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Mesoporous carbon supported Pt and Pt–Sn catalysts for hydrogenation of cinnamaldehyde

Purnakala V. Samant, Manuel F.R. Pereira, José L. Figueiredo *

Laboratório de Catálise e Materiais, Departamento de Engenharia Química, Faculdade de Engenharia da Universidade do Porto,
Rua. Dr. Roberto Frias, 4200-465 Porto, Portugal

Abstract

High surface area mesoporous carbon xerogels were prepared and used as supports for monometallic Pt and bimetallic Pt–Sn catalysts. These catalysts were tested in the selective hydrogenation of cinnamaldehyde to cinnamyl alcohol. Conversions and selectivities were found to depend on both the texture and the surface chemistry of the supports.

Keywords: Mesoporous carbon; Pt catalysts; Cinnamaldehyde hydrogenation

1. Introduction

Carbon xerogels are mesoporous materials which may find application as catalyst supports, in particular for reactions in the liquid phase. These materials can be synthesized by polycondensation of resorcinol and formaldehyde, followed by carbonization [1]. Subsequent activation can be used to introduce oxygen functional groups on the surface, which can act as anchoring sites for the metal precursors, leading to highly dispersed and stable metal catalysts. We have recently described the preparation and characterisation of such activated mesoporous carbon materials [2], which we are now evaluating as supports for metal catalysts. We have already reported on the use of these materials as supports for Pd catalysts in enantioselective hydrogenations [3], while in the present work we present preliminary data obtained in chemoselective hydrogenations.

The hydrogenation of α,β unsaturated compounds is a reaction of industrial importance, specially in the synthesis of fine chemicals. In addition, it is a suitable model reaction to investigate the effect of catalyst structure on selectivity. A comprehensive review of the state of the art has been published recently [4]. Since the reduction of the C=C bond is easier, the selectivity towards the unsaturated alcohol is generally poor. Thus, the preparation of a selective catalyst remains a challenging task. Platinum catalysts can be used, and their selectivity has been found to increase by the addition of a second metal, Sn being particularly effective in this respect [5]. Carbon materials are among the most widely used supports for this reaction, including graphite, carbon blacks, activated carbons, fullerenes, carbon nanotubes and carbon nanofibers [6–10]. Mesoporous carbons derived from polymer precursors are particularly relevant in this context, as they can be used for the preparation of carbon monolithic structures [11,12]. Oxygen containing surface groups on the carbon support have been found to play a decisive role in the anchoring of catalyst precursors [13], and to affect catalyst selectivity [9,14]. The nature of the surface groups can be tuned by gas phase or liquid phase activation methods [15]. However, not much work is reported on the use of mesoporous carbon as support for this reaction.

The present works aims at synthesizing high surface area mesoporous carbons with pore sizes ranging from 2 to 20 nm. Two materials with different surface areas were prepared, and oxygen surface groups were generated by means of controlled oxidative treatments on the parent carbons. Pt and Pt–Sn catalysts were supported on these mesoporous carbons, and their activity towards the selective formation of cinnamyl alcohol in the hydrogenation of cinnamaldehyde was investigated. Further attempts were

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* Corresponding author. Tel.: +351 22 5081663; fax: +351 22 5081449.
E-mail address: jlfig@fe.up.pt (J.L. Figueiredo).

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made at optimising the reaction conditions by changing solvents, temperature and hydrogen pressure, in order to inhibit the formation of unwanted side products, thereby controlling the selectivity towards the desired product.

2. Experimental

2.1. Synthesis of mesoporous carbon (CX)

The synthesis, characterisation and effect of activation on the surface chemistry of mesoporous carbon materials prepared by the sol gel method were previously described in detail [2], but for convenience are briefly summarised here. High-density carbon xerogels were synthesized by condensation of resorcinol and formaldehyde in a molar ratio of 2:1 using aqueous solution of sodium carbonate under subcritical temperature conditions. The gel was subsequently cured at 27, 50 and 90 °C (one day at each temperature). Water from the gel was removed by means of sequential exchanges with low volatile organic solvents, first with acetone, followed by cyclohexane. Carbonisation of the gel was carried out in nitrogen atmosphere at 800 °C, and the sodium present was removed by Soxhlet extraction in 2 M HCl. The material obtained is hereafter referred as CX.

