

## Crotonaldehyde hydrogenation on Ir supported catalysts

P. Reyes<sup>a,\*</sup>, M.C. Aguirre<sup>a</sup>, G. Pecchi<sup>a</sup>, J.L.G. Fierro<sup>b</sup>

<sup>a</sup> *Facultad de Ciencias Químicas, Universidad de Concepción, Casilla 160-C, Concepción, Chile*

<sup>b</sup> *Instituto de Catálisis y Petroleoquímica, CSIC, Madrid, Spain*

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### Abstract

Iridium supported catalysts prepared by the sol–gel and impregnation methods have been studied in the vapour-phase hydrogenation of crotonaldehyde. The influence of different preparation variables on the surface and catalytic properties was analysed. It was found that the porosity of the support has an effect on the selectivity to the unsaturated alcohol and the presence of partially reducible supports such as ZrO<sub>2</sub> and TiO<sub>2</sub> increases the selectivity to crotyl alcohol. This increase may be attributed to an enhancement of the polarisation of the C=O bond as a result of surface decoration of the metal component. The presence of chlorine ions in the metal-support interfacial region also allows, in a certain extension, a polarisation of the carbonyl bond. The effect of the reaction temperature has also been studied. It was found that a decrease in the reaction temperature led to a decrease in the crotonaldehyde conversion and in an improvement on the selectivity of the allylic alcohol. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Crotonaldehyde; Hydrogenation; Iridium catalysts; Sol–gel technique; XPS

### 1. Introduction

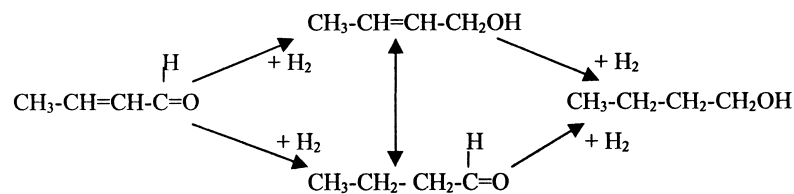
Catalytic hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes to unsaturated alcohols is an important step in the preparation of various fine chemical products. For small molecules such as acrolein and crotonaldehyde, the reaction is almost quantitatively selective to the saturated aldehydes because the hydrogenation of the olefinic double bond is favoured, both by kinetic and thermodynamic considerations. On the other hand, for larger  $\alpha,\beta$ -unsaturated aldehydes additional steric constraints produced by the substituents on the C=C double bond might influence the product selectivity. Therefore, it is desirable to find catalysts which may control the intramolecular selectivity by preferential hydrogenation of the C=O group and keep the olefinic

double bond intact. Scheme 1 shows the reaction network of crotonaldehyde hydrogenation.

Different metals and supports have been used to study the selective hydrogenation of these kinds of unsaturated compounds. Thus, metals such as Co, Pt, Ru, Rh, Os and Ir have been assayed, showing great differences in activity and selectivity. Metal supported catalysts have been modified by alloying [1,2], adding promoters [3,4], using strong interacting supports [5–8] and by inducing electronic effects. Despite the number of investigations in this field, no agreement on the nature of the effect which may have a more significant impact on the selectivity towards the unsaturated alcohol exists.

Several attempts have been made to develop a suitable catalytic system to improve the selectivity of the unsaturated alcohol. Some interesting results have been obtained by using supports that present the strong metal-support interaction (SMSI) effect such as TiO<sub>2</sub>

\* Corresponding author. Fax: +56-41-245974.  
E-mail address: preyes@udec.cl (P. Reyes).

Scheme 1. Reaction network of the hydrogenation  $\alpha,\beta$ -unsaturated aldehydes.

[9,10]. However, for a given metal supported catalyst, the selectivity can also be modified by changes in the preparation method. Thus, changes in the nature of the metallic precursor and/or the porosity of the carrier can affect significantly the surface and catalytic properties of the system. This is particularly clear for catalysts supported on an inert carrier such as  $\text{SiO}_2$  in which a reasonable increase in selectivity to the unsaturated alcohol can be obtained, using as preparation procedure the sol-gel method.

