Hydrogenation of citral over Ir/TiO$_2$/SiO$_2$ catalyst. Kinetic study.

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Introduction

The hydrogenation of an α, β unsaturated aldehyde may be strongly affected by different properties of the catalyst used in the reaction. Thus, if the selective hydrogenation of the carbonyl bond is desired, it is necessary creates the conditions to polarize the carbonyl bond of the molecule. It has been reported that one of the ways to produce sites able to polarize the C=O bond in these kind of molecule is using catalysts in SMSI state which can be obtained by reducing at high temperature a metal catalysts supported on a partially reducible support such as TiO$_2$ or Nb$_2$O$_5$ [1]. Binary oxides of TiO$_2$/SiO$_2$ has been used as supports for different reactions [2], being a promising model system for metal catalyst preparations and investigation of various aspects of strong metal support interaction effect, due to low concentration of Ti may be required to produce highly disperse TiO$_2$ on a SiO$_2$ matrix, leading to an enhancement in the TiO$_2$ specific area. Obviously this parameter should have a positive effect in the dispersion of the metal component and on the catalytic behavior. Rojas, *et al* [3], found a marked shift in activity and selectivity in the hydrogenation of C=O group of citral over Ir/TiO$_2$/SiO$_2$ HTR catalysts. The aim of this work is to provide kinetic information of the hydrogenation of citral and their partially hydrogenated products on Ir/TiO$_2$/SiO$_2$ catalyst; for each reaction the effect of the substrate concentration, hydrogen pressure, temperature and catalyst weight was studied.

Materials and Methods

Titanium isopropoxide (Aldrich, reagent grade) was dispersed in toluene (150 mL) and added an aerosil silica (Syloid-266-Grace Davidson). The obtained solid (TiO$_2$/SiO$_2$) was impregnated with an aqueous solution of H$_2$IrCl$_6$ in appropriate amount to reach an Ir loading of 1 wt.%. The impregnated solid were dried at 343 K for 6 h, calcined in air at 673 K for 4 h and reduced at 773 K (HTR) for 2 h, obtaining a Ir/TiO$_2$/SiO$_2$ HTR catalyst. The catalyst was characterized by Nitrogen adsorption at 77 K, hydrogen chemisorption at 298 K, TEM and XPS. The activity catalytic was carried out in a batch reactor at a constant stirring rate (1000 rpm). The effect of citral concentration and each intermediary of reaction was studied in the concentration range from 0.025 to 0.1 M; hydrogen partial pressure in the range from 2.07 to 6.2 bar; reaction temperature between 323 and 363 K; and the catalyst weight, ranged from 0.1, 0.2 to 0.3 g. Only one variable was modified in each experiment, keeping constant all the other variables. All these results indicate the absence of any transport limitations from the kinetic data included in this paper. Reaction products were analyzed in an GC-Varian 3400.

Results and Discussion

The results showed that Ir/TiO$_2$-SiO$_2$ catalyst is active in citral hydrogenation and produces a highly selective towards the unsaturated alcohols (geraniol + nerol). Additionally, the hydrogenation of the possible hydrogenation products was also performed under comparable conditions. Significant differences in the catalytic behavior under standardized condition was found and the activity decreases in the order: citronellal ~ citral > citronellol > nerol> geraniol This behavior is explained in terms of a strong adsorption of the molecule by the carbonyl group on the active sites which prevents the adsorption by the C=C bond and consequently, inhibits the formation of secondary reactions of citronellol and citronellal must be a consequence of an alteration in competitive adsorption which prevents the readsorption of these molecules. Table 1 summarizes the initial hydrogenation rate for the different substrates over a range of 363 K at 323 K using 0.62 bar and 0,1 M as initial concentration of substrate, it show an increase of the initial activity with increase of temperature. Figure 1 display the typical behavior of the initial concentration and hydrogen partial pressure. For the kinetic modeling was considered that the surface reactions are the rate determining (rds), while adsorption - desorption steps are considered to be in quasi-equilibrium and citral can be converted into unsaturated alcohols (UOL) on both Ir$^{\delta+}$ and Ir^0 sites, while citronellal (CAL.) is produced only on Ir^0 sites. Taking into account these observations and assuming on basis of the experimental results, the network reaction was expressed as a series of differential equations and was solved numerically by the Runge-Kutta algorithm.

Table 1. Initial activity (μmols^{-1}g^{-1}) obtained for different substrates at diverse temperatures.

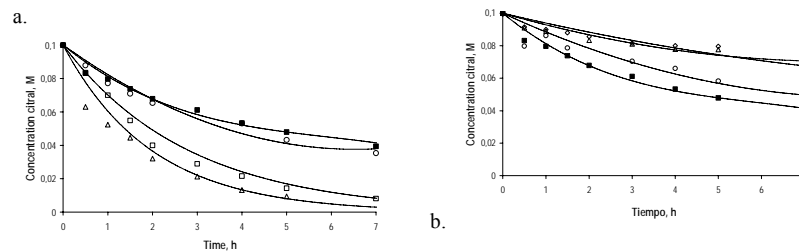|	Citral	Citronellal	Geraniol	Nerol
363 K	7,00	13,29	0,06	0,07
353 K	7,00	10,25	0,05	0,04
343 K	6,91	10,33	0,05	0,03
323 K	4,13	9,80	0,03	0,03

Figure 1. (a) Effect of the initial concentration and (b) hydrogen partial pressure on hydrogenation of citral; (■) 0.1 M; (○) 0.075 M; (◊) 0.05 M; and (Δ) 0.025 M

Significance: This summary present the kinetics of reaction over catalyst of Ir supported over binary oxides of TiO$_2$/SiO$_2$ which can be favorable in the industry as a novel type of hydrogenation catalysts synthesized by a new method..

References
1. Reyes, P., Rojas, H., Fierro. J.L.G. (2003). *Appl. Catál.* A., 248, 59.
2. Gao,X.; Wachs, X.E. (1999). *Catal. Today*. 51, 235.
3. Rojas, H., Borda, G. Reyes, P. Martínez, J., Valencia, J. (2006). XX simposium iberoamericano de catalise. Resumos dos trabahlos, 261.