

# Book of Abstracts

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# Photochemical deposition of Platinum over MWNT: making catalysts for selective hydrogenation of cinnamaldehyde

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In a recent review, attention has been called to the fact that carbon nanotubes are attractive and competitive catalyst supports when compared to activated carbon due to the combination of their electronic, adsorption, mechanical and thermal properties (Serp, et al., 2003). There are several methods that can be used to deposit metals onto the surface of a support, namely multiwalled carbon nanotubes (MWNT) Incipient wetness is still the most widely used method in spite of some known drawbacks which are mainly the high number of parameters which is necessary to control in order to obtain reproducible catalysts. Other methods like chemical vapor deposition and atomic layer epitaxy are quickly gaining importance due their ability to produce ready to use catalysts. However these methods do require rather sophisticated equipment and procedures, which may not be easy to implement. As an alternative method, photochemical deposition of noble metals is being widely studied because of its simplicity and advantages. The main advantage is the ability of spreading very effectively the metal throughout the support, thus obtaining very high dispersions resulting in higher catalytic activities.

One classical, but still very challenging application for these catalysts is the selective hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes. Two primary reaction products can be envisaged: the saturated aldehyde and the unsaturated alcohol. Cinnamyl alcohol is used as a raw material in the synthesis of perfumes, pharmaceuticals and other fine chemicals. Selective hydrogenation of cinnamaldehyde is a challenging reaction, because the C=C bond in unsaturated aldehydes shows a higher reactivity for hydrogenation over supported noble metal catalysts than the carbonyl double bond (Hajek, et al., 2003). The selectivity to cinnamyl alcohol is highly dependent on the nature of the precious metal used as a catalyst. The noble metals selectivities can be classified in the following sequence Pd < Rh < Ru < Pt < Ir (Silva, et al., 1997).

In the present study, the catalysts prepared by photochemical deposition were compared against the usual incipient wetness catalysts, normally used in these applications. The nature of the support was also investigated as MWNT were compared against TiO<sub>2</sub>. Catalyst loads were also varied in order to achieve the desired conversions.

Supported Pt (1% wt) catalysts were prepared by the photochemical deposition method over MWNT and TiO<sub>2</sub>. The metal was dispersed on the surface by photodeposition of dihydrogen hexachloroplatinate (IV) at ambient temperature. The aqueous solutions with the desired amounts of TiO<sub>2</sub> (Degussa P25) or MWNT, H<sub>2</sub>PtCl<sub>6</sub> (Alfa Aesar, 99.9%) and methanol (Riedel-de Haën, 99.8%) were sonicated for 30 minutes to prevent sintering. 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.

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The catalyst was then centrifuged, repeatedly washed with distilled water and dried in oven at 90°C for 2 days (Zhang, et al., 1998). Finally, the catalysts were calcined and reduced at 473 and 773K in flowing hydrogen and kept in a dryer until further use. Another catalyst with 5 wt% Pt loading prepared by incipient wetness method over MWNT was used for comparison purposes. The catalysts were thoroughly characterized in the usual way.

Hydrogenation of cinnamaldehyde was carried out in a 100mL well-stirred stainless steel reactor. The reaction mixture contained heptane (solvent), 140mg cinnamaldehyde, 60 $\mu$ L decane (as an internal standard for gas chromatography) and 200mg of catalyst. Nitrogen was bubbled throughout the solution several times to remove traces of dissolved oxygen. Then the reactor was pressurized with hydrogen (3 bar) in order to purge the nitrogen. Finally the temperature was set at 363K and the reactor pressurized with hydrogen to the desired 10bar immediately before starting the reaction.

As the reaction proceeds samples are withdrawn to perform quantitative analysis: conversion and product selectivity. The analysis was performed in a DANI GC-1000 Gas Chromatograph, equipped with a WCOT Fused Silica column (length 30m, 0.32mm i.d., film thickness 1 $\mu$ m) and a flame ionization detector (FID).

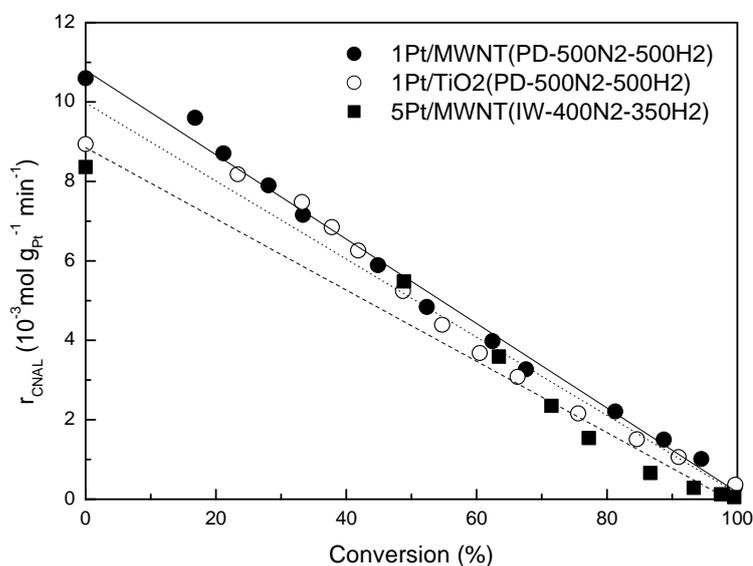


Figure. Cinnamaldehyde reaction rate as function of conversion for different Pt supported catalysts. The lines represent the linear fits: (—)1%Pt/MWNT(PD-500N2-500H2), (.....)1%Pt/TiO2(PD-500N2-500H2) (---)5%Pt/MWNT(IW-400N2-350H2).

From Figure it can be seen that the performance of the supported-Pt catalysts prepared by photochemical deposition is slightly superior to these prepared by incipient wetness. In what concerns selectivity to cinnamyl alcohol (not shown), the MWNT supported-Pt catalyst prepared by photolysis produce the best results (aprox. 40% selectivity). In conclusion this simple photodeposition method is able to produce very active catalytic materials for selective hydrogenation of cinnamaldehyde.

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