

## SELECTIVE HYDROGENATION OF FURFURAL ON Ir/TiO<sub>2</sub> CATALYSTS

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Titania-supported Ir catalysts were used in the hydrogenation of furfural. Reactions were carried out in a stirred batch type reactor at 0.62MPa and 363K using a 0.10M solution of furfural in a 1:1 mixture n-heptane –ethanol as solvent. Catalysts containing 2 wt% of Ir were reduced in H<sub>2</sub> flow at different temperatures in the range 473-773K. The catalysts were characterized by H<sub>2</sub> chemisorption, TEM, TPR, TPD of NH<sub>3</sub> and XPS. Conversion of furfural is higher at lower reduction temperatures, but leads to byproducts whereas reduction at higher temperatures shows selectivity to furfuryl alcohol close to 100%.

Keywords: iridium; TiO<sub>2</sub>; furfural.

### INTRODUCTION

There is currently an increased interest in the use of heterogeneous catalysts for the synthesis of fine chemicals. Among others, hydrogenation reactions of  $\alpha$ ,  $\beta$  unsaturated aldehydes to produce unsaturated alcohols are of great importance.<sup>1-3</sup> It involves the selective catalytic hydrogenation of carbonyl groups in the presence of olefin groups in a molecule which also contains C=C bond conjugated with the C=O bond which appears as a difficult task, since almost all metal catalysts usually give saturated compounds as main products.<sup>4-6</sup> Various attempts have been carried out in order to improve the selectivity of heterogeneous supported metal catalysts in these reactions.<sup>7-10</sup> Several research groups have reported catalysts able to selectively reduce certain conjugated aldehydes such as crotonaldehyde and cinnamaldehyde to the corresponding unsaturated alcohols.<sup>11-15</sup> Different metals and supports have been used to study the selective hydrogenation of these kinds of unsaturated compounds. Thus, metals such as Ru, Rh, Co, Pt, Os and Ir have been studied, showing great differences in activity and selectivity. Metal supported catalysts has been modified by alloying,<sup>16,17</sup> by adding promoters,<sup>18,19</sup> by using strong metal-support interaction and by inducing electronic effects.<sup>20,21</sup> Despite the number of investigations in this field, there is not an agreement on the nature of the effect which may have a more significant impact on the selectivity towards the unsaturated alcohol.

The hydrogenation of furfural is an interesting reaction since it allows obtaining furfuryl alcohol which is used in the production of liquid resins, fine chemicals and in the manufacture of lysine, vitamin C, lubricants, and dispersant agents and in the synthesis of fibers.<sup>22-24</sup> Usually, furfuryl alcohol has been obtained by hydrogenation of furfural using copper chromite as catalyst. Also, however, the toxicity and moderate activity of this catalyst has motivated the study of other alternative catalysts able to overcome the mentioned difficulties.<sup>23</sup> Thus, different catalysts, such as, copper supported on activated carbon, Raney Ni, amorphous Ni alloys, Cu-Zn mixed oxides with Al, Mn and Fe, Cu-MgO and Pt dispersed on different supports have been used in the hydrogenation of furfural. The reaction has been conducted both in vapour and in liquid phase.<sup>24-28</sup>

In this work, the hydrogenation of furfural on a series of 2wt.% Ir/TiO<sub>2</sub> catalysts have been studied. The effect of reduction temperature on surface coverage and catalytic behavior is investigated.

### EXPERIMENTAL

As support a TiO<sub>2</sub> (P-25 Degussa) with a S<sub>BET</sub> of 58 m<sup>2</sup>/g was used. The catalysts were prepared by impregnation of the support with an aqueous solution of H<sub>2</sub>IrCl<sub>6</sub> in appropriate amount to get a 2.0 wt% of Ir. Then, it was dried overnight at 393 K and calcined in air at 573 K. Different aliquots were taken from this solid to be reduced for 2 h in flowing hydrogen at 473, 573, 673 or 773 K, prior the characterization of the solid or the catalytic test.

Nitrogen adsorption at 77 K and H<sub>2</sub> chemisorption at 298 K were carried out in a Micromeritics ASAP 2010 apparatus. Temperature programmed reduction (TPR) experiments were performed in a TPD/TPR 2900 Micromeritics apparatus, using as reducing mixture a 5% H<sub>2</sub>/Ar and a heating rate of 10°/min. The same equipment was used to carry out the surface acidity measurement by temperature programmed desorption (TPD) of ammonia adsorbed by a pulse method at 373 K and desorbed in a programmed mode (10°/min) from room temperature to 873 K. Transmission electron microscopy (TEM) micrographs were obtained in a Jeol Model JEM-1200 EXII System and X-ray photoelectron spectra (XPS) were recorded using an Escalab 200R 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 samples were reduced *in situ* in H<sub>2</sub> in the chamber of this equipment at 473, 573, 673 and 773 K and once the solid was outgassed it was transported to the analysis chamber. The Ir/Ti and N/Ti atomic surface ratios were calculated from the integrated intensities of Ir 4f<sub>7/2</sub>, and Ti 2p<sub>3/2</sub> core level peaks after background subtraction and correction by the sensitivity factors<sup>29</sup> and using the C 1s line at 284.9 eV as internal standard.