The aim of the present contribution is to study the effect of the support on the activity and selectivity for crotonaldehyde hydrogenation in vapour-phase. Iridium catalysts supported on  $\text{SiO}_2$ ,  $\text{ZrO}_2\text{SiO}_2$  and  $\text{TiO}_2$  prepared by the sol-gel method and/or impregnation are compared. The catalysts have been characterised by nitrogen adsorption at 77 K,  $\text{H}_2$  chemisorption measurements at 298 K, TEM studies for particle size evaluation, XPS experiments to estimate surface composition and FTIR of adsorbed crotonaldehyde. Crotonaldehyde hydrogenation was studied, using a pulse method at a temperature range of 323–373 K.

## 2. Experimental

### 2.1. Catalysts preparation

$\text{Ir/SiO}_2$  catalysts were prepared by the sol-gel method ( $\text{Ir/SiO}_2\text{-SG}$ ) in four steps: (i) hydrolysis of tetraethyl orthosilicate (TEOS); (ii) gelation and ageing; (iii) drying and (iv) calcination. The following procedure was used: a mixture of TEOS with ethanol and  $\text{Ir}(\text{acac})_3$  (ALDRICH) dissolved in acetone to give Ir loading of 0.5 wt.% was stirred and refluxed at 318 K. The gelation pH was adjusted to 3, 5 or 9, using different hydrolysis catalysts ( $\text{HCl}_{\text{aq}}$ ,  $\text{H}_2\text{O}$  and  $\text{NH}_3(\text{aq})$ ). The reflux was maintained until gel formation was achieved. Then the temperature was

increased to 353 K and kept constant for 1 h. The obtained solids were dried at 383 K for 6 h, calcined in air at 723 K for 4 h and reduced in situ at 773 K for 2 h prior to characterisation or catalytic test. Additionally, two 0.5 wt.%  $\text{Ir/SiO}_2$  catalysts were prepared by impregnation on a silica prepared by the sol-gel method at pH = 5. An aliquot of this support was impregnated after drying ( $\text{Ir/SiO}_2\text{-IC}$ ) and another after calcination ( $\text{Ir/SiO}_2\text{-CIC}$ ). A 0.5 wt.%  $\text{Ir/ZrO}_2\text{-SiO}_2$  was prepared from TEOS and zirconium acetylacetonate [11] with 10 wt.% of  $\text{ZrO}_2$  in the mixed oxide ( $\text{Ir/SiO}_2\text{-ZrO}_2$ ). The water:solvent (*t*-butylalcohol) ratio was 4:1 and the pH was fixed at nine with ammonia solution. Then, the solids were impregnated with the appropriate amount of  $\text{Ir}(\text{acac})_3$  in acetone solution. All the samples were dried at 343 K for 24 h and calcined at 673 K for 4 h. A series of  $\text{Ir/TiO}_2$  catalysts was prepared by impregnation of  $\text{TiO}_2$  (Degussa P-25) at 398 K with an aqueous solution of  $\text{IrCl}_4$  ( $\text{Ir/TiO}_2\text{-C}$ ) or acetone solution of  $\text{Ir}(\text{acac})_3$  ( $\text{Ir/TiO}_2\text{-A}$ ). The solids were dried, calcined and reduced at 723 K as described previously.

### 2.2. Catalyst characterisation

To evaluate specific surface area, pore volume and average pore diameter, nitrogen adsorption isotherms at 77 K in the relative pressure range 0.05–0.995 were carried out in a Micromeritics Model Gemini 2370 apparatus. Hydrogen chemisorption at 298 K was carried out in a volumetric system to evaluate the  $\text{H}_2$  uptake and H/Ir. Prior to the chemisorption experiments, the samples were reduced in situ at 773 K for 2 h and then outgassed for 4 h at the same temperature.

TEM was used for the observation of supported Ir particles. These experiments were performed in a Jeol Model JEM-1200 EXII system. The samples were prepared by the extractive replica procedure.

TPR studies were carried out in a TPD/TPR 2900 Micromeritics system provided with a thermal conductivity detector. The reducing gas was a mixture of 5% H<sub>2</sub>/Ar (40 ml/min) using a heating rate of 10 K/min. Prior TPR experiments, the reduced samples were oxidised in situ in oxygen flow up to 773 K. To rule out possible redispersion of Ir particles due to these treatments, the fresh reduced samples and the reduced samples after TPR experiments were evaluated by hydrogen chemisorption. No significant changes in the hydrogen uptake were detected.

