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## EFFECT OF PARTICLE SIZE IN THE HYDROGENATION OF CROTONALDEHYDE ON SUPPORTED Pt AND Pt-Sn CATALYSTS

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### Abstract

The present work reports the effect of metal particle size on the selectivity to crotyl alcohol ( $S_{UOL}$ ) in the liquid phase hydrogenation of crotonaldehyde over  $SiO_2$  and  $\alpha-Al_2O_3$ -supported Pt and Pt-Sn catalysts. It was demonstrated that, for the monometallic catalysts, a higher particle size led to a higher  $S_{UOL}$ , while for the bimetallic catalysts, this effect was not so important.

*Keywords:* Crotonaldehyde hydrogenation, Pt-Sn catalysts, particle size effect

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## INTRODUCTION

Many unsaturated alcohols are valuable intermediates in the fragrance, flavor and pharmaceutical industries. These compounds are currently produced by selective hydrogenation of the corresponding  $\alpha,\beta$ -unsaturated aldehydes using costly stoichiometric processes. Heterogeneous catalysts, based on supported transition metals, exhibit low selectivities towards C=O group hydrogenation because C=C group hydrogenation is favored. The research efforts [1-3] are oriented to improve the selectivity to the unsaturated alcohol ( $S_{UOL}$ ) by controlling factors such as: metal-support interaction on partially reducible supports, electronic and steric influence of the support, addition of modifiers, metal particle size, steric effect of substituents in the C=C bond and the effect of pressure.

A theoretical work by Delbecq and Sautet [4] and an experimental study on monocrystals by Beccat *et al.* [5], reported that the adsorption structure of the  $\alpha,\beta$ -unsaturated aldehydes depends on the exposed planes of the metal and the substituents in the C=C bond. Thus, as the fraction of Pt (111) increases by increasing the metal particle size, higher  $S_{UOL}$  would be expected on the larger Pt particles.

In relation to the addition of a second metal, tin is widely employed due to the good results obtained. The methodology of the addition of tin seems to play an important role in the behavior of the resulting active phase. A well known technique for the preparation of bimetallic supported catalysts is the so-called Surface Organometallic Chemistry on Metals (SOMC/M), which involves the reaction of organometallic compounds of the type  $MR_4$  (M: Sn, Ge, Pb; R: methyl, ethyl, butyl) with supported transition metals [6-8]. This technique ensures an intimate contact of the base metal with the second metal (modifier). In a previous work, Santori *et al.* [9] studied the liquid phase crotonaldehyde hydrogenation on  $SiO_2$ -supported Pt and Pt-Sn catalysts prepared by SOMC/M technique, evidencing the importance of the catalyst preparation procedure to improve its activity/selectivity.

The present work reports the effect of metal particle size and of the addition of tin on the selectivity to crotyl alcohol ( $S_{UOL}$ ) in the liquid phase hydrogenation of crotonaldehyde over  $SiO_2$  and  $\alpha-Al_2O_3$ -supported Pt catalysts, in which tin is introduced by means of SOMC/M techniques.

## EXPERIMENTAL

Platinum catalysts with a content of 1 wt.% Pt, were prepared. The preparation of the sample designated Pt/ $SiO_2$  (A) is described in a previously published paper [9]. The sample Pt/ $SiO_2$  (B) was generated upon sintering the base Pt/ $SiO_2$  (A) catalyst at 1073 K in flowing  $H_2$  saturated with water. A Pt/ $\alpha-Al_2O_3$  catalyst was prepared by impregnation of  $\alpha-Al_2O_3$  Rhône Poulenc ( $10\text{ m}^2\text{g}^{-1}$ ) with Pt-acetylacetonate in a benzene solution, following the procedure of reference [10].

The bimetallic catalysts derived from the corresponding parent samples are designated: PtSn/ $SiO_2$  (A); PtSn/ $SiO_2$  (B) and PtSn/ $\alpha-Al_2O_3$ . The preparation procedure followed reference [9], with a concentration of the  $SnBu_4$  solution such as to obtain a Sn/Pt atomic ratio of 0.4 in the final catalysts.

The catalysts were characterized by  $H_2$  and CO chemisorption, Transmission Electron Microscopy (TEM) and Temperature-Programmed Reduction (TPR). The adsorption measurements were carried out in a volumetric apparatus. Samples were dried at 393 K in a flow of He, reduced at 773 K under a  $H_2$  flow for 2 h. The chemisorbed amount of  $H_2$  or CO on the platinum surface

(expressed as H/Pt and CO/Pt, respectively) was calculated by using the double isotherm method. The size distribution of particles was determined by TEM using a Jeol 100 CX instrument. To estimate the mean particle size ( $d_{\text{TEM}}$ ), the particles were considered spherical and the second moment of the distribution was employed. TPR of the catalysts were performed using a conventional dynamic equipment. The H<sub>2</sub>/Ar feed flow ratio was 1/9 and the heating rate was 10 K min<sup>-1</sup>, from room temperature to 1073 K.