The catalytic hydrogenation reaction was carried out in a stainless steel batch reactor at 363 K and a hydrogen pressure of 0.62 MPa provided with a sampling valve and a stirrer. The catalysts (0.500 g) were reduced in hydrogen in a gas reactor during 2 h at 473, 573, 673 and 773 K, cooled down to room temperature, imbibed with the solvent (a 1:1 v/v mixture

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n-heptane/ethanol) and transferred to the reactor avoiding the contact with air to prevent re-oxidation. Then, furfural and solvent was added to complete a volume of 80 mL of a 0.10 M furfural solution. After flowing with H<sub>2</sub> to remove the air, the temperature was raised to 363 K and pressurized with H<sub>2</sub> to 0.62 MPa. Samples of the liquid were taken periodically and analysed in a GC-MS Saturn 2000 (GC-MS).

## RESULTS AND DISCUSSION

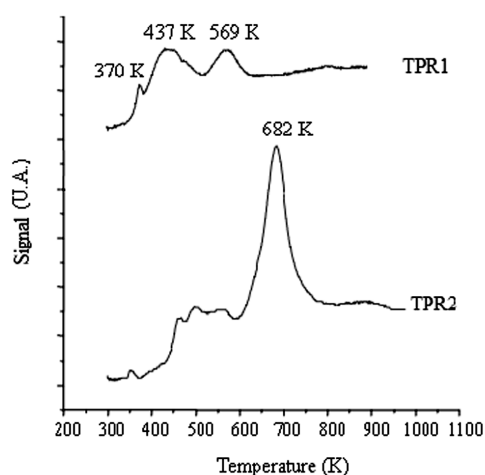
Table 1 compiles the hydrogen chemisorption results at 298 K expressed as H/Ir atomic ratios. It can be seen a slight increase in that ratio as reduction temperature raises from 473 to 573 K and it decreases slightly at 673 K and drastically at higher temperatures. This behaviour may be explained considering that at temperatures lower than 573 K, the reduction of Ir oxides is not complete and the decreases observed in the H/Ir ratio at higher temperature is a consequence of a partial coverage of the metal particles by partially reduced TiO<sub>2-x</sub> species by the SMSI effect. Thus, the metal particle sizes obtained from the chemisorption data do not make sense if the catalysts are in SMSI effect. The obtained values were compiled in Table 1 and only the value obtained by the catalysts reduced at 773 K is far from TEM values, due to surface coverage. Metal particle size values obtained by TEM are also given in Table 1. It should be mentioned that the metal particle size distribution is very narrow, in the range 1.0 to 3.5 nm for all catalysts, slightly wider for the catalysts reduced at the highest temperature. Almost no differences in the values were observed for the different catalysts, being the average close to 2.4 nm. This fact is in agreement with the previous explanation that the decrease in the H/Ir ratio is not due to changes in the metal dispersion (or metal particle size) but is due to a partial coverage of Ir crystals by TiO<sub>x</sub> species. Surface acidity studies were performed by TPD of ammonia. The obtained profiles show a wide band in the temperature range 300 to 700K. The profiles of the solids reduced at lower temperatures display intensities slightly higher and with the maximum placed at higher temperatures indicative of higher acidity and stronger acid sites respectively. These types of sites may be attributed to residual chlorine coming from the precursor H<sub>2</sub>IrCl<sub>6</sub>. At temperatures higher than 573K, the reduction of the Ir precursor has been completed as well as the evolution of HCl and the surface acidity remains almost constant.

**Table 1.** H/Ir atomic ratio, metal particle size obtained from TEM and surface acidity of Ir/TiO<sub>2</sub> catalysts

