Kinetic study of liquid-phase hydrogenation of citral over Pt and PtSn supported catalysts

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Introduction

Recent studies reported in the literature have been focused on obtaining a qualitative understanding of the reaction for liquid-phase hydrogenations by monitoring the effect of mono- and bimetallic catalysts on product distribution [1]. In order to improve the selectivity and activity to the desired component in the hydrogenation of unsaturated aldehydes, the addition of promoters, selection of solvent and modification of reaction parameters (temperature, pressure, weight of catalysts, etc) have been made [2]. Thus, the use of Sn as promoter of Pt, and the use of polar and non-polar solvents have proved that the catalytic performance can be modified increasing the selectivity to unsaturated alcohols in the hydrogenation of citral [3]. Nevertheless, there is scant information examining the influence of promoters on the kinetics of liquid-phase hydrogenation of citral. In this work we report the kinetic results of the performance of Pt and PtSn supported on silica gel (SG7) in the liquid-phase hydrogenation of citral. To evaluate the effect of the nature of solvent on kinetic parameters, a polar and non-polar solvent were used. The effect of the studied parameters was modeled using power-law equations [4].

Materials and Methods

Pt and PtSn catalysts were prepared by incipient wetness impregnation. Silica Gel 7 supplied by J. T. Baker was used as support. The amount of Pt impregnated was 1 wt% using $H_2Cl_6Pt{\cdot}6H_2O$ (Strem, 40% Pt) as precursor. In bimetallic catalysts a solution of $H_2Cl_6Pt{\cdot}6H_2O$ and $SnCl_2{\cdot}2H_2O$ (J.T. Baker, 98.7%) was employed to obtain the following molar ratio of Pt/Sn=0.5, 1.0 and 1.5. All catalysts were calcined and reduced at 500ºC. Hydrogenation experiments were carried out in a 450 ml Parr reactor. The reactions were conducted at constant hydrogen pressure of 13 bar and at 100ºC. The samples withdrawn were analyzed in a gas chromatograph coupled to mass spectrometer.

In order to obtain the optimized kinetic parameters that represent the experimental results, a Simplex-Levenberg-Marquart method was carried out for least squares estimation between estimated and experimental concentrations. The solution of ordinary differential equations that describes the mass balance was carried out by GREG-10 algorithm.

Results and Discussion

The first-order dependence on citral concentration was obtained from our kinetic studies. This kinetic is in good agreement with the proposed Langmuir-Hinshelwood model consisting of adsorption dissociative of H_2, adsorption competitive between H_2 and organic molecule and the hydrogen adsorption on the active sites being the rate-limiting. Thus, the kinetic results shown that hydrogenation of citral catalysts was more favorable kinetically in Pt as catalyst and the used model represent in good agreement the experimental reaction routes.

Table 1. Optimized kinetic parameters determined by GREG-10

Catalyst in isopropanol	First-order kinetic parameters k_i x 10^3 (lt/g_{cat}*min)						
	k_1	k_2	k_3	k_4	k_5	k_6	k_7
Pt/SG7	-	9.104	-	2.095	0.784	0.056	3.965
PtSn1.0/SG7	6.799	5.025	0.134	16.215	-	-	-

Significance

This work is relevant in the study of kinetic behavior of hydrogenation of citral.

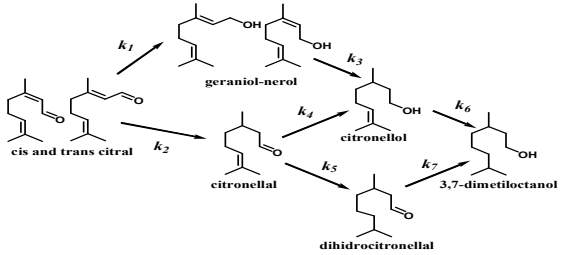

Figure 1. Reaction network for citral hydrogenation

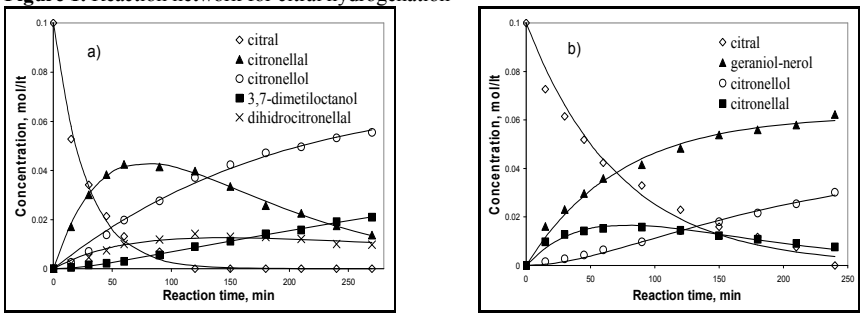

Figure 2. Experimental and modeled data in a) Pt/SG7 and b) PtSn1.0/SG7 in isopropanol as solvent. Simbols: experimental data; solid line: modeled data.

References

1. Vannice M. A., Singh U. K., *J. Catal.*, 191, 165 (2000).
2. Gallezot P., Richard D., *Catal. Rev.-Sci. Eng.*, 40(1&2), 81 (1998).
3. Barrales C., *Thesis of Master Degree*, (1997).
4. Thomas J. M., Thomas W. J. *Principles of heterogeneous catalysis*, VHC edit. (1997).