The hydrogenation of crotonaldehyde in liquid phase was performed in a batch reactor at a H<sub>2</sub> pressure of 1.0 MPa and 313 K, employing 1 g of catalyst and using isopropyl alcohol as solvent. The composition of the samples was analyzed with a Varian GC 3400 gas chromatograph, equipped with a 30 m J&W DB-WAX capillary column and a flame ionization detector.

## RESULTS AND DISCUSSION

The results of the catalysts characterization are presented in Table 1.

**Table 1**

Characterization of the studied catalysts by H<sub>2</sub> and CO chemisorption, TEM and TPR

Catalyst	H/Pt	CO/Pt	$d_{\text{TEM}}$ (nm)	$T_{\text{peak}}$ (K)	
				LT <sup>a</sup>	HT <sup>b</sup>
Pt/SiO <sub>2</sub> (A)	0.60	0.56	2.4	390	700
PtSn/SiO <sub>2</sub> (A)	0.21	0.25	2.9	430	700
Pt/SiO <sub>2</sub> (B)	0.21	0.16	6.2	390	700
PtSn/SiO <sub>2</sub> (B)	0.09	0.07	6.5	430	700
Pt/ $\alpha$ -Al <sub>2</sub> O <sub>3</sub>	0.18	0.17	11.3	490	700
PtSn/ $\alpha$ -Al <sub>2</sub> O <sub>3</sub>	0.07	0.10	12.8	380	690

<sup>a</sup> LT: Low temperature peak; <sup>b</sup> HT: High temperature peak

TEM measurements indicate that the particle size distribution of Pt/SiO<sub>2</sub>(A) is very narrow, with a mean particle diameter of 2.4 nm. The treatment of Pt/SiO<sub>2</sub>(A) at 1073 K in H<sub>2</sub> saturated with water resulted in the sintering of Pt particles to a  $d_{\text{TEM}} = 6.2$  nm. The Pt/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst presented a  $d_{\text{TEM}} = 11.3$  nm. The addition of tin on all the catalysts produces a slight increment in the mean particle size, which cannot be assigned to a further sintering of Pt, but to the selective deposition of tin onto it. Chemisorption results, for the monometallic catalysts, are in agreement with the dispersion values calculated by TEM. The bimetallic catalysts exhibited an important decrease of the chemisorbed gases, which suggests a very selective interaction of Sn with Pt.

As can be observed in Table 1, TPR profiles show two peaks of H<sub>2</sub> consumption: a first one, at low temperature, assigned to a platinum oxide having a relatively weak interaction with the support, and another peak at higher temperature, corresponding to platinum oxide with a stronger interaction with the support. For both PtSn/SiO<sub>2</sub> catalysts, it is observed an increase in the area of the low temperature peak, which can be assigned to the reduction of the platinum oxide and a fraction of tin oxide. This fact can be explained considering that platinum dissociates H<sub>2</sub> employed in the reduction of tin near it. In the PtSn/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> system, the low temperature peak appears 100 K lower than in the case of Pt/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, what may be related to the weakening of the interaction between platinum and the support, as it was reported for NiSn/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> [11].

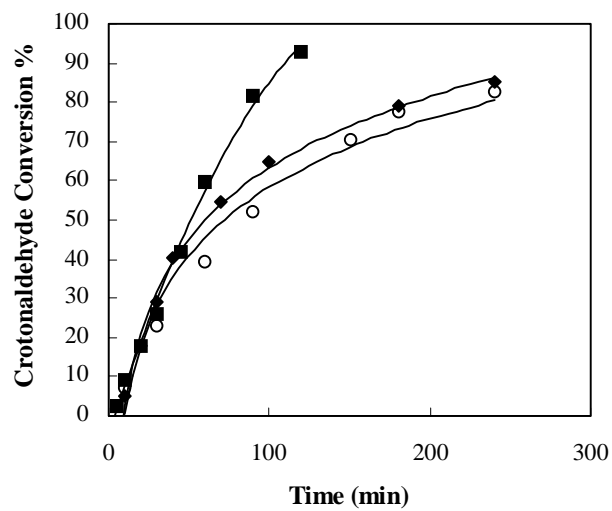
The reaction products of the crotonaldehyde hydrogenation were butanal (SAL), crotyl alcohol (UOL), butanol (SOL) and traces of hydrogenolysis compounds. Figures 1-a and 1-b represent the variation of conversion (%) vs. time (min) for the catalysts studied. Bimetallic catalysts PtSn/SiO<sub>2</sub> (A), PtSn/SiO<sub>2</sub> (B) and PtSn/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> show an increment in the hydrogenation rate compared to the monometallic ones, in spite of the important decrease in H<sub>2</sub> chemisorption. This is in agreement with previous results and it is assigned to the presence of a new active site, originated in the specific interaction between SnBu<sub>4</sub> and the corresponding monometallic catalysts during the preparation step [12].

