

Promoted platinum catalysts with close contact between platinum and promoter for the selective hydrogenation of cinnamaldehyde

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Introduction

Precision in catalyst preparation is essential to arrive at catalysts with well defined catalytic properties. A wealth of techniques such as impregnation, precipitation using bases and ion exchange have been applied with varying success.

For selective hydrogenations, Barbier and co-workers showed that the deposition of a promoter such as Sn or Fe on a Pt based catalyst via redox chemistry catalyzed by the first metal (Pt) [1] resulted in highly selective catalysts. In that case hydrogen was adsorbed on a metal based catalyst and the promoter was deposited via reduction of promoter-salt with the adsorbed hydrogen. We call this technique Reductive Deposition Precipitation (RDP). Preparation of bimetallic catalysts via RDP can also be performed below the equilibrium potential of the redox reaction. The latter situation results in underpotential deposition: adatoms can be deposited on particular sites of the metal surface whereby the equilibrium potential is shifted and enables creation of submonolayers of adatoms.

Though the advantage of RDP for catalytic performance was shown [2], detailed characterization of the interaction of promoter metals with the active metal is lacking thus far leaving the exact nature of the promoter-active phase interaction unresolved. Therefore, in this study we investigated the platinum-promoter interaction for RDP-prepared, platinum based CNF-supported, bimetallic catalysts using TEM-EDX, XPS and EXAFS. These results will be related to catalytic results using cinnamaldehyde hydrogenation as a showcase. For comparison a catalyst prepared by impregnation was included.

Materials and Methods

Platinum was deposited via HDP on CNF-ox using $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ and urea as base as described earlier [3] followed by a heat treatment in N_2 at 973 K for 2 h (Pt/CNF-973).

Tin and gallium were deposited on Pt/CNF via RDP using tin-tetrachloride or gallium nitrate solutions. Pt/CNF-973 was stirred for 1 h under hydrogen (1.2 bar) in water (acidified for SnCl_4) followed by adding of this solution via a septum to the Pt/CNF-973 slurry. After stirring for 30 min the slurry was filtered and the catalysts were successively dried overnight at 393 K, reduced and heat-treated as described earlier for Pt/CNF-973. The samples were named using the promoter weightloading as suffix i.e., Pt- SnCl_4 /RDP-0.4 is expected to have 0.4 weight-% Sn. All samples had a 3 wt% Pt loading. For reasons of comparison, tin was also added via incipient wetness impregnation.

The catalysts were tested for the cinnamaldehyde hydrogenation at low (1.2 bar) and at high (30 bar) hydrogenation pressure.

Results and Discussion

To investigate the location and state of Sn in the different catalysts TEM/EDX, EXAFS hydrogen chemisorption and XPS studies were performed (the latter two are not reported here). TEM/EDX indicated that for the RDP prepared samples Sn was always in contact with Pt however the resolution of this technique is limited and information on an atomic scale could not be obtained. Therefore an EXAFS study was performed. The table below shows the results of the fitting of the Sn-K edge data. From this table it is concluded that for the RDP prepared samples Sn is in close contact with Pt as shown by an appreciable Sn-Pt coordination. This

Catalyst	EXAFS			Catalysis at 1.2 bar	
	Scatter	N	R (Å)	Initial activity ($\text{mmol.s}^{-1}.\text{g}_{\text{Pt}}^{-1}$)	Selectivity* (%)
Pt- SnCl_4 /IWI-5	Sn-Sn	0.5	3.18	0.18	43
	Sn-Pt	1.6	2.71		
	Sn-O	5.1	2.04		
Pt- SnCl_4 /RDP-5	Sn-Sn	-	-	0.37	72
	Sn-Pt	4.8	2.74		
	Sn-O	1.1	2.08		
Pt- SnCl_4 /RDP-1	Sn-Sn	0.6	3.34	0.27	81
	Sn-Pt	5.2	2.75		
	Sn-O	0.8	2.06		
Pt/CNF-973	-	-	-	0.21	59

*Selectivity to cinnamylalcohol (%) at 50% conversion

contribution is absent in the sample prepared by IWI. When a close contact is ensured the activity and selectivity of the catalyst was enhanced. The enhancement of selectivity and activity for RDP prepared samples was also observed for Ga promoted samples thus indicating that this is a general trend.

The trends in selectivity were similar at both low and high pressure. However the activity trends were a function of the applied reaction conditions showing that trends in activity are dependent on the applied reaction conditions while this is not the case for selectivity.

Significance

The present work gives an explanation for the superior performance of RDP prepared promoted Pt catalysts for the selective hydrogenation of cinnamaldehyde. The combination of catalytic studies with thorough characterization as shown here is essential to arrive at a structure-performance relation. This relation is expected to result in rational catalyst design.

References

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