Influence of textural properties of activated carbons on Pd/carbon catalysts synthesis for cinnamaldehyde hydrogenation

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1. Introduction

In the industry, thousands of tons of porous carbon are used yearly on the market for fabrication of precious metal-supported heterogeneous catalysts. Precious metals on carbon catalysts are mainly used in liquid-phase hydrogenation, dehydrogenation, hydrolysis and oxidation reactions for fine chemical production [1–3]. Reasons for the widespread use of carbons as support are economical because it allows easy recovery, refining and recycling of the precious metals, and owing to their chemical inertness in both acid and basic media. The most used supports are activated carbons (ACs) which present several advantages: (i) an economical preparation from various natural raw materials; (ii) a high and tunable specific surface area; (iii) a variety of surface functional groups.

There are two main general routes for the introduction of metal precursors onto the carbon surface: the ion exchange and the deposition-precipitation methods. Ion exchange is the method of choice to prepare catalysts of the highest metal dispersion. In this case an oxidative functionalisation step is necessary to increase exchangeable surface functions, to yield both high metal loading and dispersion. A 4 wt.% Pd/AC with mean Pd particle size lower than 2 nm has thus been prepared [4]. However, the resulting catalyst may be thermally unstable due to the onset of anchored function decomposition from 473 K [4].

The deposition-precipitation (DP) method is another route to elaborate catalysts, which is often employed. This method does not require a pre-functionalisation of the support which constitutes a great advantage from industrial aspects. Simonov and Likholobov [5] described this route extensively in a recent review with careful attention to the different key steps in this synthesis route. They have strongly emphasized the influence of the surface chemistry of the support, showing that oxygen-rich sites did not undergo any preferential anionic adsorption. They also point out the key compulsory experimental procedures (precise introduction of the reagents, defined stirring, etc.) in order to get well-dispersed metal particles on carbon supports.

Basically the DP process is achieved by deposition of a preformed or in situ generated precious metal colloids. Depending on the process parameters the DP may generated either egg-shell or uniform distribution of the metal colloids through the carbon grains. From Simonov and Likholobov [5], and uniform distribution of the metal colloids through the grain of activated carbon seems better achieved starting from, anionic precursors in acidic medium,
e.g., \( \text{PdCl}_2^- \) in HCl solution, followed by the gradual addition of an alkaline solution. Egg-shell catalysts are attractive in dedicated applications where the target product is an intermediate in a consecutive reaction scheme, e.g., olefinic from hydrogenation of acetylenic compounds. As far as a homogeneous distribution through the grain is concerned, the relevant parameters are the distribution of macro-, meso- and micro-porosity of the support, and the nature and concentration of surface functional groups to a lesser extend. These are the parameters on which we have focused attention in the present work on Pd/AC catalysts. Besides their textural and structural characterisation, the catalysts were evaluated in the hydrogenation of 3-phenyl-2-propen, 1-al(cinnamaldehyde) as probe reaction. The hydrogenation of \( \alpha, \beta \)-unsaturated aldehydes to \( \alpha, \beta \)-unsaturated alcohols or saturated aldehydes is an important step in the preparation of various fine chemicals [6,7]. Pd is the preferred metal when saturated aldehydes are the desired products, but Pt, Ru or Ir are more efficient for the selective formation of the unsaturated alcohols.

The hydrogenation of cinnamaldehyde was chosen as model hydrogenation reaction and because this reaction is very well described in the literatures [8,9] the influence of the textural parameters can be studied in the light of previous published results. In Ref. [9], multi-walled carbon nanotubes anchored on the wall of a silica reactor is described, which have been used for the hydrogenation of \( C=C \) bonds using palladium as an active phase. High selectivities have been found for the production of hydrocinnamaldehyde which could be worth a comparison with our work.

In the present work, our purpose is to estimate the influence of the textural as well as the surface properties of a set of activated carbons on the catalytic hydrogenation performances of the resulting Pd/AC catalysts prepared by a deposition–precipitation method. This method was chosen as it usually yield uniform distribution of colloids through the grains according to Simonov and Likholobov [5].

2. Experimental

2.1. Materials

The set of five different activated carbons (AC-X, X: A, B, C, D, E) was supplied by CECA. The chemicals were provided by Aldrich and all had purity higher than 99%.

2.2. Characterisation of the supports

The supports were characterized by nitrogen sorption at 77 K and temperature-programmed decomposition (TPD) under helium.

