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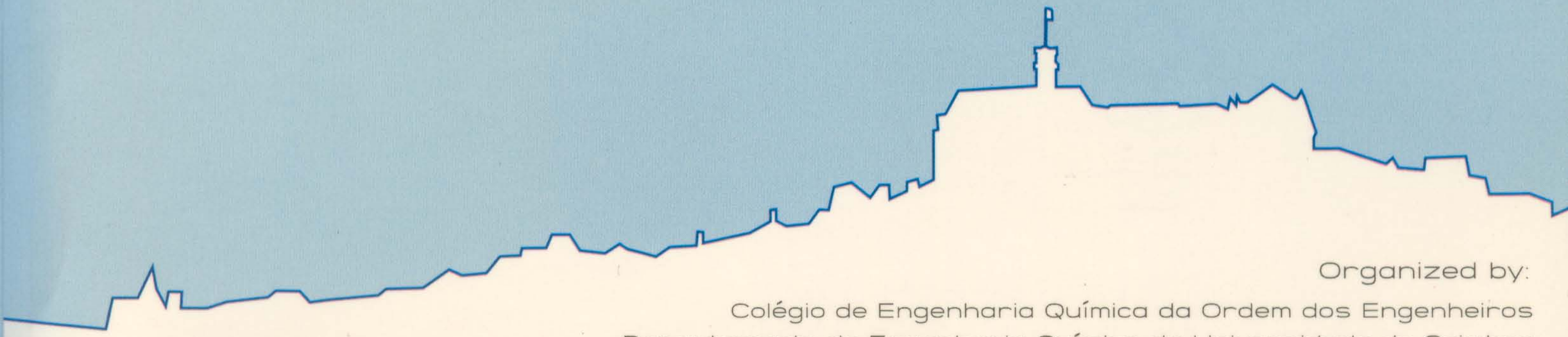

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Photochemical deposition of Platinum over MWNT: making catalysts for selective hydrogenation of cinnamaldehyde

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Keywords: *Photochemical deposition, Platinum Catalysts, Titanium dioxide, Carbon Nanotubes, Cinnamaldehyde selective hydrogenation*
Topic: Engineering Sciences and Fundamentals: Catalysis and Reaction Engineering.

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 know 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 α,β-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_2. 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_2. The metal was dispersed on the surface by photodeposition of dihydrogen hexachloroplantinate (IV) at ambient temperature. The aqueous solutions with the desired amounts of TiO_2 (Degussa P25) or MWNT, H_2PtCl_6 (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 90ºC 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, 60μL 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 1μm) and a flame ionization detector (FID).

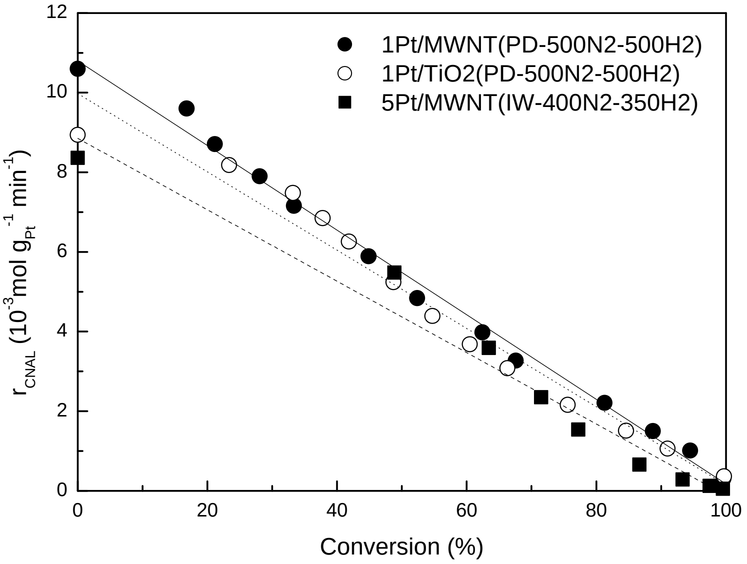

Figure. Cinnamaldehyde reaction rate as function of conversion for different Pt supported catalysts. The lines represent the linear fits: (—)1%Pt/MWNT(PD-500N2-500H2), (·····)1%Pt/TiO2(PD-500N2-500H2) (----)5%Pt/MWNT(IW-400N2-350H2).

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

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Keywords: Photochemical deposition, Platinum Catalysts, Titanium dioxide, Carbon Nanotubes, Cinnamaldehyde selective hydrogenation
Topic: Engineering Sciences and Fundamentals: Catalysis and Reaction Engineering.

