

Structure of platinum-tin on carbon nanofibers related to its performance for cinnamaldehyde hydrogenation

Arie J. Plomp, Krijn P. de Jong and Johannes H. Bitter^{1*}
¹*Inorganic Chemistry and Catalysis, Utrecht University,
3584 CA Utrecht (The Netherlands)*
*j.h.bitter@chem.uu.nl

Introduction

The selective hydrogenation of cinnamaldehyde to cinnamyl alcohol is an industrially relevant hydrogenation step [1]. Recent research showed an unprecedented high activity of platinum on carbon nanofibers (CNF) during the cinnamaldehyde hydrogenation [2, 3]. The activity of these materials was related to the amount of oxygen functionalities on the CNF surface; the lower the amount of oxygen, the higher the activity. Please note that introduction of surface oxygen is an essential step for the preparation of highly dispersed and thermally stable metal particles on CNF. Unfortunately, the highly active Pt/CNF catalyst shows a low selectivity towards the desired cinnamyl alcohol [2, 3].

In this presentation, we will show that a well-controlled preparation of platinum-tin on carbon nanofibers results in an increased activity and selectivity for the cinnamaldehyde hydrogenation. Tin is a well-known promoter-metal in combination with platinum to increase the selectivity for the hydrogenation of α,β -unsaturated aldehydes [4]. The increase in activity is remarkable and hardly noted in literature. We will discuss the prepared platinum-tin on CNF catalysts and relate the enhanced activity and selectivity to the obtained structure after synthesis.

Materials and Methods

Platinum on CNF (3 wt-%) was prepared as described earlier by Toebes et al [2]. After reduction, samples of this Pt/CNF catalyst were treated for 2 h in N₂ at 973 K to adjust the amount of oxygen on the surface. The resulting catalyst was denoted as Pt/CNF-973.

One batch of platinum-tin on CNF was prepared as described by Corro et al [5]. Pt/CNF was stirred in HCl-solution under H₂ (atm. pressure) and after 1 h, SnCl₄ was added and stirred for 30 min. After filtration, drying (393 K; overnight) and reduction (473 K; 1h; H₂/N₂-flow (10%)), the samples were treated for 2 h in N₂ at 973 K. Intended tin loading: 0.37 wt-%. This material was denoted as Pt-Sn/CNF-973 A.

A second batch of platinum-tin on CNF was prepared using incipient wetness impregnation. Pt/CNF-973 was evacuated and a solution of SnCl₄ in demi-water was impregnated until the material had a sticky appearance. This was kept under static vacuum for at least 40 h, dried (393 K; overnight) and reduced (473 K; 1h; H₂/N₂-flow (10%)). Tin loading: 0.37 wt-%. The material was denoted as Pt-Sn/CNF-973 B.

The catalysts were tested for the cinnamaldehyde hydrogenation. The catalyst was stirred in 2-propanol/water-solution at 313 K and 1.2 bar H₂ pressure. After cinnamaldehyde addition, the reaction was run for 5 hours. Samples were taken at time intervals and analyzed using a GC.

Results and Discussion

The resulting activity and selectivity of the catalysts for the cinnamaldehyde hydrogenation are depicted in Fig. 1. The initial activity of Pt-Sn/CNF-973 A is the highest, followed by mono-metallic Pt/CNF-973. Pt-Sn/CNF-973 B has the lowest initial activity. The selectivity follows the same trend: the highest selectivity is observed for Pt-Sn/CNF-973 A, followed by mono-metallic Pt/CNF-973. Pt-Sn/CNF-973 B shows the lowest selectivity.

During the synthesis of Pt-Sn/CNF-973 A, H₂ is present. Probably, this results in reduction of tin at the platinum sites and a well-defined platinum-tin alloy on the catalyst is obtained. On the other hand, tin is forced on the catalyst using impregnation for Pt-Sn/CNF-973 B, which does not result in a well-defined platinum-tin alloy. Further characterization of these catalysts, with among others EXAFS, will provide detailed information on the platinum-tin alloy. We will relate the structure to the obtained hydrogenation results.

Significance

The well-controlled preparation of platinum-tin on CNF results in a well-defined platinum-tin alloy. Both activity and selectivity for the cinnamaldehyde hydrogenation are strikingly enhanced for this catalyst.

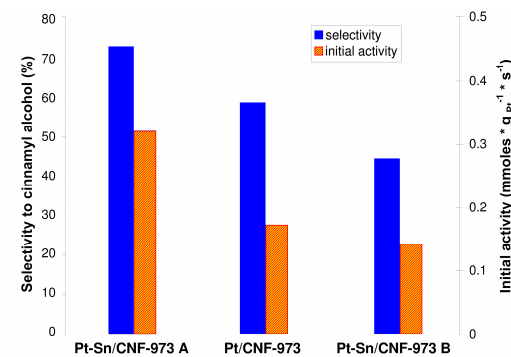


Figure 1. Cinnamaldehyde hydrogenation results for Pt-Sn/CNF-973 A, Pt/CNF-973 and Pt-Sn/CNF-973 B. The maximum observed selectivity is plotted on the left axis and the initial activity on the right axis.

References

1. Gallezot, P., and D. Richard, *Catal Rev*, 40, 81 (1998)
2. Toebes, M.L. et al, *J Catal*, 226, 215 (2004)
3. Toebes, M.L. et al, *Chem Eng Sci*, 60, 5682 (2005)
4. Ponc, V., *Appl Catal A*, 149, 27 (1997)
5. Corro, G., P. Marecot, and J. Barbier, *Stud Surf Sci Catal*, 111, 359 (1997)