Photoelectron spectra were recorded using an Escalab 200 R spectrometer provided with a hemispherical analyser, operated in a constant pass energy mode and Mg K $\alpha$  X-ray radiation ( $h\nu = 1253.6$  eV) operated at 10 mA and 12 kV. The surface Ir/Si, Ir/Ti and Zr/Si ratios were estimated from the integrated intensities of Ir 3d<sub>5/2</sub>, Zr 3d<sub>5/2</sub>, Ti 2p<sub>3/2</sub> and Si 2p lines after background subtraction and corrected by the atomic sensitivity factors [12]. The line of Si 2p at 103.4 eV was used as an internal standard. Ir peaks were decomposed into several components assuming that the peaks had Gaussian–Lorentzian shapes.

### 2.3. Hydrogenation experiments

Catalytic experiments were carried out in a pulse reactor with an on line GC. In each experiment 50 mg of catalyst were reduced in situ in flowing hydrogen (20 ml/min) in a programmed mode at 10–773 K/min and the catalytic activity was measured by injecting 1.0  $\mu$ l of organic reactant. Chemical analysis of the products was performed by gas chromatography (Varian Star 3400 CX) equipped with a flame ionisation detector). Product separation was carried out on a stainless steel column (6.6 ft.  $\times$  1/8 in. o.d.) filled with 6.6% carbowax 20 M on carbopack B 80/120 (purchased from Supelco). Column temperature was kept at 120°C. Reagents and products were identified by comparison with authentic samples. Quantitative analysis was carried out by calculating the arc of the chromatographic peaks with an electronic integrator (Chrom Jet Integrator provided by Thermo Separation Products). All the experiments were repeated at least twice, being the reproducibility better than 1%. Blank experiments showed no catalytic activity due to the supports under these conditions.

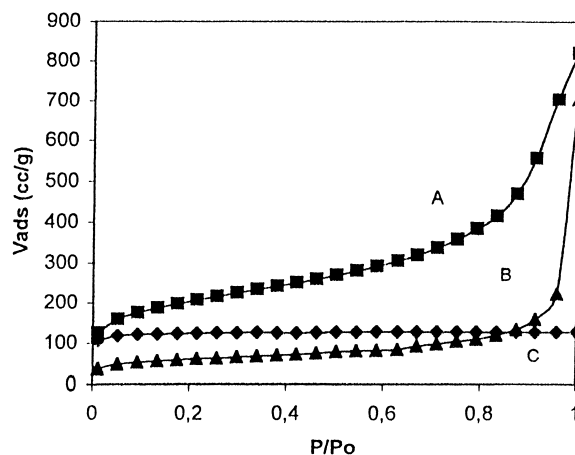


Fig. 1. N<sub>2</sub> adsorption isotherms at 77 K on representative Ir supported catalysts: (A) Ir/SiO<sub>2</sub>-5-SG (B) Ir/SiO<sub>2</sub>-9-SG and (C) Ir/SiO<sub>2</sub>-3-SG.

### 3. Results and discussion

For sol–gel silica-supported catalysts adsorption isotherms obtained at gelation pH 3 exhibit type I isotherm, indicative of essentially microporous solids. As the gelation pH increases, changes in the shape of the isotherm indicate the presence of mesoporous solids with only a small contribution of micropores. This behaviour has been explained previously on the basis of changes in the rate hydrolysis [13,14]. Fig. 1 shows representative nitrogen adsorption isotherms on Ir/SiO<sub>2</sub>. Table 1 displays the specific surface areas, pore radius and the extent of micropores contribution for different Ir supported catalysts. Significant differences in the surface area as well as in the micropores

Table 1  
Specific area, average pore radius and percent volume micropore for 0.5 wt.% Ir supported catalysts

Catalyst	$S_{\text{BET}}$ (m <sup>2</sup> /g)	$r_p$ (nm)	Micropore (%)
Ir/SiO <sub>2</sub> -3-Sg <sup>a</sup>	381	1.0	79
Ir/SiO <sub>2</sub> -5-SG	700	1.7	5
Ir/SiO <sub>2</sub> -9-SG	204	10.7	2
Ir/SiO <sub>2</sub> -5-IC	655	3.8	4
Ir/SiO <sub>2</sub> -5-CIC	672	1.7	5
Ir/ZrO <sub>2</sub> -SiO <sub>2</sub> -9	107	2.7	5
Ir/TiO <sub>2</sub> -A	71	6.8	0
Ir/TiO <sub>2</sub> -C	72	5.9	0