Abstract

In the present study, the photochemical deposition method was compared against the usual incipient wetness procedure in the preparation of supported Pt catalysts. Particular attention was given to parameters such as nature of the support (multiwalled carbon nanotubes, MWNT *vs.* titanium dioxide, TiO_2) and reduction temperature. Supported 1% wt Pt catalysts treated in hydrogen at 773K showed improved activity and selectivity towards cinnamyl alcohol (50.8 and 57.4% were observed in MWNT and TiO_2 - SMSI effect, respectively) when comparing to those untreated (45.8 and 28.9, MWNT and TiO_2, respectively). The best catalytic performance was achieved by a 5% wt Pt supported in TiO_2 catalyst treated in hydrogen at 773K. Selectivity to unsaturated alcohol as high as 63.2% at 80% conversion was observed.

1. Introduction

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, including multiwalled carbon nanotubes (MWNT). Incipient wetness is still the most widely used method in spite of some know drawbacks, which are mainly the high number of parameters 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 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 very high dispersions, resulting in higher molecular control, with a positive effect on both activity and selectivity. When a semiconductor is used as support, the photodeposition process also results in simultaneous reduction of the metal ions by conduction band electrons. Sacrificial electron donors like formaldehyde, methanol or 2-propanol are generally added to improve the rate of photodeposition. TiO_2, with approximately 3.5eV band-gap energy requires an excitation wavelength inferior to 400nm, i.e., near-UV wavelength, and in aqueous suspensions noble metals can be reduced by photoelectrons and deposited as small crystallites according to the reaction:

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$$M^{n+} + \frac{n}{2}H_2O \xrightarrow{h\nu} M^0 + nH^+ + \frac{n}{4}O_2$$

with the following relative reactivity pattern: $Ag^+ > Pd^{2+} > Au^{3+} > Pt^{4+} >> Rh^{3+} >> Ir^{4+} >> Cu=Ni=Fe=0$ (Herrmann, 1995).

Nano-scale catalyst design to molecular controlling of the metal phase is a key factor to prepare more selective catalysts. In the XXI century, selectivity is going to be driving force in catalyst design and engineering, due to cost effectiveness and environmental protection. Selective catalytic hydrogenation of organic substrates containing unsaturated functional groups is an important step in the industrial preparation of fine chemicals. As an example, allylic alcohols are obtained on the hydrogenation of the carbonyl group in α,β-unsaturated aldehydes and are valuable intermediates for the production of perfumes, flavoring additives, pharmaceuticals and agrochemicals. Recently, many studies have been concerned with these reactions, using manly acrolein, crotonaldehyde, cinnamaldehyde and citral. The development and characterization of catalysts for the selective hydrogenation of α,β-unsaturated aldehydes with special emphasis on cinnamaldehyde has been reviewed by Gallezot (Gallezot *et al.*,1998). Cinnamyl alcohol is obtained by the hydrogenation of cinnamaldehyde (figure 1) and can be used as a raw material in the synthesis of perfumes and pharmaceuticals. The influence of the nanostructured carbon supports on the hydrogenation of cinnamaldehyde was studied by Plainex (Plainex *et al.*, 1994) who found that a Ru/nanotube catalyst, which contained fullerenes, was up to 92% selective for cinnamyl alcohol and Lashdaf (Lashdaf *et al.*, 1998) who observed a selectivity of 60% using 5%Ru/C60. Unfortunately, the selectivity towards unsaturated alcohols, the desired products, is difficult to achieve because thermodynamics favors the hydrogenation of the C=C over the C=O bond by about 35 kJ mol^{-1} and because for kinetic reasons, the reactivity of the olefinic bond is higher than that of the carbonyl. In spite of these drawbacks the selectivity towards unsaturated aldehydes using heterogeneous catalysts can be improved by changing numerous conditions like type of solvent, support and metal, addition of a second metal or metal reduction temperature. Regarding the nature of the metal, some results show that unpromoted Ir and Os catalysts are considered to be rather selective for unsaturated alcohol formation while Pt, Ru and Co are moderately selective and Pd, Rh and Ni are nonselective (Gallezot *et al.*,1998).

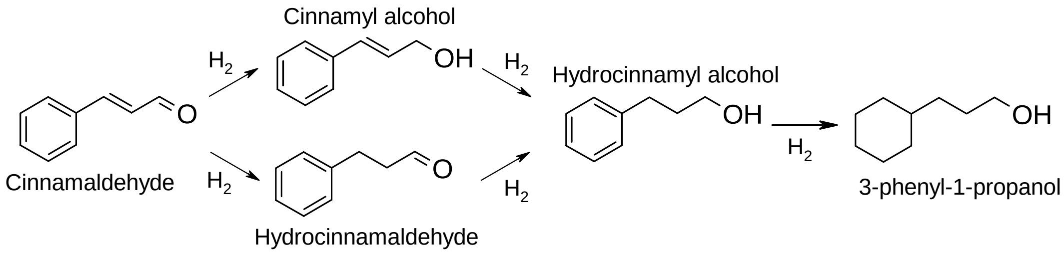

Figure 1 –Scheme of cinnamaldehyde hydrogenation.