Equivalent BET specific areas were determined from N\(_2\) adsorption at 77 K using a Micromeretics ASAP 2000 apparatus on samples (50 mg) previously outgassed for 7 h at 523 K and 10\(^{-4}\) Pa. The external surface areas and the microporous properties were estimated using the t-plot method with a carbon black as in Ref. [10].

The surface oxygen-containing groups of the supports were characterized by temperature-programmed desorption (TPDc-He) of the decomposition products from heating the materials in He. For each analysis, 0.2 g of the support was heated (5 K min\(^{-1}\)) in helium flow (25 mL min\(^{-1}\)) from room temperature up to 1073 K. The effluent composition was continuously monitored by on line sampling by a quadruple mass spectrometer (Pfeiffer Vaccum Omniram). The amounts of CO and CO\(_2\) were obtained by using calibration with the decomposition of a hydrated calcium oxalate standard. The desorption profiles of CO and CO\(_2\) are characteristic of specific surface groups (carboxylic acid, lactone, phenol, etc.) [4,11].

2.3. Preparation of the catalysts

A \( \text{H}_2\text{PdCl}_4 \) solution, prepared by dissolving \( \text{PdCl}_2 \) in 0.1 M HCl at 323 K, was added after cooling to the activated carbon (20 mL g\(_{\text{AC}1}\)). A 1 M NaOH solution was added to reach pH 12. The pH was kept constant for 1 h during the precipitation process. The resulting solid was filtered, washed with distilled water several times to avoid residual chlorine impurities and dried in air at 353 K. The catalysts were reduced in 3% \( \text{H}_2/\text{Ar} \) flow at 523 K for 2 h. The final catalysts were labelled Pd/AC-X, respective to the AC precursor.

2.4. Characterisation of the catalysts

The catalysts reducibility was determined by temperature-programmed reduction (TPR) experiments in a flow apparatus (AutoChem 2910, Micromeritics), eventually connected to a quadrupole mass spectrometer (Pfeiffer Vaccum Omniram). Prior to analysis, the sample (0.4 g) was flushed 1 h with argon (25 mL min\(^{-1}\)) before heating from 273 to 800 K (20 K min\(^{-1}\)) in a \( \text{H}_2/\text{Ar} \) (3/97) mixture (15 mL min\(^{-1}\)). The amounts of \( \text{H}_2 \) consumed or evolved were monitored continuously.

The accessibility to the Pd phase was estimated from the chemisorption of CO. The CO chemisorption was carried out by volumetry with automatic adsorption system (ASAP 2010 Chemi, Micromeritics) and using the double isotherm method. After outgassing at 523 K for 12 h, reactivation under hydrogen flow at the same temperature for 1 h for each catalyst. The sample was evacuated at 10\(^{-4}\) Pa for 1 h at the same temperature, and then cooled down to 313 K. The CO chemisorption isotherm was then determined in the pressure range 13–80 kPa. After outgasing at the same temperature for removing weakly bonded CO, a second CO-chemisorption isotherm was determined in the same pressure range. The difference between the two isotherms extrapolated to zero pressure was assigned to irreversibly adsorbed CO. Assuming a surface stoichiometry \( \text{Pd}/\text{CO} \), of unity, the fraction of exposed Pd atoms \( D = \text{Pd}_i/\text{Pd}_f \) can then be estimated as \( D = \text{CO}/\text{Pd}_f \) (molar ratio).

2.5. Catalytic experiments

The liquid-phase hydrogenation of cinnamaldehyde (CAL) was carried out in a sealed stainless-steel autoclave (Engineers Autoclave 0.1 L). Prior to the reaction, the prereduced Pd/AC-X catalyst (0.05 g) was in situ reactivated in solvent (cyclohexane) at 423 K under 1 MPa \( \text{H}_2 \) pressure for 2 h in a 200 mL autoclave. The catalytic test was then carried at 333 K under 1 MPa \( \text{H}_2 \) pressure. The introduction of cinnamaldehyde was taken as time zero. Samples were withdrawn periodically and analyzed with a gas chromatograph (HP-4890D) using an RTX S-Amine capillary column (30 m × 0.25 mm × 0.52 \( \mu \)m). Undecane was used as internal standard. The catalytic properties were illustrated by the initial rate, CAL conversion, product selectivity and turn over frequency (TOF, s\(^{-1}\), number of CAL molecule converted per surface Pd atom and per second):

\[
\text{CAL conversion} (\%) = 100 \times \frac{\left[ \text{CAL}_i \right] - \left[ \text{CAL}_f \right]}{\left[ \text{CAL}_i \right]}
\]

selectivity of product X (\%) = \( \frac{X_i}{\sum X_i} \)

\[
\text{TOF} (\text{s}^{-1}) = \frac{\text{rate (mol g}^{-1}\text{ s}^{-1})}{\text{Pd}_i (\text{mol g}^{-1})}
\]

