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## High-throughput Screening of Tin Modified Platinum Catalyst Used for Liquid Phase Hydrogenation of Crotonaldehyde

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### Introduction

Recent years the high-throughput screening (HTS) of catalysts has obtained both great scientific and practical interest [1]. The hydrogenation of unsaturated aldehydes to the corresponding alcohol is frequently applied for the preparation of fine chemicals. In this study crotonaldehyde (UAL) was hydrogenated to crotyl alcohol (UOL) in the liquid phase on a series of pure and tin modified platinum catalysts. The selective introduction of tetraethyl tin as precursor compound onto supported metals is based on the Controlled Surface Reaction (CSR) between adsorbed hydrogen and tin tetra-alkyl compounds [2]. Upon using SnEt<sub>4</sub> in the CSR an anchored Primary Surface Complex (PSC) is formed can be written as follows:



After fast screening a number of tin modified platinum catalysts 2.2%Pt/SiO<sub>2</sub> and 5%Pt/Al<sub>2</sub>O<sub>3</sub> (Degussa, did not require re-reduction) catalysts, as leads, were chosen for detailed study. The effect of tin content and the mode of introduction has been investigated.

### Materials and Methods

Both *in situ* modification with Sn(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub> and the catalytic reaction was carried out in automated high-throughput high pressure slurry phase reactor equipped with 16 autoclaves (V=15ml) (SPR16, AMTEC GmbH, Germany). The modification was done prior to UAL hydrogenation either by adsorption at RT or *in situ* CSR at 50°C. Methylcyclohexane was used as a solvent (V = 8 ml), and the amount of UAL was 0.5 ml (c = 0.7 mol/l). The analysis of the reaction mixture (UAL, UOL, butyraldehyde (SAL), butanol (SOL) was done by GC.

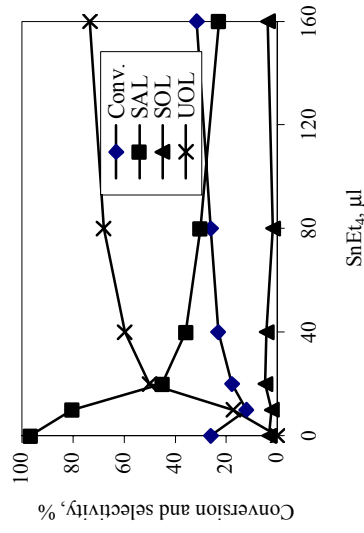
### Results and Discussion

The increase of the amount of SnEt<sub>4</sub> added to 5%Pt/Al<sub>2</sub>O<sub>3</sub> and 2.2%Pt/SiO<sub>2</sub> catalysts markedly enhanced the selectivity of UOL (see Table 1 and Figure 1, respectively). Tin modified 5%Pt/Al<sub>2</sub>O<sub>3</sub> is more active and selective to SOL than 2.2%Pt/SiO<sub>2</sub>.

**Table 1. Hydrogenation of UAL on 5%Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. Effect of the amount of SnEt<sub>4</sub>.**

SnEt <sub>4</sub> (μl)	Conv. (%)	SAL (%)	SOL (%)	UOL (%)
0	95	66	31	3
5	99	<1	68	31
10	98	<1	63	36
30	99	<1	48	51
60	97	<1	32	68
80	96	<1	22	78

SnEt<sub>4</sub> was added at 50 °C, 0.5 MPa H<sub>2</sub> and kept on the catalyst for 2 h. Then UAL was added and the reaction was performed at T = 35°C, P<sub>H<sub>2</sub></sub> = 2 MPa, t = 4 h, 1000rpm.



**Figure 1.** The effect of SnEt<sub>4</sub> added by adsorption on the performance of 2.2%Pt/SiO<sub>2</sub> catalyst.

**Table 2. The effect of modification in the hydrogenation of UAL on 5%Pt/Al<sub>2</sub>O<sub>3</sub> catalyst.**

Mode of tin addition	t (h)	Conv. (%)	SAL (%)	SOL (%)	UOL (%)
ex situ 50°C (PSC)	3	66	43	17	40
ex situ 50°C (PSC)	4	78	39	22	39
ex. red. 450°C (Pt-Sn)	3	56	62	16	22
in situ 25°C	4	83	13	17	70
in situ 50°C	4	96	1	22	78

80 μl SnEt<sub>4</sub> was used for modification. UAL was added after modification and the reaction was performed at T = 35 °C, P<sub>H<sub>2</sub></sub> = 2 MPa, 1000rpm.

As seen in Table 2 *in situ* modification of 5%Pt/Al<sub>2</sub>O<sub>3</sub> catalyst results in much higher UOL selectivity than *ex situ* CSR [2], followed by decomposition of PSC in the liquid phase or in H<sub>2</sub> at 450°C. The highest selectivity of crotyl alcohol eached on tin modified 5 wt.% Pt/Al<sub>2</sub>O<sub>3</sub> at 96% conversion was ca. 80 %. It is suggested that "Sn"-Pt<sup>0</sup> "metal ion-metal nanocluster" ensembles play a crucial role in selectivity control to crotyl alcohol [3].

### Significance

HTS screening and development of catalysts has both industrial and fundamental importance.

### References

- Thomson, S., Hoffmann, C. Ruthe, S., Schmidt, H.W. and F. Schuth, F., *Appl. Catal. A: General* 220, 253 (2001).
- Margitfalvi, J.L., Borbáth, I., Hegedűs, M. and Tompos, A., *Appl. Catal. A: General* 229, 35 (2002).
- Margitfalvi J.L. and Göbölös S. in "Catalysis- Science and Technology, Specialist Chemistry Reports" (J.J. Spivey and G.W. Roberts, Eds.) Vol.17, p. 1, Royal Society of Chemistry, London, 2004.