In the present study the photochemical prepared catalysts 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$_2$.

2. Experimental

2.1 Catalyst preparation

Pt catalysts supported on titania (1 and 5%wt, 1Pt/TiO2 and 5Pt/TiO2, respectively) and on MWNT (1%wt Pt, 1Pt/MWNT) were prepared by the photochemical deposition method. The metals were dispersed on the surface by liquid phase photodeposition of dihydrogen hexachloroplantinate (IV). The aqueous solutions with the desired amounts of TiO$_2$ (Degussa P-25) or MWNT, H$_2$PtCl$_6$ (Sigma-Aldrich, 8%) 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. The catalyst was then centrifuged and dried in oven at 363K for 2 days (Zhang, *et al.*, 1998). Finally, the catalysts were calcined and reduced at 773K in flowing hydrogen (1Pt/TiO2-773 and 1Pt/MWNT-773) and kept in a dryer until further use. A catalyst with 5% wt Pt loading prepared by incipient wetness method over MWNT (5Pt/MWNT) and a commercial 1% wt Pt supported in charcoal (1Pt/C, Johnson Matthey, Charcoal type 18 powder) were used for comparison purposes.

The amount of platinum deposited in the support was controlled indirectly by UV-vis spectroscopy. One sample was withdrawn at the beginning and another at the end of the photodeposition process. The 261 nm band was checked using an UV-vis spectrometer (Jasco V560). The absence of measurable band at the end of the photodeposition indicates that all the platinum was successful deposited.

2.2 Catalyst characterization

The textural characterization of the materials was based on the N_2 adsorption isotherms, determined at 77K with a Coulter Omnisorp 100CX apparatus. BET surface areas (S_{BET}) were calculated, as well as the micropore volumes (V_{micro}) and mesopore surface areas (S_{meso}) determined by the *t*-method, using the standard isotherm for carbon materials proposed by Rodríguez-Reinoso (Rodríguez-Reinoso *et al*., 1987). The metal dispersion was determined by H_2 chemisorption at room temperature in a U-shaped tubular quartz reactor after a thermal treatment to remove contaminant species from the catalyst surface. Pulses of H_2 were injected through a calibrated loop into the sample at regular time intervals until the area of the peaks became constant. The amounts of H_2 chemisorbed were calculated from the areas of the resultant H_2 peaks. The H_2 was monitored with a SPECTRAMASS Dataquad quadrupole mass spectrometer. X-ray photoelectron spectroscopy (XPS) was used to determine the surface atomic composition of platinum supported catalysts in a VG Scientific ESCALAB 200A spectrometer using a non-monochromatized AlKα radiation (1486.6eV). The sample powders were mounted directly on a double-sided adhesive tape. The pressure in the analysis chamber was inferior to 10^{-8}mbar during data collection. Binding energy (BE) spectra were recorded in the regions of C 1s, Ti 2p, O 1s and Pt 4f. The spectrums thus obtained were analyzed by XPSpeak 4.1 software by deconvoluting the peaks with mixed Lorentzian–Gaussain functions after background subtraction. Surface analysis for topographical and analytical characterization was carried out by scanning electron microscopy (SEM) with a Jeol JSM-6301F electron microscope. The sample powders mounted on a double-sided adhesive tape and observed at different magnifications under two different detection modes, secondary and back-scattered electrons.

2.3 Catalytic hydrogenation

Hydrogenation of cinnamaldehyde was carried out in a 100mL well-stirred stainless steel reactor. The reaction mixture contained heptane (Aldrich, 99%), 140mg cinnamaldehyde (Fluka, 98%), decane (Fluka, 98%, as internal standard for gas chromatography) and 250mg of catalyst. Nitrogen was bubbled throughout the solution several times to remove traces of dissolved oxygen. The reactor was then 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 proceeded samples were withdrawn to quantitative analysis: conversion and product selectivity. The analysis was performed in a DANI GC-1000 Gas Chromatograph, equipped with a split/splitless injector, a capillary column (WCOT Fused Silica 30m, 0.32mm i.d., coated with CP-Sil 8 CB low bleed/MS 1μm film) and a flame ionization detector.

