853 K, cooling to room temperature in Ar and chemisorption of hydrogen in the H₂–Ar mixture at room temperature or B, cooling of the reduced catalyst from 853 K to room temperature in the same flowing H₂–Ar mixture.

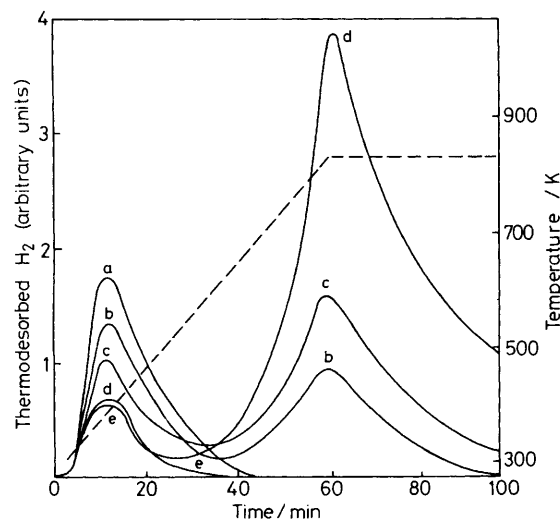


Figure 1. Hydrogen thermodesorption spectra for Rh–Sn/SiO₂ catalysts at varying Sn/Rh_s ratios. ----- temperature (K), ——— thermodesorbed H₂; (a) Sn/Rh_s = 0, B pretreatment; (b) Sn/Rh_s = 0.3, B pretreatment; (c) Sn/Rh_s = 1, B pretreatment; (d) Sn/Rh_s = 2.4, B pretreatment; (e) Sn/Rh_s = 2.4, A pretreatment.

Two species have been identified by their different desorption temperatures (Figure 1). At increasing Sn/Rh_s (ratio of Sn atom per surface Rh atom) the low temperature desorption peak decreases both for A and B pretreatment. In contrast, the second desorption peak only appears for samples containing tin and submitted to B type chemisorption. Moreover, the area under this peak increases linearly with Sn/Rh_s within the precision range of the method, ±20%. The highest temperature used was only 853 K which is *ca.* 60 K below the true peak temperature (which was measured by a device capable of reaching temperatures as high as 1053 K). This limitation was overcome by isothermal treatment for 2 h at 853 K in order to measure the total quantity of thermodesorbed hydrogen.

This behaviour can be correlated with the variation in activity and selectivity of these catalysts in the hydrogenation of ethyl acetate and the increase in Sn/Rh_s ratio. Monometallic supported rhodium is active in this reaction but the selectivity to form ethanol is very low (50%) because of the formation of methane and ethane. As Sn/Rh_s increases above 0.3, selectivity becomes higher (70%) and even reaches 95% for Sn/Rh_s = 1. Simultaneously the activity linearly increases with Sn/Rh_s, suggesting a change in the active species as the catalyst is transformed from a monometallic to a bimetallic one.

Catalytic hydrogenation generally involves adsorbed hydrogen species, so it seems logical to correlate the nature and amount of the two observed species with the hydrogenation activity of ethyl acetate. There appears to be a direct linear relationship between the hydrogenation activity of ethyl acetate and the amount of high temperature desorbable hydrogen (Figure 2).

In conclusion, this catalyst exhibits two adsorbed hydrogen species. The first, associated with rhodium, is slightly modi-

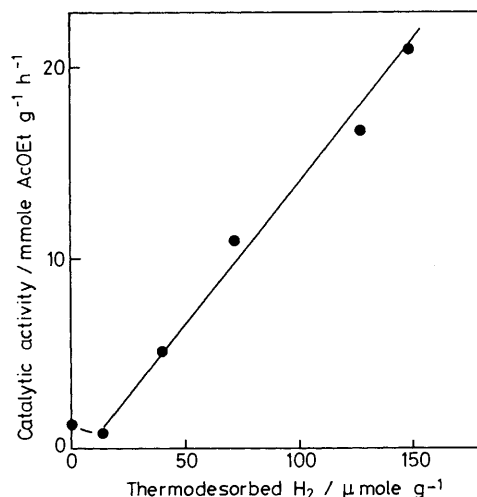


Figure 2. Relationship between the hydrogenation activity of ethyl acetate [measured at 543 K, *P*(H₂) 4.5 MPa, *P*(AcOEt) 0.5 MPa] and the amount of high temperature desorbable hydrogen.

fied by the addition of tin, while the second one, associated with tin, appears to be directly connected to the catalytic activity and selectivity of the bimetallic catalysts.

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