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**ABSTRACTS**

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### High temperature activation of noble metal catalysts supported on carbon multi-walled nanotubes for selective hydrogenation of unsaturated aldehydes

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Selective catalytic hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes represents today an important route in the industrial preparation of fine chemicals. Heterogeneous catalysts are normally less selective than the homogeneous, but easier to handle. Therefore, there is still room for improvement especially regarding catalyst selectivity to the unsaturated alcohol. Our work shows that the surface chemistry also plays an important role on selectivity. We describe an activation procedure for platinum and iridium metal catalysts supported on carbon nanotubes, which improves significantly both selectivity and activity. In the case of platinum, selectivity towards the unsaturated alcohol increased 8 times to a maximum of 66% at 79% conversion.

**Keywords:** Carbon Nanotubes, Cinnamaldehyde Selective Hydrogenation, Surface Chemistry

# High temperature activation of noble metal catalysts supported on carbon multi-walled nanotubes for selective hydrogenation of unsaturated aldehydes

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## Introduction

Selective catalytic hydrogenation of organic substrates containing unsaturated functional groups is an important step in the industrial preparation of fine chemicals. Allylic alcohols are obtained by the reduction of the carbonyl group in  $\alpha,\beta$ -unsaturated aldehydes and are valuable intermediates for the production of perfumes, flavoring additives, pharmaceuticals and agrochemicals. Different heterogeneous catalysts have been tested with several degrees of success [1]. Carbon nanotubes (CNT) have been targeted for several applications in catalysis, especially because of their superior electronic, adsorption, mechanical and thermal properties when compared to activated carbon. In a recent review, attention has been called to the enormous potential of multi-walled carbon nanotubes (MWCNT) as support in the development of efficient catalysts [2]. Nitric acid treatment of the CNT is a current procedure used to increase the oxygen surface groups on the substrate. Although these groups are desired to increase the anchoring spots on the surface, which are required adsorb the metal active phase, they can have a negative effect in the catalytic properties of the system. In order to purge the surface from those oxygenated groups we tested some different thermal treatments. From our experience with noble metal catalysts supported on activated carbon, we know that these treatments affect the dispersion of the metal phase, reducing the activity of the catalyst. In this study we performed a high temperature activation of our CNT supported catalysts and investigated their performances using the hydrogenation of cinnamaldehyde as model reaction.

## Experimental

MWCNT were prepared by chemical vapor deposition of ethylene using Fe/Al<sub>2</sub>O<sub>3</sub> as catalyst following a procedure described elsewhere [3]. Monometallic catalysts supported on HNO<sub>3</sub>-oxidized multi-walled carbon nanotubes containing 1 to 3 wt% of platinum or iridium were prepared using wet impregnation techniques. After calcination and reduction to the desired temperatures, the catalysts were used in the liquid phase hydrogenation of cinnamaldehyde. The reaction was carried out in a 100mL stainless steel autoclave at 363K and 10bar H<sub>2</sub> pressure. Product analysis was done by gas chromatography (DANI-1000, with a column WCOT Fused Silica 30m, 0.32mm i.d., coated with CP-Sil 8 CB low bleed/MS 1 $\mu$ m film).

## Results and discussion

Temperature-programmed desorption (TPD) results indicate that a post-reduction treatment at 973K allows the control of the catalyst surface composition by reducing the concentration of oxygenated groups on the surface. Following nitric acid oxidation, carbon materials often

contain large amounts of surface groups namely carboxylic, lactones, anhydrides and carbonyl/quinone [4]. After a 973K thermal treatment under nitrogen all but traces of carbonyl/quinone groups (detected in CO desorption spectra) are removed from the surface. Higher temperatures are required to remove them completely from the surface.

The post-reduction treatment has a pronounced effect on both activity and selectivity towards unsaturated alcohols. On the other hand the metal particle size distribution remained practically unchanged. According to Toebe *et al.* [5] the adsorption of cinnamaldehyde molecule is conditioned by the amount of oxygen groups present at the support surface. When the surface contains a significant amount of oxygen surface groups, the adsorption of cinnamaldehyde on the polar carbon surface is weak. Removing most of these groups allows the molecule to adsorb strongly over the non-polar support. This explanation is in line with the observed results, where a catalyst containing 1 wt.% platinum showed a 8 fold increase on selectivity towards cinnamyl alcohol (conversion of 79%) after the 973K treatment (Figure 1). Similar results were observed in case of 2 wt.% iridium catalyst supported in MWCNT.

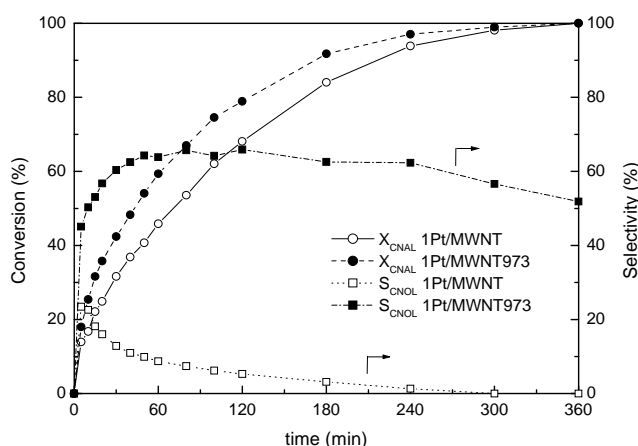


Figure 1 Effect of post-reduction treatment on the conversion and selectivity towards unsaturated alcohol with a platinum catalyst supported on MWCNT.

## Conclusions

High temperature treatments (973K) allowed us to obtain a less polar surface by removing oxygen functional groups from the surface. This activation step had a positive effect on both selectivity and activity. Platinum and iridium catalysts proved to be quite selective towards the unsaturated cinnamyl alcohol.

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