3. Results and discussion

3.1. Characterisation of the activated carbons

The adsorption isotherms of nitrogen performed at 77 K on the set of original raw activated carbons are shown in Fig. 1A.
According to the IUPAC classification, the adsorption isotherms mainly belong to the type I, typical of microporous materials. The key features of microporous are present here: an infinite slope at low-relative pressure followed by very little nitrogen adsorption up to bulk condensation. Further, the extent of adsorption at low-relative pressure already gives some information about the degree of micro-porosity. On the other hand, all curves exhibit H4 type hysteresis loops, which can be attributed to some adsorption between grapheme sheets, but in overall, this phenomenon is rather limited as compared to micropores filling [12].

If we now go into more details, it can be noticed that, depending on the material studied, the slope of the adsorption isotherms in the monolayer–multilayer regime (from p/p0 = 0.1 up to p/p0 = 0.8) is not the same for all the materials. This process goes along an almost horizontal line in the case of sample AC-E, but it gets steeper when going from AC-D to AC-A. In the case of AC-E, it can be deduced that the material is essentially microporous, with very little external surface (large grains). Two reasons can explain the significant slopes observed in the case of materials AC-D to AC-A: (i) a very wide pore size distribution inducing a significant adsorption in a wide range of relative pressure; (ii) a large extent of external surface inducing a significant monolayer multilayer adsorption process. These two explanations do not exclude one another. Other information can be deduced from the curves at low-relative pressure: the position of the knees gradually shifts to the high-relative pressures from AC-E to AC-A which strongly suggests a decrease of the microporous character.

The t-plots in Fig. 1B were constructed using a non-porous carbon black as reference. Analysis of the t-plots provided the values of the external areas, S\text{EXT}, from the slope of the linear regression of the conventional multilayer region (0.4 nm < t < 0.7 nm). The total microporous volume, V\text{mic}, was calculated from the intercept with the y-axis (see Table 1).

Some additional information can also be obtained from the part of the t-plot in the range 0.25 nm < t < 0.4 nm. According to the literature, this break-up of the curve can be attributed to the existence of ultramicropore, with size inferior to 0.8 nm [13,14]. However, the slope of this line is strongly dependent on the reference chosen as demonstrated by Fernandez-Colinas et al. [10] with a set of four non-porous references. This strong influence of the nature of the reference over the t-plot curves is an issue that Singh [15] first discussed when the α method was proposed. The partial microporous volume corresponding to this range of smaller micropores was labelled V\text{mic}. As shown in Fig. 1B, all t-plots curves yield similar ultramicropore volumes (similar y-axis extrapolation).

The S\text{EXT} values obtained by applying the BET equation to the nitrogen adsorption isotherms in the usual domain 0.05 < p/p0 < 0.25 are reported in Table 1. The equivalent BET specific surface areas are comprised between 420 and 930 m² g⁻¹. It can also be noticed that the ratio S\text{mic}/S\text{EXT} varies from 0.55 to 0.75 for samples AC-A to AC-E which classically means that the more microporous the activated carbons are, the smaller is their specific surface area.

The oxidation degree of the surface is assessed by the TPDec-He method. The quantification of CO and CO₂ emissions during temperature ramping in inert atmosphere provides information about oxygen groups present at the surface, and more precisely about the nature of these oxygen groups and their thermal stability. It has been found that CO₂ emissions occur in the temperature range 423–773 K whereas CO emissions are significant above 673 K. This implies that CO emissions are the indication of more stable surface oxygen-containing groups. The results reported in Table 1 show that CO₂ emissions are in the range 0.070–0.280 mmol g⁻¹ which is five times less than the amount evolved from the same material having undergone a mild oxidation step using an aqueous NaClO solution [4] (labelled AC-A-OXY, n\text{CO}_2 = 1.130 mmol g⁻¹). The huge increase in the evolved CO₂ amount is clearly correlated to the oxidation of the material and, according to the literature, these emissions are due to the presence of specific acidic functional groups (mainly carboxylic acid, lactone and anhydride) [16]. The amounts of evolved CO recorded for all materials are slightly higher than CO₂, with an average value of 0.400 mmol g⁻¹. For the most part, this emission provides evidence of very stable surface oxygen-containing groups, i.e., both quinone and phenol groups. It can be noted that the importance of the CO₂ emissions strongly depends on the sample, whereas it does not in the case of CO emissions. This suggests that all activated supports studied possess the same amount of highly stable surface oxygen-containing functions whereas the amount of those of low stability depends on the sample. These differences will be further discussed later in the paper.