<sup>a</sup> From isotherm DRK (543 m<sup>2</sup>/g).

contribution can be noted. Thus, catalyst prepared by the sol-gel procedure at pH 3 exhibits essentially the presence of micropores whereas in that prepared at pH 5, the isotherm indicates mainly the presence of mesopores with a small contribution of micropores. On the other hand, the Ir/ZrO<sub>2</sub>SiO<sub>2</sub> sample prepared at pH 9 in the presence of ammonia solution shows an isotherm, which may be considered as type IV in the BDDTs classification. Even though it is well known that the BET equation is not valid for microporous solids, the obtained values were also included as reference because only the sample prepared at pH 3 in the presence of HCl is essentially microporous. Pore radius obtained from Gurvitch's rule indicates differences in line with the previous discussion. The catalysts supported on TiO<sub>2</sub> exhibit type IV isotherms which is characteristic of mesoporous solids.

Fig. 2 displays TPR profiles of representative calcined supported iridium catalysts. The samples Ir/SiO<sub>2</sub>

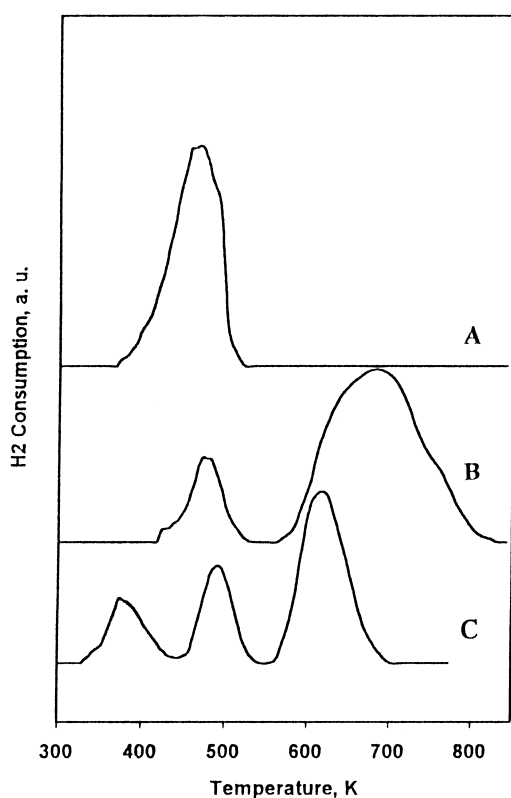


Fig. 2. TPR profiles of representative Ir supported catalysts: (A) Ir/SiO<sub>2</sub>-5-SG (B) Ir/ZrO<sub>2</sub>-SiO<sub>2</sub> and (C) Ir/TiO<sub>2</sub>-A.

exhibit a single peak centred at 463 K attributed to the reduction of iridium oxide particles to Ir [15–17]. The sample Ir/ZrO<sub>2</sub>-SiO<sub>2</sub> shows an additional broad and smaller peak centred at 650 K. The fact that in this solid the reduction takes place at higher temperature and its intensity is low, indicates that Ir species remain trapped into the porous structure of the carrier with a strong metal support interaction making the reduction process more difficult. In the Ir/TiO<sub>2</sub> samples, the profiles exhibit peaks at 383 and 465 K due to the reduction of iridium oxide species and a broad peak around 610 K due to the reduction of IrO<sub>x</sub> strongly interacting with the TiO<sub>2</sub> surface and with some contribution of the partial reduction of the support. The H<sub>2</sub>-consumption of these Ir/TiO<sub>2</sub> samples is slightly higher than that required for the complete reduction of iridium oxides indicating a partial reduction of TiO<sub>2</sub> in intimate contact with the metal.