2.2. Preparation of carbon by the mixed resorcinol–cresol route

Resorcinol and cresol were mixed in equal proportion (1:1) and formaldehyde was added to it in molar ratio (2:1). 0.1 M sodium carbonate was used as catalyst, and the appropriate amount of water was added to have 200/60 mass ratio. The carbon xerogel was obtained by following the same steps as for CX. The carbon material obtained is hereafter denoted as RCCX.

2.3. Surface modification and catalyst preparation

Surface modification of CX was carried out with 5% O_2 in nitrogen at 400 °C for 12 h. The burn-off obtained was 18% (referred as CX-18). 5% Pt was loaded on CX and RCCX by the incipient wetness method using hexachloroplatinic acid as precursor (PtCX, PtRCCX). Pt–Sn catalysts with 1.25% Sn and 5% Pt were also prepared on CX and CX-18 (PtSnCX and PtSnCX-18) by step wise impregnation, where the tin precursor (tin chloride) was introduced first, as described previously [13]. The catalysts were reduced using 0.1 M sodium formate at 60 °C under constant stirring.

2.4. Catalyst characterisation

The samples were characterised by nitrogen adsorption, XPS and TPD.

Nitrogen adsorption isotherms at 77 K were obtained on a Coulter Omnisorp 100 CX sorptometer, and were subsequently analysed by the *t*-plot using the standard isotherm for carbon materials. The mesopore surface area (S_{meso}) and micropore volume (V_{micro}) were calculated in this way, and are included in Table 1, together with the BET surface areas.

Table 1
Properties of the supports

Support	S_{BET} (m^2/g)	S_{meso} (m^2/g)	V_{micro} (cm^3/g)	CO (μmol/g)	CO_2 (μmol/g)
CX	724	524	0.12	217	709
CX-18	1084	672	0.16	7223	1232
RCCX	475	117	0.10	1680	942

The amounts and types of surface functional groups were studied by temperature programmed desorption (TPD). The analyses were carried out in a custom built set-up consisting of a U-shaped quartz micro reactor cell, placed inside an electrical furnace, with helium flow of 25 ml/min. The samples were subjected to a 5 °C/min linear temperature rise up to 1100 °C. A SPECTRAMASS Dataquad quadrupole mass spectrometer was used to monitor the desorbed CO ($m/z = 28$) and CO_2 ($m/z = 44$) signals [15]. XPS analysis was carried out in a VG Scientific ESCALAB 200A spectrometer using non-monochromatized Mg Kα radiation (1253.6 eV) to determine the surface chemical composition of the metal catalysts on carbon. The Pt 4f and Sn 3d high resolution spectra were analysed by deconvoluting the peaks with mixed Lorentzian–Gaussian functions.

2.5. Catalytic tests

The hydrogenation reaction was conducted in a well-stirred high temperature high-pressure stainless steel autoclave reactor. Typically, nitrogen was bubbled through the solution to remove any traces of dissolved oxygen from the reaction medium before passing hydrogen, followed by a hydrogen purge, repeated 2–3 times. Finally, the reactor was brought to the desired temperature (either room temperature or 60 °C) and pressurised by hydrogen (at atmospheric pressure or 5 bar). In a catalytic run, the reaction mixture contains 0.37 g of cinnamaldehyde, 20 ml of toluene (or equal volume of toluene and 1.78 M KOH) under vigorous stirring. Toluene was preferred as a solvent, in order to avoid the formation of hydrocinnamaldehyde diethylacetal, which is sometimes observed when ethanol is used [5]. Small portions of the liquid mixture were withdrawn periodically for GC analysis, in order to determine the cinnamaldehyde conversion and product distribution.

The products were identified on the basis of their mass spectra using GCMS. Quantitative analysis was performed with a DANI GC-1000 gas chromatograph, equipped with a WCOT Fused Silica column (CP-Sil 8 CB low bleed/MS, 30 m, 0.32 mm. i.d., 1 μm film thickness) and FID. All the products were calibrated by diluting with toluene. Cinnamaldehyde (Fluka, 99.8%) was used after distillation. Hydrogen was supplied by AirLiquide.