### Table 1

<table>
<thead>
<tr>
<th>Support</th>
<th>S\text{EXT} (m² g⁻¹)</th>
<th>V\text{mic} (cm³ g⁻¹)</th>
<th>S\text{EXT} (m² g⁻¹)</th>
<th>S\text{mic}/S\text{EXT}</th>
<th>TPDec-He\text{a} (mmol g⁻¹)</th>
<th>n\text{CO}_2</th>
<th>n\text{CO}</th>
<th>n\text{CO}_2/n\text{CO}</th>
</tr>
</thead>
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<tr>
<td>AC-A</td>
<td>901</td>
<td>0.24</td>
<td>391</td>
<td>0.57</td>
<td>0.07</td>
<td>0.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AC-B</td>
<td>928</td>
<td>0.25</td>
<td>393</td>
<td>0.58</td>
<td>0.09</td>
<td>0.42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AC-C</td>
<td>850</td>
<td>0.24</td>
<td>404</td>
<td>0.57</td>
<td>0.12</td>
<td>0.46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AC-D</td>
<td>696</td>
<td>0.21</td>
<td>264</td>
<td>0.62</td>
<td>0.21</td>
<td>0.46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AC-E</td>
<td>428</td>
<td>0.15</td>
<td>114</td>
<td>0.74</td>
<td>0.28</td>
<td>0.52</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AC-A-OXY</td>
<td>820</td>
<td>0.23</td>
<td>334</td>
<td>0.58</td>
<td>1.13</td>
<td>1.26</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\* Values obtained from integration of the TPDec-He profiles.

\* From Ref. [4].

3.2. Characterisation of the catalysts

The activated carbons exhibit typical point of zero charge (PZC) of pH 3–5 as shown in Fig. 2 in the case of samples Pd/AC-A and
Pd/AC-B. It must be noted that Pd/AC-D and Pd/AC-E gave similar PZC values despite different TPDec curves (see later). Thus, in acidic media, the overall surface is positively charged and its interaction with PdCl4 2/C0 species is clearly favoured. Otherwise, it has been shown in the past that the activity of Pd catalysts prepared according to the DP process could be influenced by any change in the nucleation or the precipitation time [17]. In this work, the precipitation process started only a few minutes after the addition of the metal (t = 3 min), minimising the contact time between the PdCl4 2/C0 species and the carbon surface. This resulted in a homogeneous adsorption of the metallic precursor onto the support. The activated carbons can hence be considered as chemically equivalent and only differ by their textural properties. The quantities of palladium introduced estimated by elemental analysis are reported in Table 2. Negligible amounts of residual chlorine were found in the final catalysts (600 ppm).

The TPR profiles of the catalysts are shown in Fig. 3. The experiments were carried out from 273 up to 800 K, as preliminary studies have demonstrated that no metal reduction occurs above this temperature. The various patterns provide evidence of three peaks of hydrogen evolution or consumption. It is well known that large Pd particles are able to absorb H2 within their structure to form a Pd–β-H phase [18]. This Pd–β-H phase which forms at room temperature is unstable at T > 340–360 K and can be detected in the TPR pattern from the H2 released around this temperature. The amount of hydrogen involved in the formation of the hydride phase, expressed from the H2/Pd ratio (where H2 represents the amount of H2 desorbed at around 350 K), is moreover dependent on the palladium particle size. The smaller Pd particles (<2 nm) are unable to form the β-hydride phase and the H2/Pd ratio increases with increasing the Pd particle size [18]. The TPR profiles of Pd/AC-A, B, C show small contributions of H2 evolution, but that of Pd/AC-E differs clearly with a significant contribution of H2 evolution from Pd–β-H phase. This behaviour reflects a higher proportion of large Pd particles in this sample, which cannot be estimated easily due to overlapping of H2 evolution and consumption around 370 K.