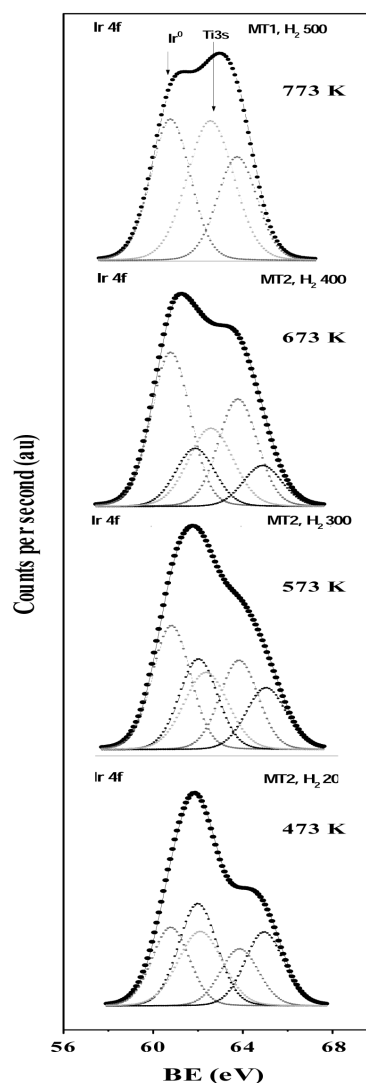
Catalyst	H/Ir	d <sub>CHEM</sub> (Å)	d <sub>TEM</sub> (Å)	μmoles NH <sub>3</sub> /g
2%Ir/TiO <sub>2</sub> (I-473)	0.57	16	20	0.95
2%Ir/TiO <sub>2</sub> (I-573)	0.68	14	22	0.83
2%Ir/TiO <sub>2</sub> (I-673)	0.56	17	24	0.71
2%Ir/TiO <sub>2</sub> (I-773)	0.09	102	25	0.70

The TPR profile displayed a peak centred at 437 K assigned to the reduction of Ir species which is overlapped with the evolution of HCl and a second peak centred at 550 K attributed to iridium oxide species with higher interaction with the support. It is likely that during this second step also occurs a partial reduction of the titania by hydrogen spillover (Figure 1).

Figure 2 shows the XPS spectra of Ir 4f. In the same region of the Ir 4f core level (4f<sub>7/2</sub> and 4f<sub>5/2</sub>) appears a peak due to Ti 3s, and therefore the spectra are more complex. The two components of Ir peaks may be deconvoluted in two components, one corresponding to Ir<sup>0</sup> at 60.9 eV and the other assigned to a partially oxidised Ir<sup>δ+</sup> at 62.0 eV, as can be seen. The presence of Ir<sup>0</sup> increases as reduction temperature increases. Additionally, two signals were also detected



**Figure 1.** Temperature programmed reduction of Ir/TiO<sub>2</sub> catalysts



**Figure 2.** XPS spectra of Ir 4f core level of Ir/TiO<sub>2</sub> catalysts

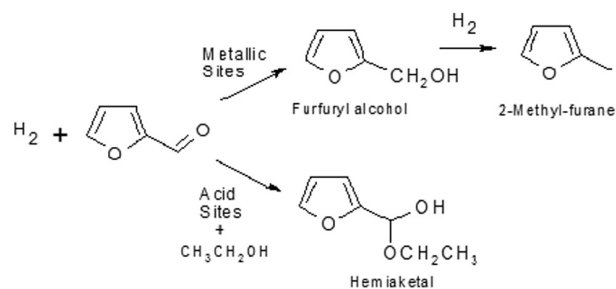
for O 1s. The binding energies of these signals, located at 529.9 and 531.6 eV correspond to O<sup>2-</sup> and surface OH respectively. On the other hand, the Ti 2p core level spectra were similar for all the studied samples without changes in the B.E (458.6 eV), corresponding to Ti<sup>4+</sup> as the main component. The presence of partially reduced Ti

species was not possible to detect. Table 2 compiles the BE of Ir 4f<sub>7/2</sub> and O 1s core level spectra as well as the Ir/Ti atomic surface ratio. In brackets, the extent of each proportion is given. It can be seen that the Ir/Ti atomic surface ratio remains almost constant in the temperature range 473-573 K and it decreases slightly at higher temperatures. This behaviour may be understood taking into account that the metal dispersion remains almost constant as revealed by TEM results. On the other hand in the temperature lower than 573 K the reduction of Ir species is not complete and at higher temperatures a partial surface coverage of Ir crystals by TiO<sub>2-x</sub> species occurs and consequently, a decrease in the Ir/Ti ratio takes place.

**Table 2.** Binding energy (eV) of Ti 2p<sub>3/2</sub>, O 1s, Ir4f<sub>7/2</sub> core level and Ir/Ti atomic surface ratio of Ir/TiO<sub>2</sub> catalysts

Catalyst	Ti 2p <sub>3/2</sub>	O 1s	Ir 4f <sub>7/2</sub>	Ir/Ti at
2%Ir/TiO <sub>2</sub> (I-473)	458.5	529.9 (85) 531.5 (15)	60.9 (44) 62.1 (56)	0.054
2%Ir/TiO <sub>2</sub> (I-573)	458.6	529.8 (85) 531.5 (15)	60.9 (58) 62.0 (42)	0.054
2%Ir/TiO <sub>2</sub> (I-673)	458.5	529.9 (87) 531.6 (13)	60.9 (75) 62.0 (25)	0.047
2%Ir/TiO <sub>2</sub> (I-773)	458.7	530.0 (88) 531.5 (12)	60.8 (90) 62.1 (10)	0.044

