

## Liquid Phase Hydrogenation of Citral with Pt and PtSn Supported Catalysts to Obtain Geraniol, Nerol and Citronellol

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### Introduction

The addition of tin as promoter to transition metals has been widely used during the last decade in order to improve the catalytic properties of these metals. Particularly, the alloys of tin with platinum have been shown to greatly enhance the selectivity of the hydrogenation of the  $\alpha,\beta$ -unsaturated aldehydes. Effectively, compared to pure Pt, the yield in unsaturated alcohols, a product showing interesting properties in the fine chemical industry, is increased [1]. The origin of this catalytic effect is not totally understood and several hypotheses exist: Sn can act as an inert, side-blocking agent that changes the adsorption site of the molecules, and Sn can introduce electronic effects on Pt, modifying its adsorption properties [2].

### Materials and Methods

Pt and PtSn catalysts were prepared by incipient wetness impregnation. Silica Gel of high superficial area was used as support (Silice Gel 7, J. T. Baker, Sg = 680 m<sup>2</sup>/g). The amount of Pt impregnated was 1% wt for all catalysts. In bimetallic catalysts Pt content was 1% wt also and Sn was added to obtain the following atomic relation of Pt/Sn=0.5, 1.0 and 1.5. All catalysts were calcined and reduced at 500°C.

Hydrogenation experiments were carried out in a Parr reactor model 4560. The reactions were conducted at constant hydrogen pressure of 13 bar and at 100°C. The samples withdrawn were analyzed in a gas chromatograph coupled to a mass spectrometer.

### Results and Discussion

In this work we report the results of the performance of Pt and PtSn catalysts in the liquid phase hydrogenation of citral. The supports employed were silica gel (SG7) and the metal loading was 1% Pt with a Pt/Sn atomic relation of 0.5, 1.0 and 1.5. In addition the effect of the solvent was studied using hexane and 2-propanol. Excellent results were obtained when the PtSn/SG7 with a Pt/Sn ratio of 1 was used with 2-propanol as solvent: citral conversion was 100% and the selectivity towards geraniol-nerol mixture was 64% and 36% of citronellol. This result was attributed to electronic and geometric effects when tin was added as promoter [3]. If tin was not present (Pt/SG7) citral conversion was the same but the products obtained were 3,7-dimethyl-octanol and dihydrocitronellal. 2-propanol used as solvent had an important effect in selectivity towards geraniol-nerol mixture and this was attributed to polarization of C=O bond of molecule of citral by this solvent in the reaction environment [4]. When the solvent used was hexane a broad range of products was obtained: for PtSn/SG7, 39% geraniol-nerol mixture, 54% citronellol and by-products such as 3,7-dimethyl-octanol, citronellal, dihydrocitronellal, isopulegols and menthols were observed. The selectivity results to geraniol, nerol and citronellol for Pt and PtSn supported on SG7 catalysts employed in this work are presented in the table 1.

Table 1. Selectivity towards geraniol-nerol mixture and citronellol.

Catalyst	solvent	%S geraniol-nerol	%S citronellol
Pt/SG7	hexane	0	0
	2-propanol	0	55
PtSn0.5/SG7	hexane	0	50
	2-propanol	57	43
PtSn1.0/SG7	hexane	37	55
	2-propanol	64	36
PtSn1.5/SG7	hexane	21	43
	2-propanol	60	17

### Significance

These results have great relevance in the fine chemical industry.

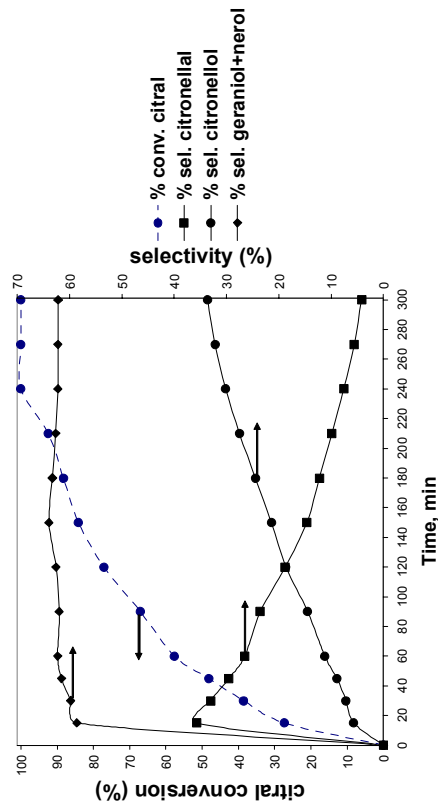


Figure 1. Citral conversion and selectivity vs. time to PtSn/SG7 catalyst with Pt/Sn=1.0 and 2-propanol as solvent. 0.1 M citral/solvent, T=100°C, H<sub>2</sub> pressure=13 bar.

### References

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