Table 2 summarises the hydrogen chemisorption, TEM and XPS results. The average Ir particles size, *d* has been calculated from the equation [18]  $d = 1.11/(H/Ir)$  (nm) where H/Ir represents an estimation of metal dispersion. It can be seen that metal dispersion in Ir/SiO<sub>2</sub> catalysts is very high compared with values of the catalysts prepared at gelation pH of 5 and 9. However, at pH 3, the hydrogen uptake is lower which may be explained considering that at this pH the rate of hydrolysis is higher and it is likely that Ir may remain trapped in the porous structure of the support and not available for hydrogen chemisorption. This explanation is also supported by TEM results in which the iridium particle sizes are smaller compared with the

Table 2

H/Ir ratios, particle size, binding energies (eV) of Ir 4f<sub>7/2</sub> core electrons and surface atomic ratios evaluated from XPS of 0.5 wt.% Ir supported catalysts<sup>a</sup>

Catalyst	H/Ir	Particle size (nm)		Ir 4f <sub>7/2</sub> B.E. (eV)	Ir/M
		Chemisorption	TEM		
Ir/SiO <sub>2</sub> -3-SG	0.27	4.1	2.1	60.4	0.0012
Ir/SiO <sub>2</sub> -5-SG	0.59	1.9	3.0	60.4	0.0011
Ir/SiO <sub>2</sub> -9-SG	0.50	2.2	3.2	60.4	0.0008
Ir/SiO <sub>2</sub> -5-IC	0.58	1.9	3.0	60.3	0.0011
Ir/SiO <sub>2</sub> -5-CIC	0.53	2.0	2.8	60.3	0.0011
Ir/ZrO <sub>2</sub> -SiO <sub>2</sub>	0.48	2.3	2.9	60.5	0.0003
Ir/TiO <sub>2</sub> -A	0.064	17.2	3.0	60.7	0.0216
Ir/TiO <sub>2</sub> -C	0.055	20.0	3.2	60.6	0.0173

<sup>a</sup> M:Si or Ti.

other catalysts. The Ir/ZrO<sub>2</sub>-SiO<sub>2</sub>-9 catalyst has similar H/Ir ratios compared with Ir/SiO<sub>2</sub>-9 counterpart as shown in Table 2. The low H/Ir ratios obtained for Ir/TiO<sub>2</sub> catalysts are the expected values for catalysts having the SMSI effect. In fact, the drop in hydrogen uptake can not be attributed to a change in the particle size as it is shown by TEM. Particle size obtained by chemisorption and TEM are in good agreement. The exception already mentioned are the catalysts supported on TiO<sub>2</sub> and the Ir/SiO<sub>2</sub>-3-SG catalysts in which the value obtained by TEM is approximately one half of that given by chemisorption. It is likely that in this sample, part of the iridium remains strongly interacting with the support and not accessible to the probed molecule. Additionally, in the micrographs of this sample, a narrow particle size distribution centred around 2 nm having some larger particles was obtained indicating that these larger particles remain outside the porous network of this catalyst.

The Ir 4f<sub>7/2</sub> core level spectra were recorded for all the reduced iridium catalysts and the binding energies are also collected in Table 2. For Ir/SiO<sub>2</sub> catalysts the position of the peak is approximately 60.4 eV corresponding to Ir<sup>0</sup> species. For those catalysts supported on ZrO<sub>2</sub>-SiO<sub>2</sub> and TiO<sub>2</sub>, there is a slight shift to higher binding energies indicating the presence of Ir<sup>0</sup> and Ir<sup>δ+</sup> species. These results are expected considering the SMSI effect exhibited by these supports. Additionally, the atomic ratios Ir/M (M = Si or Ti) are also given in Table 2. The Ir/Si ratios remain almost constant for all the Ir/SiO<sub>2</sub> catalysts and the values are independent on the preparation method, as it was expected from chemisorption and TEM results. The

low Ir/Si ratios in the Ir/ZrO<sub>2</sub>-SiO<sub>2</sub> catalysts are indicative of the presence of metal particles trapped into the support. Ir/TiO<sub>2</sub> ratios are much higher than those catalysts previously discussed. This is explained considering the lower surface area of the support and the preparation method (impregnation). The samples prepared from the organometallic precursor have higher Ir/Ti ratios in line with chemisorption results.