3. Results and discussion

3.1. Catalyst characterisation

The textural properties of the three supports used are included in Table 1. It may be observed that CX presents much larger BET and mesoporous surface areas than RCCX. Oxidation of CX had a large impact on the textural properties of the support, with increases in the range of 30%, both for S_{meso} and V_{micro}.

The oxygen groups present on the surface of the supports were characterised by TPD, as shown in Fig. 1. These groups decompose with evolution of CO_2 (carboxylic acids, anhydrides and lactones) or CO (anhydrides, phenols, carbonyls). The total amounts of CO and CO_2 released were calculated by integrating the areas under the corresponding TPD spectra, and are also included in Table 1. Since the most acidic groups release CO_2, while the less acidic and basic groups release CO, the ratio CO_2/CO gives some indication on the acidity of the surface [15]. Fig. 1 shows that the oxidised support (CX-18) has a much larger amount of surface oxygen than the parent material (CX); moreover, all carboxylic acid groups (which evolve as CO_2 at low temperatures) have been decomposed, leading to a much less acidic surface. It is also interesting to note that the carbon xerogel obtained by the alternative route (RCCX) has a much larger amount of surface oxygen than CX, in spite of its lower surface area.

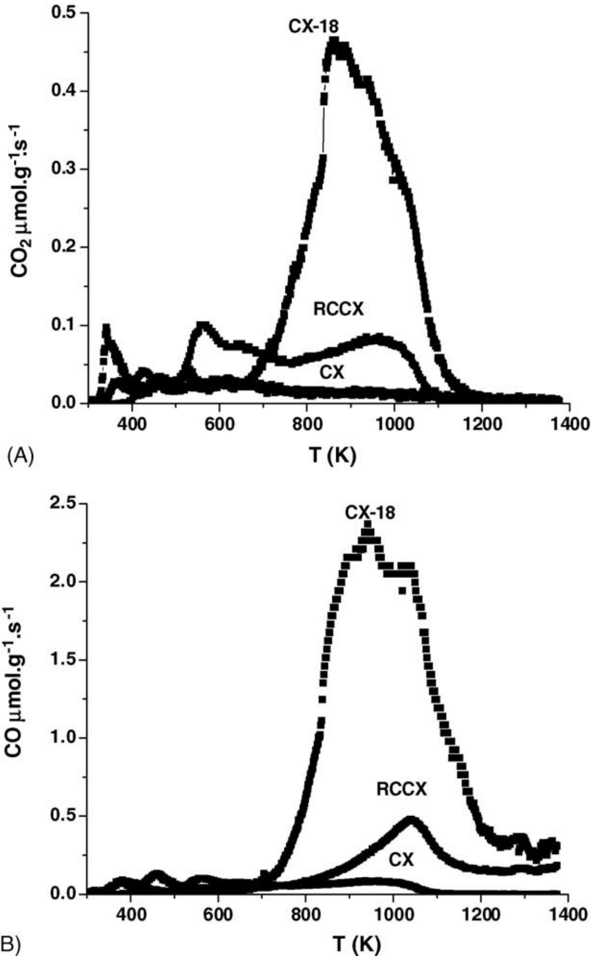


Fig. 1. TPD spectra for CX, RCCX and CX-18: (A) evolved CO_2 and (B) evolved CO.

