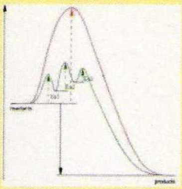
8º Encontro da Divisão de Catálise e Materiais Porosos da Sociedade Portuguesa de Química



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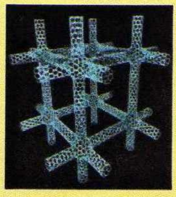

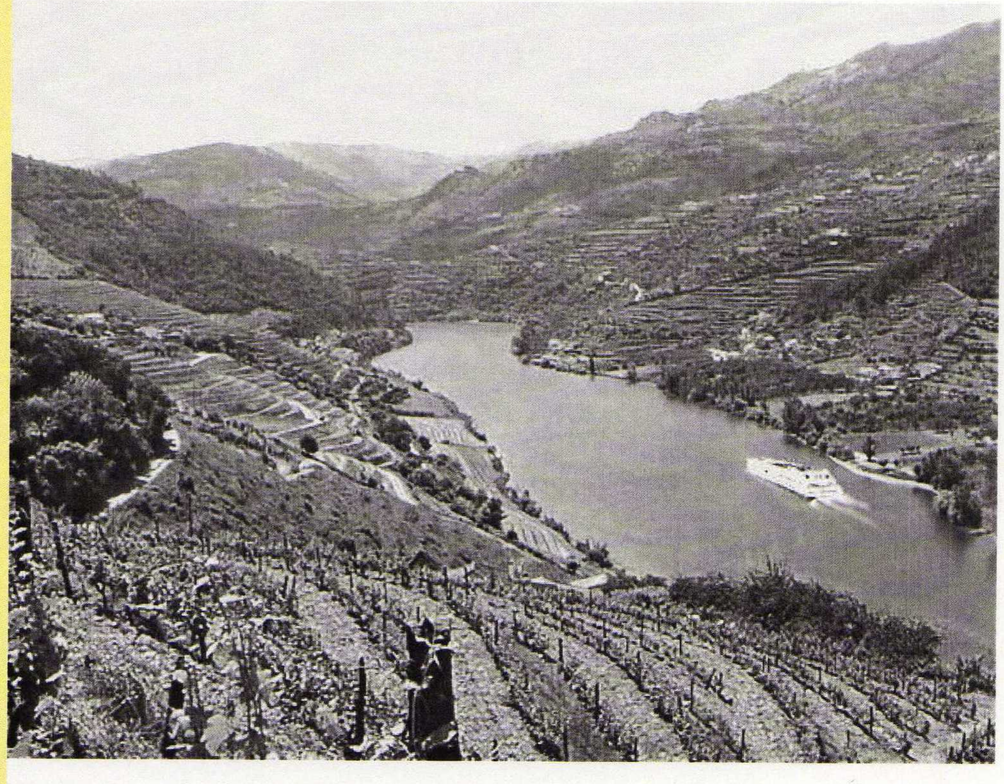

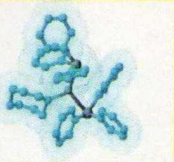

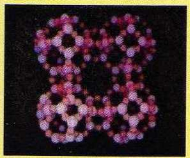

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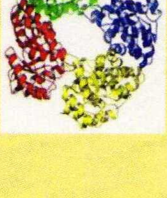

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Carbon xerogel as catalytic support for noble metal based selective hydrogenation reactions

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Abstract

Nitric acid treated carbon xerogel was used as support to prepare Pt, Ir and Ru monometallic catalysts. The introduction of oxygen surface groups was important to increase metal dispersion but proved to limit selectivity to cinnamyl alcohol during the hydrogenation of cinnamaldehyde. After an activation treatment to remove unwanted surface groups, Pt catalysts exhibited the highest selectivity, 73%, followed by Ir with 65% and finally Ru with only 32% (measured at 50% conversion).