The catalytic activity of all the catalysts was evaluated in the hydrogenation of crotonaldehyde in a pulse reactor in the temperature range of 323–373 K. In all the cases, three main reaction products were obtained: crotyl alcohol (CROH), butyraldehyde (BUHO), butyl alcohol (BUOH) and hydrocarbons as minor products. In most of the catalysts, a slight change in conversion level was detected upon successive pulses reaching a steady state after five to seven pulses. These changes in conversion are accomplished with changes in selectivity as shown in Fig. 3 for one of the representative samples. It can be seen that during the first pulse, the surface of the catalyst is slightly modified by the adsorption of the reactant and when such modification reaches a steady state the conversion level and selectivity are almost constant. Obviously, these two facts are depending on the temperature. It should be noted that eventhough the metal component (Ir) is supported on an inert support as SiO<sub>2</sub> reasonable selectivity to CROH was obtained. Fig. 4 summarises, steady-state conversions and selectivity to different products as a function of the reaction temperature for one of the Ir/TiO<sub>2</sub> catalysts. It can be seen that in the temperature ranging between 323 and 373 K, the main product is BUHO. With regard to the selectivity

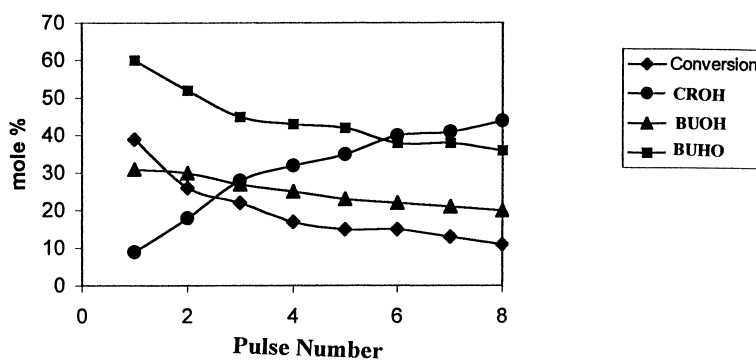


Fig. 3. Hydrogenation of crotonaldehyde at 373 K over Ir/SiO<sub>2</sub>-9-SG. Conversion levels and selectivity vs. number of pulses.

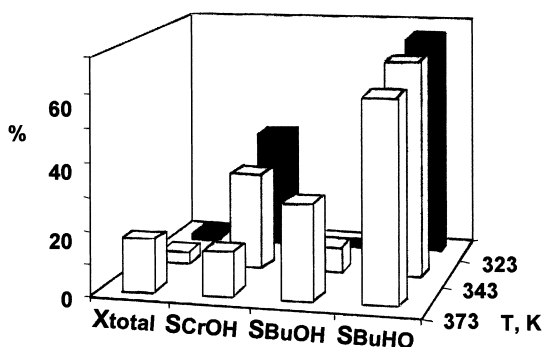


Fig. 4. Conversion levels and selectivity at different temperatures for Ir/TiO<sub>2</sub>-A catalyst.

to CROH, it increases significantly as temperature decreases while BUOH shows the opposite trend. Similar trends were observed for all the studied catalysts with differences in selectivity levels. The increase in the selectivity to BUOH upon increasing temperature is explained taking into account that the rate of isomerisation of CROH to BUHO and the rate of hydrogenation of CROH and BUHO are favoured at higher temperature [19]. Table 3 summarises the conversion levels, the selectivity to CROH and the activation energy for the studied catalysts. The results indicate that the surface properties of the support affect both the activity and the selectivity. Thus, in Ir/SiO<sub>2</sub> catalysts which have similar metal particle size but considerable differences in surface porosity the presence of mesopores induces an increase in the selectivity to CROH. Thus, Ir/SiO<sub>2</sub>-3-SG catalyst which displays the highest contribution of micropores