The results of selectivities to the different products obtained are gathered in Table 2. For the monometallic catalysts, the selectivity to UOL increased with the platinum particle size, for all the range of conversions, as stated in previously published experimental and theoretical studies [4,5,13]. Data of Table 2 show that S<sub>UOL</sub> of monometallic catalysts is improved upon addition of tin and the effect of the particle size is not so important as for monometallic catalysts.

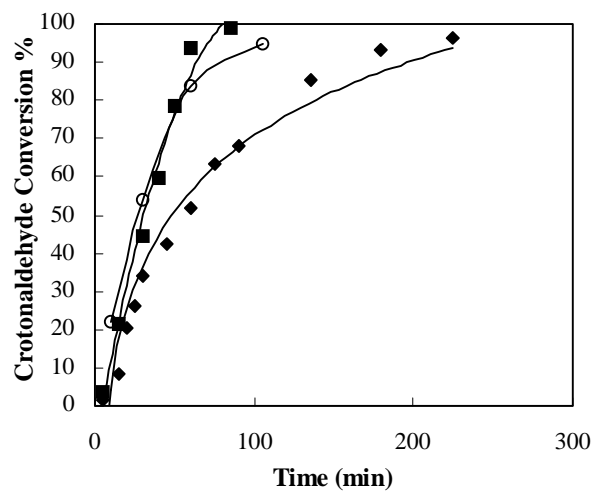
**Table 2**

Selectivity of the catalysts in the liquid phase hydrogenation of crotonaldehyde

Catalyst	Conversion = 20%			Conversion = 80%		
	SAL	SOL	UOL	SAL	SOL	UOL
Pt/SiO <sub>2</sub> (A)	65	20	15	60	31	9
PtSn/SiO <sub>2</sub> (A)	37	9	54	25	27	48
Pt/SiO <sub>2</sub> (B)	61	18	21	57	29	14
PtSn/SiO <sub>2</sub> (B)	30	12	58	20	28	52
Pt/ $\alpha$ -Al <sub>2</sub> O <sub>3</sub>	56	20	24	37	45	18
PtSn/ $\alpha$ -Al <sub>2</sub> O <sub>3</sub>	40	19	41	24	41	35



**Fig. 1a:** Conversion (%) vs. time (min) for the monometallic catalysts: (○) Pt/SiO<sub>2</sub>(A); (■) Pt/SiO<sub>2</sub>(B); (◆) Pt/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>



**Fig. 1b:** Conversion (%) vs. time (min) for the bimetallic catalysts: (○) PtSn/SiO<sub>2</sub>(A); (■) PtSn/SiO<sub>2</sub>(B); (◆) PtSn/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>

The beneficial effect of the addition of Sn, in agreement with our previous results can be described as follows: in these bimetallic catalysts Sn is present as both Sn(0) and Sn(II,IV), measured by XPS [9]. This ionic tin is responsible for an adequate polarization of the C=O group, leading to an improvement in  $S_{UOL}$ .

Theoretical calculations conducted with modeled platinum catalysts, concluded that the adsorption of  $\alpha,\beta$ -unsaturated aldehydes on Pt(111) faces led to the preferential hydrogenation of the C=O group [14]. The contribution of these kinds of faces is more important in low dispersed catalysts, a fact that explains the sequence of  $S_{UOL}$  obtained with the monometallic catalysts: Pt/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> > Pt/SiO<sub>2</sub>(B) > Pt/SiO<sub>2</sub>(A). The addition of tin leads to nonuniformities and imperfections of these faces, reducing the Pauli repulsion of the C=C group in such a manner that hydrogenation of both groups may become competitive. In this way, the positive effect on  $S_{UOL}$  of enlarging the particle size, becomes less important. That is why the increment of the selectivity to UOL observed in the bimetallic PtSn catalysts should be assigned exclusively to the effects introduced by tin, mentioned in the above paragraph.

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