Introduction

There is currently an increased interest in the use of heterogeneous catalysts for the synthesis of fine chemicals. The heterogeneous catalytic process is always easier to handle than any other process and leads to a lower amount of waste products, thus lower risk for the environment. Research focused on chemo- and regio-selective catalytic hydrogenation of unsaturated compounds to produce fine chemicals is rapidly growing. In the past few years considerable effort has been dedicated to the development of a catalytic system able to perform selective hydrogenation of the carbonyl function of α,β-unsaturated aldehydes into unsaturated alcohols (Figure 1) with a high yield, thus avoiding the use of toxic reducing agents (metal hydrides) commonly applied in preparative organic chemistry.

The unsaturated alcohols are important intermediates in organic synthesis of fine chemicals for several industries such as flavor, fragrance, pharmaceutical and agrochemical. Unfortunately, high selectivities towards these alcohols are difficult to achieve, since thermodynamics favors the hydrogenation of the C=C over the C=O bond by about 35 kJ mol^{-1} and due to kinetic reasons, as the reactivity of the olefinic bond is higher than that of the carbonyl. To increase selectivity, this thermodynamic constraint must be reduced or even removed by a preferential adsorption of the carbonyl function at the catalyst surface.

It has been found that selectivity towards the allylic alcohol is highly dependent on the nature of the precious metal used. Metals such as Pt, Os, Ir, Pd, Rh and Ru among others have been studied, leading to differences in activity and selectivity. Gallezot and Richard [1] reported 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.

Because support plays an important role in catalyst design, in order to optimize the dichotomy between metal and support, the use of a material whose properties can be fine tuned is highly desirable. Carbon xerogel (CX) is a relatively recent member of the carbon family and the possibility of, to a certain extent, adjust the surface area and pore width, among other textural properties makes its use very attractive.

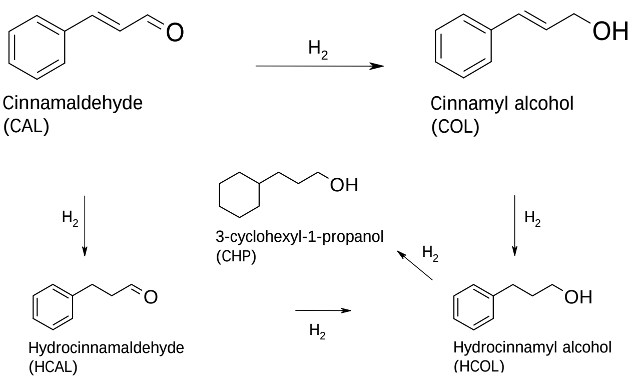

Figure 1 – Reaction pathway for the selective hydrogenation of cinnamaldehyde

In this work we studied the effect of high temperature activation of CX supported noble metal catalysts on their performances using the hydrogenation of cinnamaldehyde as model reaction.

Materials and methods

An aqueous organic gel was prepared by polycondensation of resorcinol with formaldehyde (1:2), adapting the procedure described by Job *et al.* [2]. Accordingly, 56.57 g of resorcinol (Aldrich, 99%) were added to 113 mL of deionised water in a glass flask. After complete dissolution, 82 mL of formaldehyde solution (Sigma, 37 wt. % in water, stabilized with 15 wt. % methanol) were also added. In order to achieve the 6.0 value for the initial pH of the precursor solution, sodium hydroxide solution (2 N) was added dropwise under continuous stirring. The gelation step was allowed to proceed at 358 K during 3 days, after which the gel displayed a dark red colour. At this point, the consistency of the material allowed the sample to be shaped as desired (ground to small particles *ca.* 0.2 mm). The gel was further dried in oven from 333 K to 423 K during several days, defining a heating ramp of 20 K/day and maintaining 423 K for 3 days. After drying, the gel was pyrolyzed at 1073 K under a nitrogen flow (100 mL min^{-1}) in a tubular vertical oven. The gel was then treated in nitric acid solution to create oxygen surface groups, washed with water until neutrality of the rinsing waters and dried in oven for 2 days at 413 K.

