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ABSTRACTS

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Photochemical deposition: a simple and effective approach to catalyst preparation for cinnamaldehyde hydrogenation

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Photochemical deposition of noble metals over metal oxide supports has the advantage of spreading very effectively the metal throughout the support, thus leading to high dispersions. Materials with catalytic properties can be prepared in this way and used in many applications including selective hydrogenation of unsaturated organic substrates containing oxygenated functional groups, like steroids or α,β -unsaturated aldehydes, which are used in the industrial preparation of fine chemicals.

Titania supported Pt and Ir catalysts were prepared by photodeposition. They were used in the cinnamaldehyde selective hydrogenation to test their activity and selectivity. The photodeposition method was able to produce materials with an outstanding performance for selective hydrogenation of cinnamaldehyde, leading to a selectivity as high as 64% towards cinnamyl alcohol at 79% conversion under mild operating conditions.

Keywords: Heterogeneous catalysis, Selective hydrogenation, Fine chemistry

Photochemical deposition: a simple and effective approach to prepare hydrogenation catalysts

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Introduction

Photochemical deposition of noble metals in different supports is gaining importance because of its simplicity and advantages. Its main advantage is the ability of spreading very effectively the metal throughout the support, thus leading to high dispersions. In addition, when the photodeposition process is carried out over a semiconductor, results in concomitant reduction of the deposited metal ions, mainly through the action of conduction band electrons. To improve the rate of photodeposition is usual to add a sacrificial electron donor like formaldehyde, methanol or 2-propanol [1]. This method can be applied to the preparation of a variety of catalysts, including noble metal catalysts supported in TiO₂. Following preparation, fine-tuning of the catalytic properties is a fundamental step when high activity and selectivity are sought.

Selectivity is nowadays a key factor in catalyst design. Selectivity improvement means not only reducing the amount of by-products from an environmental point of view, but also cost effectiveness on production and separation steps. Research for new catalytic materials that can selectively hydrogenate organic substrates containing unsaturated functional groups, like steroids or α,β -unsaturated aldehydes is in our days a very active domain of investigation. For example, allylic alcohols obtained by reduction of the carbonyl group in α,β -unsaturated aldehydes are valuable intermediates in the production of perfumes, flavoring additives, pharmaceuticals and agrochemicals.

In this study high temperature activated catalysts (calcined and reduced to 773K) were compared to non activated ones (only reduced by photodeposition process) using the liquid phase hydrogenation of cinnamaldehyde as model reaction.

Experimental

Noble metal catalysts supported on titania were prepared by the photochemical deposition method. The metal was dispersed on the surface by photodeposition of dihydrogen hexachloroplatinate (IV) or ammonium hexachloroiridate (III) at ambient temperature. The aqueous solutions with the desired amounts of TiO₂ (Degussa P-25, 50 m² g⁻¹, 20% rutile, 80% anatase), metal precursor and methanol were sonicated for 30 minutes. The suspension was then irradiated by a low-pressure mercury vapor lamp with an emission line at 253.7 nm (aprox. 3W of radiant flux) for 4h [2]. The catalyst was then filtered, repeatedly washed with distilled water and dried in oven at 90°C for 2 days. Some catalyst were the calcined and reduced to 773K. Techniques like nitrogen adsorption at 77K, SEM/EDS, H₂ chemisorption and TEM analysis were used to characterize the catalytic materials. In order to assess metal particle size H₂ chemisorption measurements were performed.

Liquid phase hydrogenation of cinnamaldehyde was carried out in a 100mL stainless steel autoclave at 363K and 10bar. Small aliquots of the reaction mixture were taken throughout the reaction to perform quantitative analysis (computing conversion and product selectivity).

Results and discussion

H₂ chemisorption lead to identification of metal particles with 20nm of diameter in a 5 wt.% Pt catalyst. In order to confirm particle size, samples were analyzed by TEM and the results provided particles with ca. 5nm. This result can be explained in terms of decoration of Pt particles by partially reduced TiO_x moieties. Since catalysts were reduced at high temperatures strong metal support interaction (SMSI) can be responsible for low H/Pt ratios indicating a partial surface coverage effect instead of sintering of the metallic phase. This effect is also responsible for improved selectivity towards unsaturated alcohol. The beneficial effect of SMSI over activity and selectivity towards carbonyl group reduction in hydrogenation reactions is known from the literature [3]. The same 5 wt.% Pt catalyst revealed a maximum selectivity to cinnamyl alcohol of 64% at 79% conversion (Figure 1b), against 26% maximum selectivity at 29% conversion under similar conditions for the untreated catalyst (Figure 1a). In addition to the above reported data, similar results were found for Ir supported catalysts, but with smaller metal particles (ca. 2nm).

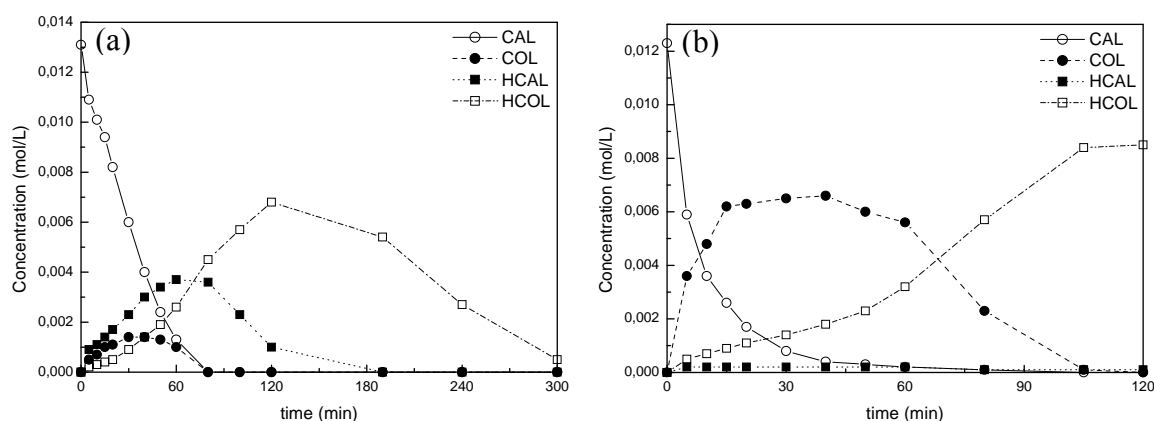


Figure 1 Concentration profiles for cinnamaldehyde hydrogenation using (a) 5Pt/TiO₂ and (b) 5Pt/TiO₂-773 catalysts.

Conclusions

Catalysts prepared by photodeposition revealed outstanding activity and selectivity for selective hydrogenation of cinnamaldehyde into cinnamyl alcohol.

SMSI effect may be responsible for titania supported catalysts higher activity and selectivity. Under the same conditions Pt catalyst was slightly more selective, despite being less active, than Ir catalyst.

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