3. Results and Discussion

3.1 Catalyst characterization

Textural analysis of both supports showed that TiO_2 had a BET surface area of 31.5m^2 g^{-1} whereas MWNT 172m^2 g^{-1}. Due to the production mechanism of these materials, both MWNT and TiO_2 are essentially non-porous with all the observed surface area due to adsorption on the external surface.

The presence of the metallic phase only produced a slight decrease of the BET surface area of the catalyst regarding the naked support and can be explained in terms of support aggregation assisted by metal particles.

3.2 XPS results

Independently of the support used, all the catalysts showed a significant percentage of platinum oxides (PtO or PtO_2), about 40% in case of photodeposition catalysts and 50% for incipient wetness catalysts. In spite of this no noticeable differences were observed in the characteristic regions for each support (Ti2p and O1s for TiO2, C1s for MWNT) between the naked and Pt containing samples. For 1Pt/TiO2-773 the $4f_{7/2}$ BE was assigned to 71.3eV (Pt^0) and 74.3eV (PtO) while $2p_{3/2}$ was 459.5eV (TiO_2). The peak at 530.4 eV was in agreement with O1s electron binding energy for TiO_2 molecules. Slight oscillations around these values were observed to all other TiO_2 supported catalysts. In 1Pt/MWNT-773 the $4f_{7/2}$ BE was assigned to 71.3eV (Pt^0) and 74.3eV (PtO) as they did for the TiO_2 support. All platinum peaks were adjusted with the constraint that ratio $Pt4f_{5/2}$ and Pt $4f_{7/2}$ is 6.81/8.65.

3.3 Cinnamaldehyde hydrogenation

In Table 1 are collected the main results obtained in the liquid-phase hydrogenation of cinnamaldehyde. The catalysts prepared by photodeposition show remarkable selectivities towards unsaturated alcohols and elevated activities when compared to 5Pt/MWNT (prepared by incipient wetness).

Within those prepared by photochemical deposition without any thermal treatment 1Pt/MWNT is much better than 1Pt/TiO2.

Table 1 – Initial reaction rates (mmol g_{Pt}^{-1} min^{-1}) for cinnamaldehyde conversion and maximum selectivity towards cinnamyl alcohol (%), with respective conversion (%) between brackets.

Catalyst	$r_{CNAL,0}$ (mmol g_{Pt}^{-1} min^{-1})	% $S_{CNOL,MAX}$ (X_{CNAL})
1Pt/MWNT	8.62	46 (17)
1Pt/MWNT-773	10.6	51 (17)
1Pt/TiO2	7.11	29 (39)
1Pt/TiO2-773	8.94	57 (33)
1Pt/C	23.8	6 (49)
5Pt/MWNT	8.36	43 (49)
5Pt/TiO2	3.28	36 (29)
5Pt/TiO2-773	2.50	63 (80)

The thermal treatment at 773K under hydrogen had a visible positive effect in the selectivity. Moreover, it was more significant for the titania supported catalyst. This may be related with the strong metal-surface interaction (SMSI) effect which is induced in metal oxides when group VIII metals are reduced at high temperatures (773K). Comparing all 1% wt Pt catalysts one can easily see that the commercial catalyst is the most active. As a result of its high activity the selectivity towards the saturated aldehyde reaches 70% (49.4% conversion) when only 5 minutes passed.

On the other hand, part of the high selectivity observed with 5Pt/MWNT could be explained in terms of metal particle size. Using SEM we observed Pt clusters very well dispersed and up to 100nm diameter. Gallezot (Gallezot *et al.*,1998) also reported an improvement in selectivity when particle size increased, but not to this order of magnitude.