Monometallic catalysts supported on HNO_3-oxidized carbon xerogel containing 1 wt.% of platinum, iridium and ruthenium were prepared by wet impregnation under inert atmosphere using as metal precursors $[Pt(COD)(CH_3)_2]$, $[(Ir(\mu\text{-}SC(CH_3)_3)(CO)_2)_2]$ and [Ru(COD)(COT)], respectively. After filtering and drying in oven overnight (393 K) the catalysts were calcined in nitrogen and reduced with hydrogen (Pt/CX and Ru/CX at 623 K and Ir/CX at 773 K). A post-reduction thermal treatment (PRT) under nitrogen at 973 K was also performed (Pt/CX973, Ir/CX973 and Ru/CX973) in order to remove surface groups.

Techniques like nitrogen adsorption-desorption at 77 K, temperature programmed desorption (TPD), transmission electron microscopy (TEM) and H_2 chemisorption were used to characterize the catalytic materials.

Liquid phase hydrogenation of cinnamaldehyde was carried out in a 100 mL stainless steel autoclave at 363 K and 10 bar. Small aliquots of the reaction mixture were taken throughout the reaction to perform quantitative analysis (conversion and product selectivity) by gas chromatography (DANI GC-1000, with a column WCOT Fused Silica 30 m, 0.32 mm i.d., CP-Sil 8 CB low bleed/MS 1 μm film coating).

Results and discussion

TPD experiments performed on the CX before and after acid activation (Figure 2) clearly show the difference in the amount of surface groups in both samples. Following nitric acid oxidation, carbon materials often develop large amounts of surface groups namely carboxylic (released in TPD at 573 K), anhydrides (800 K), phenols (950 K), lactones (1000 K) and carbonyl/quinone (1100 K) [3]. The effect of the oxidation with nitric acid over the textural and surface properties of CX can be observed in Table 1.

Table 1. Textural properties and released amounts of CO and CO_2 for CX before and after nitric acid treatment

Sample	S_{BET} ($m^2 g^{-1}$)	S_{MES} ($m^2 g^{-1}$)	V_{MIC} ($cm^3 g^{-1}$)	CO (μmol g^{-1})	CO_2 (μmol g^{-1})	CO/CO_2
CX	627	180	0.18	1 172	616	1.9
CX-HNO_3	20	-	-	16 403	18 842	0.9

The severity of the acid treatment caused the CX structure to collapse forming large aggregates of carbon as shown by the drastic decrease of the specific BET surface area whereas the acidity increased due to a lower CO/CO_2 ratio.

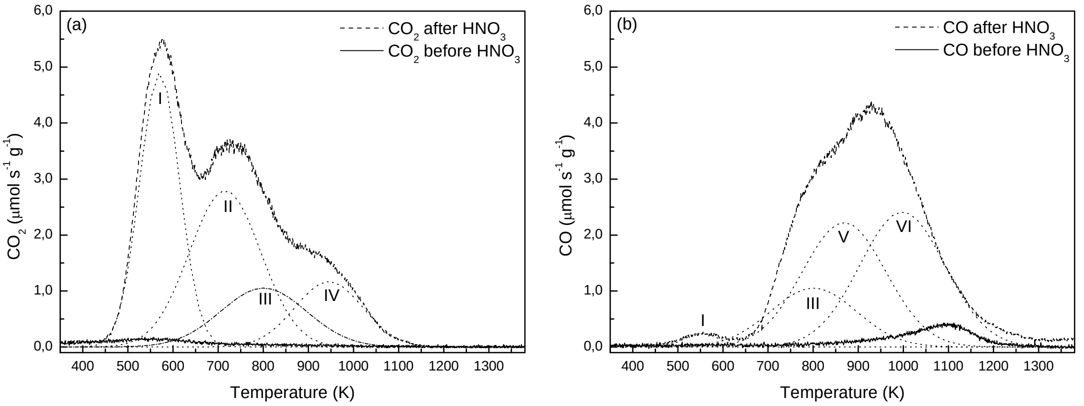

Figure 2 – TPD spectra for CX before and after HNO_3: (a) CO_2 and (b) CO profile. See text for the meaning of roman numerals

