



Structural properties of alumina- and silica-supported Iridium catalysts and their behavior in the enantioselective hydrogenation of ethyl pyruvate

A.B. Dongil^a, B. Bachiller-Baeza^{a,b,*}, I. Rodríguez-Ramos^{a,b}, A. Guerrero-Ruiz^{b,c}, C. Mondelli^d, A. Baiker^d

^a Instituto de Catálisis y Petroleoquímica, CSIC, Marie Curie 2, 28049 Madrid, Spain

^b Grupo de Diseño y Aplicación de Catalizadores Heterogéneos, Unidad Asociada UNED-CSIC (ICP), Spain

^c Dpto. Química Inorgánica y Técnica, Fac. de Ciencias, UNED, C/Senda del Rey n° 9, 28040 Madrid, Spain

^d Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zurich, Hönggerberg, HCI, CH-8093 Zurich, Switzerland

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ABSTRACT

Iridium catalysts were prepared using alumina or silica as supports and two preparation methods, incipient wetness impregnation and flame spray pyrolysis. These catalysts were characterized, after reduction in hydrogen, by transmission electron microscopy, infrared spectroscopy of adsorbed CO and microcalorimetry of CO chemisorption. Aliquots of these catalysts were tested in the ethyl pyruvate hydrogenation using cinchonidine as a chiral modifier. Different enantioselectivities to (R)-ethyl lactate were obtained depending on the support material and the preparation method. Based on the structural characterization it is proposed that the different enantioselectivities are mainly due to different surface structure of the iridium nanoparticles caused by the support interaction.

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1. Introduction

The application of platinum group metals modified with cinchona alkaloids as heterogeneous enantioselective catalysts for asymmetric hydrogenations has been widely studied and covered in various reviews [1–5]. Platinum is the most successful metal for the hydrogenation of α -ketoesters and other activated ketones while Pd has shown very remarkable performance in the hydrogenation of activated carbon double bonds. However, only a few studies reported the suitability of Ir-based materials for this type of reactions [6–12]. For example, Ph_3P stabilized Ir/SiO₂ catalyst modified by a chiral diamine, derived from cinchona alkaloids, exhibits high activity and high enantioselectivity (up to 96% enantiomeric excess, ee) for the hydrogenation of simple aromatic ketones [11]. Also, Ir (20 wt%)/SiO₂ impregnated catalysts modified with cinchonidine afforded in the hydrogenation of methyl pyruvate activities comparable to those achieved by the corresponding cinchonidine-Pt/Al₂O₃ reference system, although with comparatively moderate ee (30%) [12]. The possibility to employ Ir catalysts with lower metal loading (1–5 wt%) has also been explored [13]

and attempts have been made to support iridium particles on a polymeric matrix [14].

The enantioselective hydrogenation of ethyl pyruvate, which has frequently been applied as a model reaction, is generally considered as a structure sensitive reaction [1,2,15]. Briefly, in these catalytic systems, the chiral active sites are generated on the catalytically active metal surface by adsorption of the modifier (cinchona alkaloid) through its aromatic quinoline moiety. The reactant is assumed to adsorb on a metal site adjacent to the modifier and consequently particles large enough to accommodate the diastereomeric modifier–reactant complex are required. However, very small colloidal Pt particles have also rendered very high ee's in methyl pyruvate hydrogenation [16], and therefore the debate about the optimal size of the Pt-crystallites is not closed. On the other hand, several parameters influence the enantioselective reaction [1,2,17,18]: the proper choice of solvent, catalyst pretreatment and reaction conditions (modifier/reactant ratio, temperature). Consequently, considerable research has been devoted to find the optimal conditions to produce a catalyst with high activity and selectivity [1–5]. With respect to the catalyst, the size and morphology of the active metal particles and the presence of contaminants are known to affect the catalytic performance and can be varied with reductive pretreatments [17,19]. These catalyst parameters are crucial since they influence the

* Corresponding author. Fax: +34 915854760.

E-mail address: b.bachiller@icp.csic.es (B. Bachiller-Baeza).

modifier orientation and its adsorption strength on the metal, the enantioselectivity being favored with strong interactions [20–23].

More recently, catalysts prepared by flame synthesis have been tested in this type of reactions [24–26]. Interestingly, better performances in terms of activity and/or enantioselectivity have been found for the flame-made catalysts than for reference catalysts prepared by conventional methods as shown for the hydrogenation of ethyl pyruvate and ethyl 3-methyl-2-oxobutyrates with Rh/Al₂O₃ or the hydrogenation of 4-methoxy-6-methyl-2-pyrone with Pd/Al₂O₃. Apart from that, flame synthesis is very attractive from both the academic and industrial point of view as it allows the preparation of the catalysts in a single step and, by properly adjusting the synthesis parameters, a narrow particle size distribution can be obtained.

