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LIQUID-PHASE HYDROGENATION OF UNSATURATED ALDEHYDES: ENHANCING SELECTIVITY OF MWCNT CATALYSTS BY THERMAL ACTIVATION

Bruno F. Machado¹, Helder T. Gomes^{1,2}, Philippe Serp³, Philippe Kalck³, Joaquim L. Faria¹

¹Laboratório de Catálise e Materiais, Laboratório Associado LSRE/LCM, Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, Portugal

²Departamento de Tecnologia Química e Biológica, Escola Superior de Tecnologia e de Gestão, Instituto Politécnico de Bragança, Portugal

³Laboratoire de Chimie de Coordination UPR CNRS 8241, composante ENSIACET, Toulouse University, France

bmachado@fe.up.pt

Introduction

In a recent review, the importance of carbon nanomaterials as catalytic supports, namely of nanotubes (single- and multi-walled) and nanofibers, was explored [1]. An interesting application of these materials as supports is the preparation of noble metal catalysts for the selective hydrogenation of α,β -unsaturated aldehydes, valuable intermediates in the industrial preparation of fine chemicals. Allylic alcohols, for example, are obtained by the reduction of the carbonyl group and are used in the production of perfumes, flavoring additives, pharmaceuticals and agrochemicals. Selectivity towards unsaturated alcohols is limited by kinetic and thermodynamic reasons but can be improved by creating proper conditions. One of the most important factors is the nature of the active metal phase in the catalyst. Ir and Os are considered to be rather selective while Pt, Ru and Co are only moderately selective [2]. The way these and other metals are dispersed over the surface of the support can also influence the performance of the catalyst. Liquid-phase oxidation with nitric acid is a common technique used to enhance metal dispersion by introducing high amounts of oxygenated surface groups which act as anchoring sites for the metal phase. Some of these remaining groups are often found to negatively influence the catalytic properties of the system. They can be removed by high temperature thermal treatments, which normally affect the dispersion of the metal phase, thus leading to a loss of performance. However, in this study we found the opposite effect for our carbon nanotubes supported catalysts used in the liquid-phase hydrogenation of cinnamaldehyde.

Experimental

Multi-walled carbon nanotubes (MWCNT) were prepared by chemical vapor deposition of ethylene using Fe/Al₂O₃ as catalyst following a procedure described elsewhere [3]. Monometallic catalysts supported on MWCNT oxidized with nitric acid, containing 1 wt. % Pt or Ir were prepared using the wet impregnation technique and characterized by N₂ adsorption isotherms, transmission electron microscopy (TEM), thermogravimetric analysis (TGA) and temperature programmed desorption (TPD). After calcination and reduction, the catalysts were used in the liquid-phase hydrogenation of cinnamaldehyde. The reaction was carried out in a 100 mL stainless steel reactor at 363 K and 10 bar total pressure. Products were analyzed by gas chromatography (DANI-1000, with a column WCOT Fused Silica 30 m, 0.32 mm i.d., coated with CP-Sil 8 CB low bleed/MS 1 μ m film).

Results and discussion

Following nitric acid oxidation, carbon materials often contain different types and amounts of surface groups, namely carboxylic acid and anhydride, lactone and carbonyl/quinone [4]. According to a technique developed in our group [4] it is possible to identify these oxygenated surface groups by deconvolution of the TPD spectra. These TPD spectra indicate that a post-reduction treatment (PRT) performed at 973 K reduces the concentration of the

oxygenated surface groups. After this treatment only traces of carbonyl/quinone groups (detected in CO desorption spectra) remain on the surface. Metal particle size is an important parameter that could be seriously compromised by this high temperature treatment but H₂ chemisorption measurements corroborated by TEM rule out any significant metal sintering effect. The thermal stability exhibited by the catalysts is based on a strong covalent bond between the carboxylic groups in the oxidized surface and the metal precursor. The PRT had a pronounced effect on both activity and selectivity towards the desired cinnamyl alcohol (COL). According to Toebes *et al.* [5] the adsorption of cinnamaldehyde molecule over Pt/GNF catalysts is conditioned by the amount of oxygen groups present at the support surface and their removal allows the molecule to strongly adsorb over the non-polar support, yielding hydrocinnamaldehyde (HCAL). This explanation is not in line with our observed results, where a Pt/MWCNT catalyst showed an 8 fold increase on selectivity towards COL (conversion of 79%) after the 973 K treatment (Figure 1). Similar results were observed with an iridium catalyst supported in the same MWCNT.

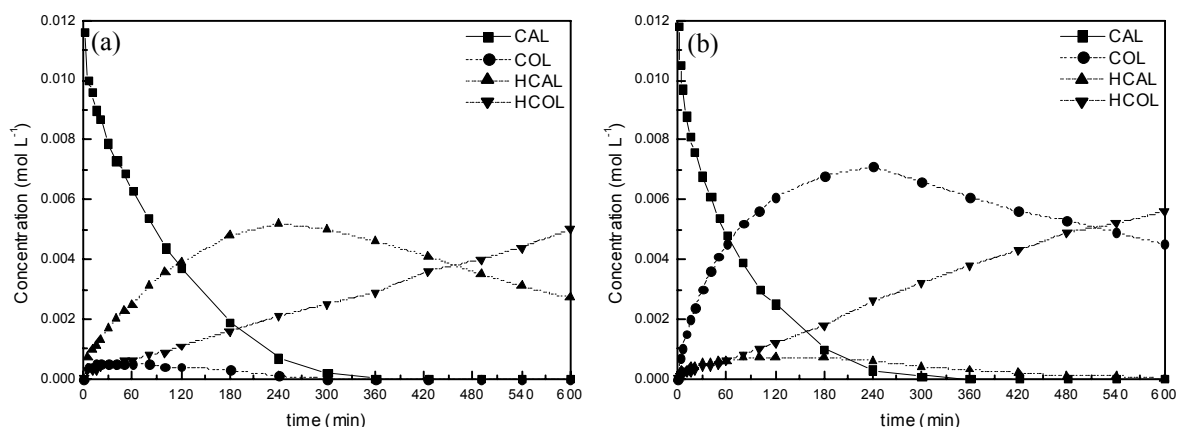


Figure 1 Effect of post-reduction treatment on the conversion and selectivity towards unsaturated alcohol with a 1 wt. % platinum catalyst supported on MWCNT: (a) before PRT; (b) after PRT.

Conclusions

The activation step produces a positive effect on selectivity and enhances the catalytic activity by a factor of 2. Platinum and iridium catalysts proved to be equally selective towards the unsaturated cinnamyl alcohol. Variance with the results in Pt/GNF may result from different orientation of the graphitic planes in both carbon materials, as well as different interaction of the metal phase with the support.

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