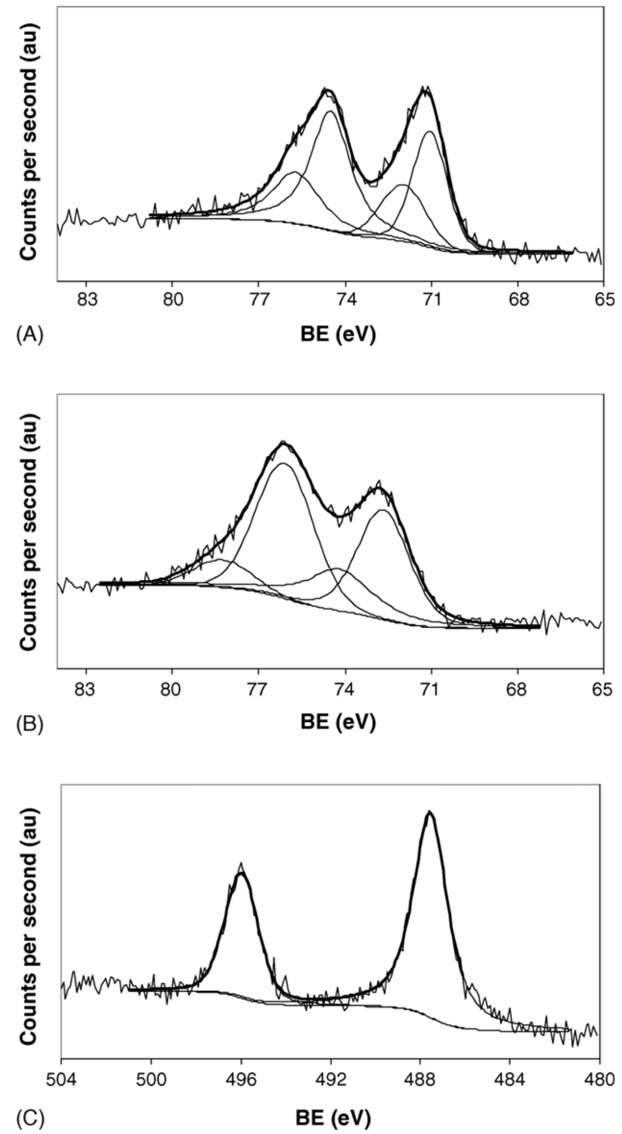


Fig. 2. XPS spectra of: (A) Pt in PtCX-18; (B) Pt in PtSnCX-18 and (C) Sn in PtSnCX-18.

The Pt 4f and Sn 3d spectra of PtCX and PtSnCX-18 are shown in Fig. 2. The binding energies of the Pt $4f_{7/2}$ and Sn $3d_{5/2}$ levels are collected in Table 2. Pt^0 and Pt^{2+} are detected in both catalysts, while only oxidised Sn is found in the bimetallic catalyst. Both peaks in the Pt spectrum of the bimetallic catalyst are shifted to higher binding energies with respect to the monometallic catalyst. This may be due to the electronic modification of the surface Pt atoms, which may be in a Pt–O–Sn state, as discussed by Coloma et al. [16].

Table 2
Binding energies (eV) of the Pt $4f_{7/2}$ and Sn $3d_{5/2}$ levels for mono (PtCX-18) and bimetallic (PtSnCX-18) catalysts

Catalyst	Pt $4f_{7/2}$	Sn $3d_{5/2}$	Pt^{2+}/Pt^{0}
PtCX-18	71.0	–	
	72.0		0.58
PtSnCX-18	72.7	487.5	0.62
	74.3		

3.2. Catalytic tests

The products obtained in the hydrogenation of cinnamaldehyde (CA) were cinnamyl alcohol (CALC), hydrocinnamaldehyde (HCALD) and hydrocinnamyl alcohol (HCALC). Other possible reaction products such as methylstyrene, phenylpropane and acetals, were not detected in the present work. Therefore, the reaction pathways involved in the hydrogenation of cinnamaldehyde are those shown in Scheme 1.

Fig. 3 shows the cinnamaldehyde conversion and the selectivity towards the unsaturated alcohol obtained in the presence of the four catalysts after 20 h of reaction time at 1 bar and room temperature. The same pattern was observed in both cases, namely: PtSnCX-18 > PtSnCX > PtCx > PtRCCX. The selectivity was defined as:

$$S_{\mathrm{CALC}} = \frac{[\mathrm{CALC}]}{[\mathrm{CALC}] + [\mathrm{HCALD}] + [\mathrm{HCALC}]}.$$