A second peak corresponding to hydrogen consumption appears for all samples with maximum ranging from 400 to 440 K. This peak shifts to lower temperature from Pd/AC-A to Pd/AC-E. In agreement with Neri et al. [19], this hydrogen consumption can be confidently attributed to the reduction of Pd precursors (PdCl4 2, oxo- and/or hydroxo-Pd species). It is worthy to note that for the well-defined reduction peak of Pd/AC-A and Pd/AC-B, the quantitative analysis of hydrogen taken up reveals a H2/Pd of ca. 1.2, in good agreement with the reduction of Pd2+ to Pd0. The observed excess of hydrogen consumption can be assigned to spillover of hydrogen from the palladium particles to the carbon support [18,20]. The shift from 400 to 440 K of the TPR peak reflects a lower reducibility of the Pd precursors particles. This is generally associated with particles in stronger interaction with the support, may be due to either smaller sizes or to higher amounts of chlorine in the precursor [19]. In spite of the similarity of chlorine content in the final catalysts (ca. 600 ppm), one cannot rule out the latter explanation. Regarding the size of the Pd precursor particles, it is measured by Zeta potential measurements as a function of pH in the case of (○) Pd/AC-A and Pd/AC-B (∙).

Table 2
Some characteristics of the Pd/AC-X catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pd (wt.%)</th>
<th>S_{BET} (m² g⁻¹)</th>
<th>V_{micro} (cm³ g⁻¹)</th>
<th>TPR, H2/Pd (mol/mol)</th>
<th>CO_{irrev}/Pd ratio (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/AC-A</td>
<td>4.4</td>
<td>938</td>
<td>0.25</td>
<td>1.17</td>
<td>0.38</td>
</tr>
<tr>
<td>Pd/AC-B</td>
<td>4.4</td>
<td>904</td>
<td>0.25</td>
<td>1.24</td>
<td>0.34</td>
</tr>
<tr>
<td>Pd/AC-C</td>
<td>4.1</td>
<td>915</td>
<td>0.25</td>
<td>0.78</td>
<td>0.26</td>
</tr>
<tr>
<td>Pd/AC-D</td>
<td>4.1</td>
<td>659</td>
<td>0.21</td>
<td>0.82</td>
<td>0.24</td>
</tr>
<tr>
<td>Pd/AC-E</td>
<td>4.8</td>
<td>388</td>
<td>0.14</td>
<td>0.52</td>
<td>0.13</td>
</tr>
</tbody>
</table>

a Values calculated from catalysts corrected mass (i.e., without mass induced by metal loading).

b Calculated from the TPR results using the reduction peaks located at 393 and 523 K.
c Estimated from extrapolation on the Y-axis of the chemisorption isotherms in the pressure range 13–80 kPa.

Fig. 2. Zeta potential measurements as a function of pH in the case of (○) Pd/AC-A and Pd/AC-B (∙).

Fig. 3. TPR profiles of the catalysts: (a) Pd/AC-A; (b) Pd/AC-B; (c) Pd/AC-C; (d) Pd/AC-D; (e) Pd/AC-E.
correlated with the size of Pd\textsuperscript{0} particles in the final catalysts which will be commented below.

Finally, there is a high-temperature TPR peak of H\textsubscript{2} consumption at ca. 500 K. The ratio H\textsubscript{2}/Pd is not informative to identify the nature of reduced species due to large peak overlap. In order to gain more information, some TPR experiments were followed with MS-coupling. They show that H\textsubscript{2} consumption at 500 K is associated with CH\textsubscript{4} evolution. We therefore propose that this peak is associated with a Pd\textsuperscript{0}-assisted hydrogasification of the carbon support. Similar observations and explanations were recently proposed by Dantas Ramos et al.\cite{20} for Pd/carbon catalysts.

From TPR experiments one can propose that Pd/AC-X catalysts are composed of Pd particles of varying sizes with a higher proportion of large particles for Pd/AC-E. The experiments of CO chemisorption and TEM examination are in agreement with this proposition (see below).