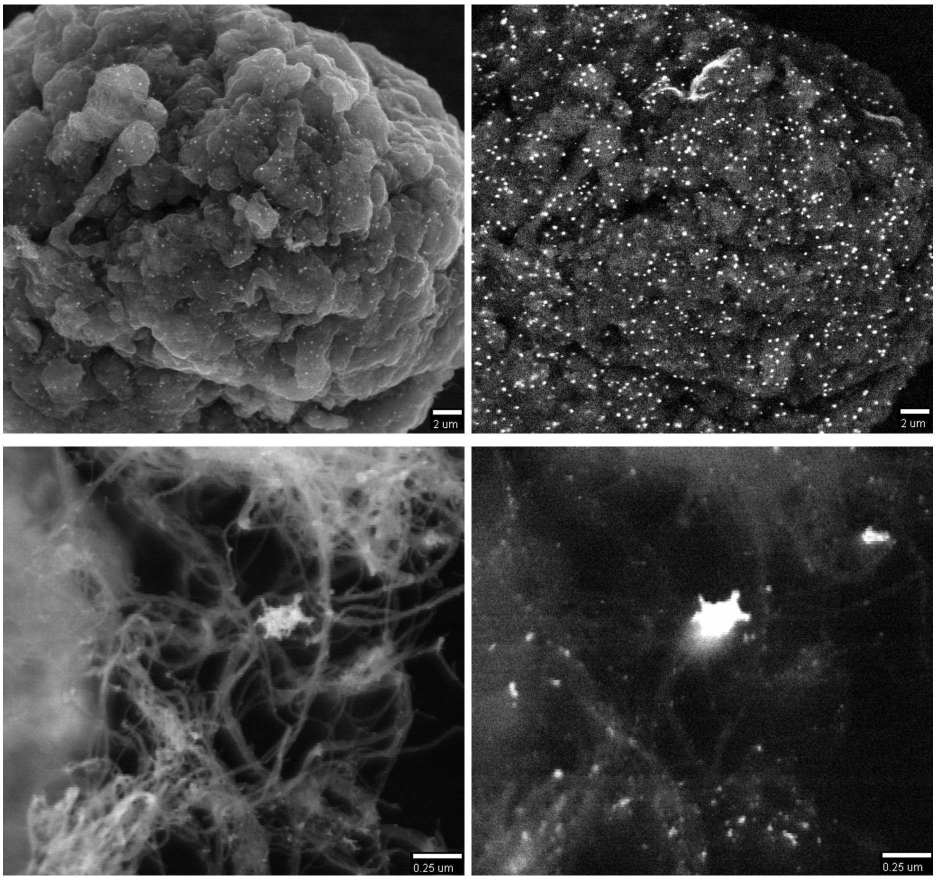

Figure 2 – Secondary electron SEM micrographs images of 5Pt/MWNT (a) and 1PtMWNT (c), and corresponding backscattered electron micrographs (b) and (d), respectively.

Comparison of SEM micrographs in the secondary electron mode with those in the backscattered electron mode shows in the latter the typical brilliance due to the presence of metal (Figure 2).

In a typical hydrogenation reaction, the final product after five hours of conversion is the saturated hydrocinnamyl alcohol (Figure 3). The maximum selectivity for the unsaturated alcohol, based on product distribution was attained at 17% conversion and it is 51%.

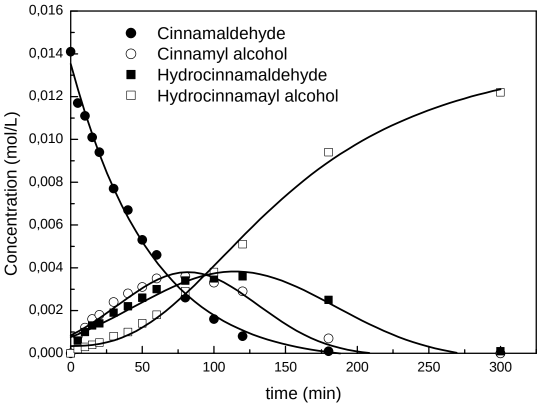

Figure 3 – Typical concentration profiles for the hydrogenation of cinnamaldehyde (1Pt/MWNT-773).

Using 5Pt/TiO2 as it is (before thermal treatment) the final product after 6 hours reaction is the complete hydrogenated cinnamaldehyde molecule (i.e., 3-phenyl-1-propanol). This was not the case for the other prepared catalysts where hydrocinnamyl alcohol was the preferential product. Nishiyama

(Nishiyama *et al*., 1997) also reported the formation of 3-phenyl-1-propanol when using a Rh/SiO_2 catalyst.

After an H_2 thermal treatment at 773K of the 5Pt/TiO_2 catalyst, the final product is the saturated alcohol. Moreover, selectivity to cinnamyl alcohol remained as high as 63.2% when 1 hour passed (80% conversion). Selectivity towards the saturated aldehyde never exceeded 10% throughout the reaction, showing excellent C=O bond activation. Hence, the increase in platinum load, from 1 to 5% wt, had a very positive effect on cinnamyl alcohol selectivity proving to be the best catalyst.

4. Conclusions

Photodeposition method is able to produce very active catalytic materials for selective hydrogenation of cinnamaldehyde. Comparing TiO_2 catalyst performance before and after the thermal treatment it is possible to observe an increase in selectivity. This effect is more pronounced on the 5% wt Pt catalyst than on the 1%, increasing significantly cinnamyl alcohol selectivity. Although not as effective as TiO_2 (with SMSI effect) MWNT still showed remarkable selectivities proving to be a material worth studying in the future.

Acknowledgements

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