has also the highest restriction to the access of the crotonaldehyde to metal crystallites placed into the porous network and consequently, the reaction takes place essentially in the external surface of the catalyst, being the hydrogenation of C=C bond the almost exclusive reaction. On the other hand, in Ir/SiO<sub>2</sub>-5-SG and Ir/SiO<sub>2</sub>-9-SG catalysts, the presence of mesopores allows the diffusion of the reactant through the pore structure increasing the time that the reactant is in contact with the catalyst, therefore, the hydrogenation of C=O bond proceeds in large extension to give the unsaturated alcohol. Similar results have been recently published by Claus et al [20] for Ag catalysts. Ir/ZrO<sub>2</sub>-SiO<sub>2</sub> catalysts which present the lowest catalytic activity show the highest selectivity to CROH which may be indicative of SMSI effect. Ir/TiO<sub>2</sub> samples exhibit comparable catalytic behaviour, being slightly higher the activity in those prepared by impregnation of TiO<sub>2</sub> with the organometallic precursor. The samples prepared by ex-chloride precursor show lower activity which may be attributed to a slight decrease in the hydrogenation ability due to the presence of chlorine ion which seems to produce only small effect on the selectivity. In these catalysts, the surface decoration of iridium particles by TiO<sub>x</sub> species may be responsible of the higher selectivity to CROH. The activation energy in all SiO<sub>2</sub> catalysts is almost constant, being slightly higher for the catalysts which present the SMSI effect, in agreement with values previously reported by Dandeker and Vannice [21]. It is remarkable to point out that in spite of previous results, showing that supports having SMSI effect are more appropriate to obtain highly

Table 3

Catalytic activity expressed as conversion level and selectivity to the products crotylalcohol (CROH), butyraldehyde (BUHO) and butylalcohol (BUOH) of 0.5 wt.% Ir supported catalysts

Catalyst	Conversion (%)			Selectivity to CROH (%)			E <sub>a</sub> (kJ/mol)
	323 K	343 K	373 K	323 K	343 K	373 K	
Ir/SiO <sub>2</sub> -3-SG	5	8	15	7	5	3	22
Ir/SiO <sub>2</sub> -5-SG	5	7	10	24	16	10	20
Ir/SiO <sub>2</sub> -9-SG	13	16	41	31	15	5	22
Ir/SiO <sub>2</sub> -5-IC	7	13	15	25	24	16	23
Ir/SiO <sub>2</sub> -5-CIC	2	6	7	14	14	6	25
Ir/ZrO <sub>2</sub> -SiO <sub>2</sub> -9	1	3	4	41	27	23	41
Ir/TiO <sub>2</sub> -A	4	7	19	32	20	11	29
Ir/TiO <sub>2</sub> -C	3	5	19	35	25	13	31

selective catalysts to crotyl alcohol, inert support as SiO<sub>2</sub> having an appropriate porosity may exhibit comparable performance. With regard to the high selectivity to CROH found for the Ir/ZrO<sub>2</sub>-SiO<sub>2</sub>-9 catalyst, it can be explained that the ZrO<sub>2</sub> may be slightly reduced in H<sub>2</sub>, generating ZrO<sub>x</sub> species which may migrate on the surface of Ir crystallites. This migration occurs mainly in mesoporous systems. Additionally, this catalyst also exhibits high Zr/Si atomic surface ratio which makes more favourable the migration of ZrO<sub>x</sub> and consequently increases the selectivity.

#### 4. Conclusions

Using the sol–gel procedure in the preparation of several silica-supported iridium catalysts, it is possible to obtain efficient systems with significant differences in textural and surface properties. Changes in the porosity of silica due to pH gelation, induce changes in the selectivity of the reaction of the hydrogenation of crotonaldehyde in vapour phase. At pH 3 the Ir/SiO<sub>2</sub> catalyst is essentially microporous and at higher pH values an important increase in the mesoporosity is observed. TEM results show only small changes in metal particle sizes for all the studied catalysts. XPS results suggest that the metal component is present mainly as Ir<sup>0</sup> and only slight shift in the binding energy of Ir 4f core level for Ir/ZrO<sub>2</sub>-SiO<sub>2</sub> and Ir/TiO<sub>2</sub> catalyst indicates the presence of Ir<sup>δ+</sup>, which is the expected behaviour for catalysts having SMSI effect. Different conversion levels and selectivities were obtained for the studied catalysts at a given temperature. The selectivity to the allylic alcohol increases as temperature decreases and the presence of mesopores also improve the selectivity to the unsaturated alcohol. Additionally, the support having the SMSI effect allows an increase in the selectivity by polarisation of the C=O bond.

These results indicate that reasonable selectivities to the unsaturated alcohol in an inert support (SiO<sub>2</sub>), with comparable values than those exhibited by the

catalysts supported on TiO<sub>2</sub>, can be obtained by controlling the porosity of the carrier.

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