The hydrogenation of furfural was studied at 393 K and 0.62 MPa in a batch reactor. The results showed a continuous decrease in the furfural concentration and the generation of furfuryl alcohol as reaction product. In those catalysts reduced at 473 and 573 K a hemiacetal generated by a side reaction between furfural and ethanol also appears. Figure 3 shows a scheme of the hydrogenation of furfural on Ir/TiO<sub>2</sub> catalysts. Significant differences in the TOF level as well as in the extent of the side reaction which leads to a hemiacetal were observed in the series of studied catalysts as can be seen in Figure 3. This side reaction takes place on acid sites of the catalysts, and as it was previously discussed, the acidity of this catalyst series is affected by the residual chlorine on the catalysts due to the differences in the reduction temperature. Therefore, the formation of hemiacetal may be favoured in those catalysts with higher surface acidity in agreement with the obtained results.



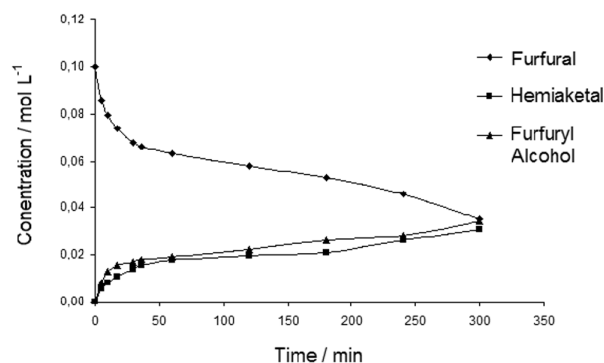
**Figure 3.** Scheme of reaction during furfural hydrogenation on Ir/TiO<sub>2</sub> catalysts

Table 3 shows the selectivity to furfuryl alcohol at 30% of conversion for the studied iridium catalysts. The formation of a hemiacetal takes place on acid sites which directly interact with the C=O bond, leading to a protonated species and allowing the access of a weak nucleophilic specie such as ethanol. Thus, ethanol is a solvent and also reactant giving a by-product in the hydrogenation of furfural. As the reduction temperature of the catalyst increases, the surface acidity gradually decreases (Table 1) due to the SMSI effect and the route to produce furfuryl alcohol is enhanced.

**Table 3.** Initial reaction rate, TOF and selectivity to furfuryl alcohol at 30% of conversion in the hydrogenation of furfural at 363 K and 0.62 MPa on Ir/TiO<sub>2</sub> catalysts

Catalyst	Initial reaction rate, mol L <sup>-1</sup> g <sup>-1</sup> min <sup>-1</sup>	TOF (seg <sup>-1</sup> )	Selectivity (%)
2%Ir/TiO <sub>2</sub> (I-473)	0.127	0.073	21.2
2%Ir/TiO <sub>2</sub> (I-573)	0.071	0.040	55.0
2%Ir/TiO <sub>2</sub> (I-673)	0.036	0.030	100
2%Ir/TiO <sub>2</sub> (I-773)	0.029	0.143	100

Figure 4 shows the evolution of furfural and the reaction products for a representative catalyst. It can be seen a decrease in the concentration of furfural with a dependence close to first order. The products display a pseudo exponential increase in their concentration, with differences according to the preferred route. Table 3 compiles the initial reaction rates, TOF and the selectivity at 30% of conversion. It can be seen that the highest activity is displayed by the catalysts reduced at lower temperature because they exhibit a higher amount of Ir surface atoms but also higher surface acidity. Conversely, in those reduced at higher temperatures, present in a SMSI state, they show lower amounts of metallic surface atoms and surface acidity, and consequently, the activity in the hydrogenation of furfural is lower and no side reaction occurring on acid sites takes place.



**Figure 4.** Evolution of the concentration of furfural and reaction products in the hydrogenation of furfural on Ir/TiO<sub>2</sub> (I-573) catalyst at 363 K and 0.62 Mpa of hydrogen pressure

## CONCLUSIONS

The results showed that Ir/TiO<sub>2</sub> catalysts may develop a surface coverage by partially reduced species of the support, TiO<sub>2-x</sub>, whose extent depends on the reduction temperature, being higher as the reduction temperature increases. Additionally, if H<sub>2</sub>IrCl<sub>6</sub> is used as metal precursor, low reduction temperatures leave residual chlorine on the catalyst surface, thus, increasing the surface acidity, leading to bifunctional catalysts. These latter catalysts, in the furfural hydrogenation reaction, produce hemiacetal as side product, whereas in those with lower acidity only furfuryl alcohol is formed.

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