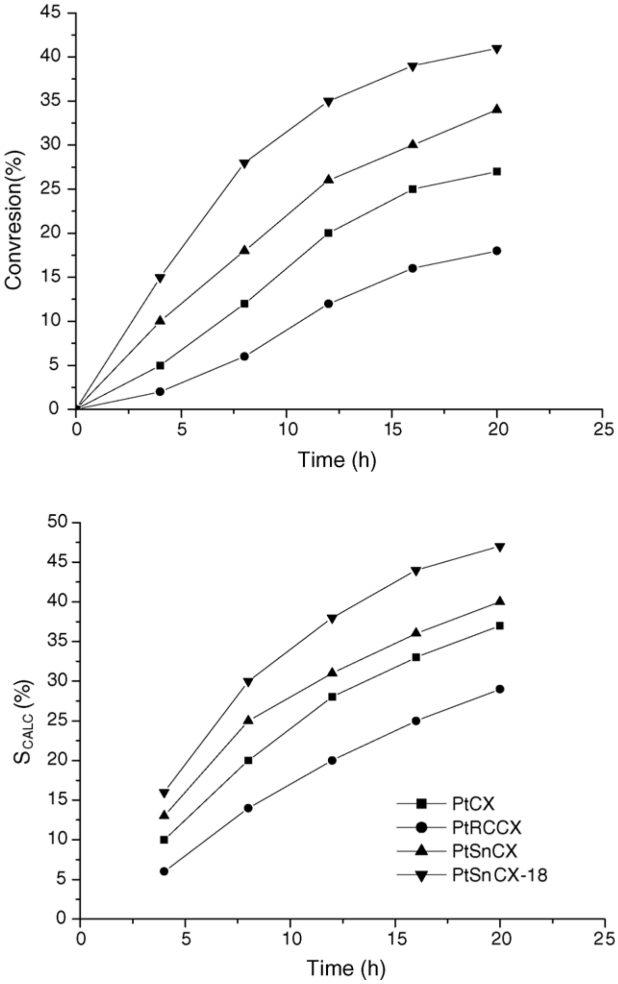
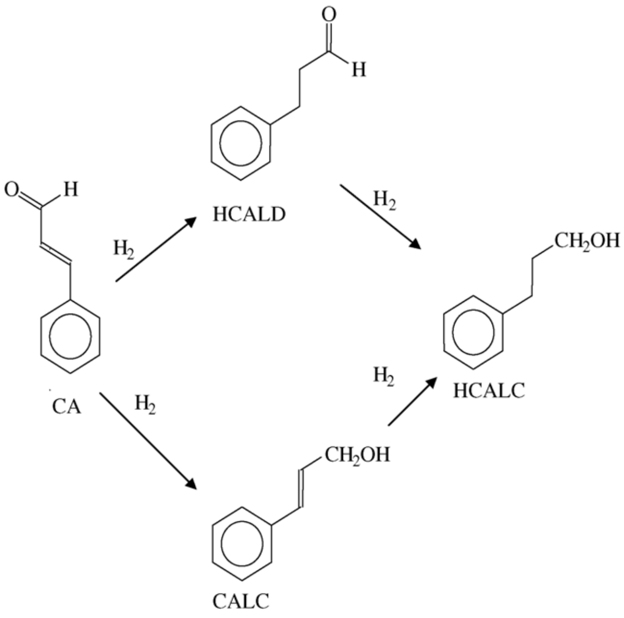


Fig. 3. Conversion of cinnamaldehyde and selectivity for cinnamyl alcohol on different catalysts at room temperature, 1 bar pressure of H_2.

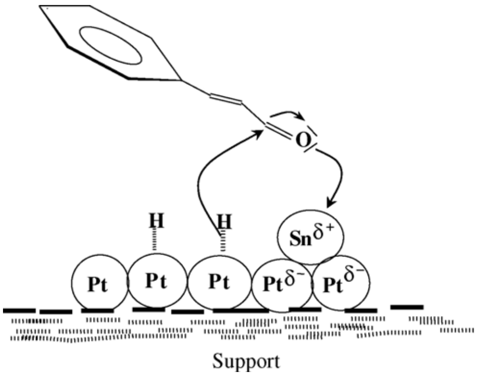
The performance of PtRCCX was quite poor in comparison with PtCX, possibly as a result of the much lower surface area of the support, which in turn is expected to lead to a poor platinum dispersion, as we previously found in the case of activated carbon supported Pt catalysts [17]. As expected, the bimetallic catalysts were better than the monometallic, particularly the catalyst prepared on the oxidised support (CX-18).