Deconvolution of the TPD spectra of CX identified high amounts of carboxylic (I and II in Figure 2), phenols (V) and carbonyl/quinones (VI), and lower amounts of anhydrides (III) and lactones (IV). These surface groups, mainly carboxylic, act as anchoring sites for metal particles and are able to increase metal dispersion. Catalyst characterization results showed Pt particles around 3 nm, 2 nm for Ir and 1 nm for Ru. The catalytic results from the liquid-phase hydrogenation of cinnamaldehyde are gathered in Table 2. CX supported catalysts exhibited enhanced activity and selectivity after PRT. This treatment at 973 K allowed for a better control of the catalyst surface by removing oxygen containing groups. In all cases a significant improvement could be observed in the production of COL. The most outstanding result was established with Pt where a complete shift in HCAL to COL selectivity was noticed (Figure 3). The best performance without PRT was observed with the Ir catalyst and this can be explained in terms of a higher processing temperature during calcination step (necessary to remove the sulfur), allowing for a partial removal of the surface groups. For this reason the enhancement observed after PRT was not as pronounced as that observed for Pt. Ru catalysts were, in spite of very active, very selective towards the undesired HCAL. Even though it was not the preferred molecule a remarkable selectivity of 65% was observed.

Table 2. Catalytic results obtained in the liquid-phase hydrogenation of cinnamaldehyde with the CX supported catalysts

Catalyst	S_{COL} (%)*	S_{HCAL} (%)*	S_{HCOL} (%)*
1Pt/CX	20	39	18
1Pt/CX973	73	7	6
1Ir/CX	57	20	9
1Ir/CX973	65	20	8
1Ru/CX	5	65	8
1Ru/CX973	32	42	14

*Values obtained at 50% conversion of cinnamaldehyde

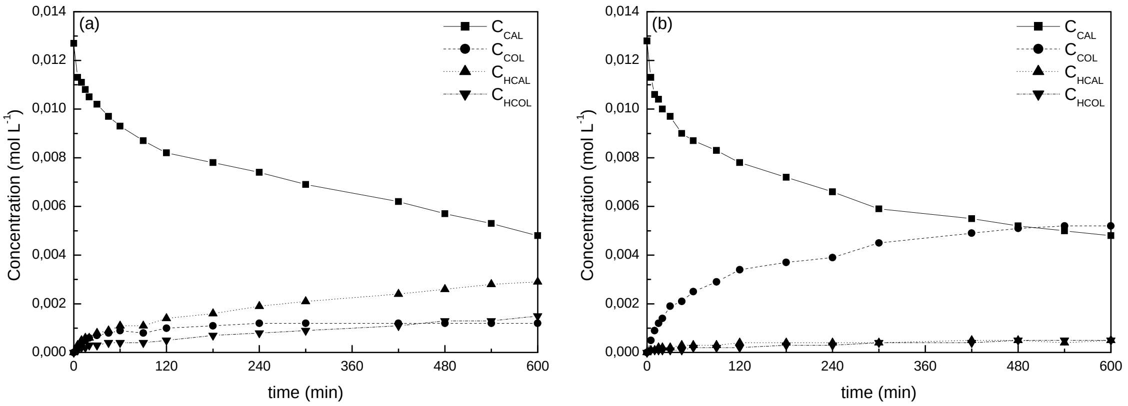

Figure 3 – Concentration profiles for (a) Pt/CX and (b) Pt/CX973

High temperature treatment (973 K) of the catalysts removed a significant amount of oxygen functional groups from the surface, especially carboxylic and anhydrides. This activation step had a positive effect on both activity and selectivity. Platinum and iridium catalysts proved to be quite selective towards the unsaturated cinnamyl alcohol, while ruthenium produced high yields of the saturated aldehyde.

Acknowledgements

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