Being aware of the critical importance of the choice of the metal and trying to find an alternative for Pt catalysts, here we have studied the asymmetric hydrogenation of ethyl pyruvate to ethyl lactate on supported Ir catalysts using cinchonidine as chiral modifier. A central aspect of our study is the influence of the structural properties of the supported iridium catalysts on their catalytic performance. For that purpose we prepared differently supported (silica, alumina) Ir catalysts applying two different preparation methods (incipient wetness impregnation, flame spray pyrolysis). Data on the preparation and characterization of flame-made supported platinum group metal catalysts are scarce and to our knowledge the synthesis of iridium catalysts by this method is reported here for the first time. The catalysts were characterized using TEM, and by following the chemisorption of CO by FT-IR and microcalorimetry.

2. Experimental

2.1. Catalysts preparation

Materials applied were: γ -alumina, silica (Aerosil), H₂IrCl₆·6H₂O (Aldrich), Tetraethyl orthosilicate (TEOS, Fluka, puriss.), aluminum(III) acetylacetonate (ABCR, 99%) and iridium(III) acetylacetonate (Acros, 97%).

Four different catalysts were prepared by impregnation and flame spray pyrolysis with an Ir loading of 5 wt%. Ir/SiO₂ and Ir/Al₂O₃ were prepared by incipient wetness impregnation with a H₂IrCl₆·6H₂O solution. The catalysts were calcined in air at 573 K for 2 h. For the flame synthesis of Ir/SiO₂-fm and Ir/Al₂O₃-fm, the precursors, iridium acetylacetonate and TEOS or aluminum acetylacetonate, were dissolved in 100 mL of 50/50 (vol.%) MeOH/AcOH and stirred until the solution became transparent and finally filtered. The precursor mixture was fed at 5 mL min⁻¹ through the nozzle of the flame reactor as described in detail elsewhere [27].

The specific surface area of the as-prepared catalysts was determined by nitrogen adsorption at 77 K using the BET method (Micromeritics ASAP 2010 volumetric system). All samples were outgassed at 423 K for 1 h prior to analysis. The iridium content of

the catalysts, shown in Table 1, was determined with inductively coupled plasma optical emission spectroscopy (ICP-OES) technique (Perkin Elmer Optima 3300 DV) after dissolution in a mixture of acids (HNO₃, HCl, H₂SO₄ and HClO₄).

2.2. Characterization

2.2.1. Electron microscopy

Transmission electron microscopy (TEM) studies of the samples were carried out in a JEOL JEM-2100F microscope at 200 kV. The instrument has a point resolution of 0.19 nm and is equipped with a high-angle annular dark field (HAADF) detector and a 2k × 2k ULTRASCAN 1000 CCD camera. The samples were prepared by grinding and ultrasonic dispersal in an acetone solution. The surface weighted mean diameter (d) of the Ir particle size was calculated based on a minimum of 200 particles, using the following equation where n_i is the number of particles with diameter d_i :

$$d = \frac{\sum_i n_i d_i^3}{\sum_i n_i d_i^2}$$

2.2.2. Microcalorimetry: CO chemisorption

The metallic dispersion and metal particle size were determined from the CO chemisorption isotherms. These measurements were performed volumetrically with simultaneous measure of the heats evolved in each pulse by a Tian Calvet heat-flow calorimeter (Setaram C-80 II) operated isothermally at 330 K and connected to a glass vacuum-dosing apparatus. The apparatus has been described in detail elsewhere [28]. Doses of approximately 2×10^{17} molecules of the probe gas were introduced into the system to titrate the surface of the metal catalysts. For these experiments, the catalysts were first in situ reduced under hydrogen flow at 773 K for 2 h, outgassed overnight at the same temperature, and finally cooled down to 330 K. The metal dispersion was obtained from the total amount of CO uptake at monolayer coverage. This coverage is considered to be achieved when the evolved heat falls in the physisorption field (40 kJ mol⁻¹).

2.2.3. FTIR experiments

The catalysts were pressed into self-supported wafers, ca. 10 mg cm⁻². An in situ glass made IR cell with CaF₂ windows was used for the IR experiments. The samples were outgassed overnight prior to the experiments. The reduction treatments were carried out increasing the sample temperature, at 10 K min⁻¹, up to 773 K in a H₂ flow (ca. 25 mL min⁻¹) and hold at that temperature for 2 h. Then, the catalysts were outgassed at 773 K for 1 h. The IR spectra of the reduced samples were recorded before and after exposure to 6–8 kPa of CO at room temperature. Subsequently, the IR spectra of the wafers were recorded again after evacuating the samples with dynamic vacuum at 373, 473 and 573 K for 1 h. All spectra were collected using a Fourier transform infrared spectrometer (Nicolet 5 ZDX) equipped with a liquid nitrogen-cooled MCT (mercury-cadmium-telluride) detector at a resolution of 4 cm⁻¹ in

Table 1
CO adsorption data and particle size calculated by TEM.

Catalyst	Ir content (% wt)	S _{BET} (m ² g ⁻¹)	CO adsorption			TEM d (nm)
			N ads (μmol g ⁻¹)	d (nm)	q^0_{ads} (kJ mol ⁻¹)	
Ir/SiO ₂	3.5	295	91	2.3	145	2.9
Ir/Al ₂ O ₃	3.9	135	102	2.2	160	1.3
Ir/SiO ₂ -fm	0.3	134	–	–	–	–
Ir/Al ₂ O ₃ -fm	3.2	230	49	3.7	160	3.5

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