Scheme 1.

According to Marinelli et al. [18], the selectivity towards the unsaturated alcohol depends on the presence of sites on the catalyst which can activate the carbonyl group and allow an easy supply of hydrogen atoms. The higher selectivity of the bimetallic catalysts for the unsaturated alcohol (CALC) can be explained by the promoting effect of Sn. Indeed, the XPS results showed that tin is in the oxidised state, and therefore, the active sites can be described as Pt^{0}–$Sn^{\delta+}$. Then, cinnamaldehyde can adsorb preferentially on these sites by the C=O group, via donation of a lone pair of electrons from the oxygen atom; at the same time, hydrogen chemisorbed on Pt can attack the carbon atom in the carbonyl group, as shown in Scheme 2. It can be assumed that, on monometallic Pt catalysts, the reactant adsorbs by π-complexing of the C=C bond, which therefore, will be preferentially hydrogenated.

To take full advantage of the higher intrinsic selectivity of PtSn, the reactant should approach the active site “head-on”



Scheme 2.

(Cf. Scheme 2), leading to the preferential hydrogenation of the C═O bond. This situation should be favoured on a mesoporous support. On the other hand, activated carbons have smaller slit-shaped pores (micropores), where the reactant can only enter ‘‘sideways’’ [19]. Such an approach to the active site will favour the hydrogenation of the C═C bond, leading to lower selectivity to the desired product, CALC.

We have previously reported on Pt and PtSn catalysts supported onto activated carbons, and studied extensively the effect of the oxidising treatments [13]. It was concluded then that the oxidative treatment allows for higher dispersion of the metal phase, leading to higher activity, both of the monometallic Pt and the bimetallic Pt–Sn catalyst. The better performance of PtSnCX-18 compared to PtSnCX can be ascribed to the presence of oxygen surface groups on the support, prior to reduction. Coloma et al. [20] studied the gas-phase hydrogenation of crotonaldehyde over Pt catalysts supported on carbon black. They reported that both the activity and the selectivity towards the unsaturated alcohol increased when the support had been previously oxidised. They observed that important amounts of hydrogen remained on the support after reduction, possibly occupying the active sites created on the carbon surface upon decomposition of the oxygen groups. These hydrogen species could affect the behaviour of the catalysts by a polarising effect on the carbonyl bond. There are conflicting reports in the literature on the effects of surface oxygen. In our own work with Pt and Pt–Sn catalysts supported on activated carbons, lower S_{CALC} were obtained on the oxidised supports [21]. However, it should be pointed out that in this case the oxidation had been performed with nitric acid, leading to an acidic surface, while in the present work the support was oxidised at higher temperature with oxygen, leading to a more basic material (as indicated by the ratio CO/CO_2, Table 1), which should favour the production of CALC [22].

Table 3
Hydrogenation of CA over PtSnCX and PtSnCX-18

Catalyst	P (bar)	T (°C)	Conv. (%)	S_{CALC} (%)	S_{HCALD} (%)	S_{HCALC} (%)
PtSnCX	5	60	75	75	15	10
PtSnCX-18	5	30	66	78	12	10
PtSnCX-18	1	60	74	75	15	9
PtSnCX-18	5	60	96	68	1	37

Solvent: toluene and 1.78 M KOH (1:1), 50 mg catalyst, 0.37 g CA. Conversions and selectivities determined after 20 h, except the last entry, after 8 h.

It has also been reported that the presence of strong bases like KOH enhance the selectivity [4,22]. Therefore, we have also tested the best catalysts under such conditions, using a KOH/toluene biphasic solvent. The results are summarised in Table 3, showing improved performance of the bimetallic catalysts in comparison to the use of toluene alone at room temperature and pressure (Fig. 3).In addition, it is observed that higher temperature and pressure increase the conversion, but limit the selectivity to CALC. Further gains in selectivity are expected when the reaction conditions are optimised for this system.

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