The size of Pd particle size was estimated from irreversible CO chemisorption measurements and TEM examination. The fraction D of exposed Pd atoms decreased from Pd/AC-A down to Pd/AC-E with values ranging from 0.38 to 0.13 (Table 2). This observation is confirmed by TEM analysis (Fig. 4). Apart from the Pd/AC-E, all materials exhibit a good metal dispersion (with regards to the 4–5% metal loading), the major part of it being made of small particles (smaller than 4 nm) and few larger ones (larger than 15 nm). Further, a correlation is demonstrated in Fig. 5 between the specific surface area is reported and the Pd dispersion. A strong increase of the dispersion from 0.13 to 0.38 can be observed with the corresponding specific surface area increasing from 380 up to

![Fig. 4. Transmission electron microscopy performed on the different samples: (a) Pd/AC-A; (b) Pd/AC-B; (c) Pd/AC-C; (d) Pd/AC-D; (e) Pd/AC-E.](image-url)
It is worth noting that this increase of specific surface area is mainly due to a higher extent of $S_{\text{EXT}}$ (Table 2).

The surface and textural properties in the final catalysts have also been examined from TPDec-He and N$_2$ sorption. No major change can be observed regarding the textural properties of ‘‘AC-X’’ in Pd/AC-X in comparison with the parent AC-X starting support. The variation of the specific surface area is in the range ±8–9% depending on the support. Observing a decrease in the specific surface area is something quite common as some pore blocking might be expected, however, increasing the specific surface area is more intriguing. Some extent of pore blocking occurs in the case of the most microporous samples (Pd/AC-D and Pd/AC-E) for which the metal introduction results in a quantitative decrease of microporous volume. On the other hand, the slight increase in specific surface area for Pd/AC-A and Pd/AC-C samples could be explained by different reasons: (i) a quantitative surface expansion by gasification process; (ii) a decomposition of low stable surface oxygen group, leading to some microporous network liberation. The first explanation is not supported by TPR experiments with MS coupling which do not provide evidence of CH$_4$ evolution for these samples. Regarding the second explanation, the same TPR experiments have provide evidence of CO$_2$ release at the onset Pd precursor reduction. In reduction conditions, the least thermally stable oxygen surface groups (carboxylic acid groups) were decomposed. Moreover, it has been demonstrated, by using the t-plot method, that all materials do have similar secondary micro-porosity. Therefore, at this stage, it is not possible to give a straightforward answer to this issue.

With regards to the chemical properties of the surface, TPDec-He of the final catalysts have shown a decrease in comparison to the starting AC-X supports, of the carbonylic group amounts which reach low and similar values whatever the catalysts.

3.3. Catalytic experiments

The formal reaction scheme of CAL hydrogenation is reported in Fig. 6.

To assess the role of external mass transfer on the reaction rate, the influence of agitation speed was studied from 600 to 1600 rpm using Pd/AC-B as catalyst. No significant change in cinnamaldehyde conversion was noticed above 1000 rpm which means that the reaction then proceeds under chemical control. Hence, all further reactions were carried out at 1200 rpm.

The apparent activation energy $E_a$ determined in the temperature range 320–350 K with Pd/AC-B as catalyst is 70 kJ mol$^{-1}$. This value is in good agreement with the value reported by Zhang et al. [21]; with a 5% Pd/C commercial catalyst, they found a value of 65 ± 5 kJ mol$^{-1}$ in toluene as solvent.

The CAL conversion profiles on Pd/AC-X catalysts are shown in Fig. 7. They all exhibit a similar shape, indicating a similar reaction process. The initial rate increases more or less gradually from 5.4 × 10$^{-3}$ to 10.8 × 10$^{-3}$ mol Pd g$^{-1}$ s$^{-1}$, when moving from Pd/AC-E to Pd/AC-A (Table 3). The turn over frequency TOF, number of CAL molecules converted per second and per surface Pd atom, are also reported in Table 3. The TOFs observed are similar regardless the textural properties and/or size of Pd particles of the catalysts. They are of the same order of magnitude as those reported in literature; for instance, Girot-Fendler et al. [7] reported a TOF value of 6.7 s$^{-1}$ for a Pd/graphite and hydrogenation carried out in isopropanol/water.

The selectivities in hydrocinnamaldehyde (HCAL) obtained for the five catalysts reach 90 at 90% CAL conversion. Thus, in our conditions of reaction, a mixture of HCAL and phenylpropanol (PP) was always obtained without detection of any traces of cinnamyl alcohol (COL). It is well known that palladium is more prone to hydrogenate the C=C bond than the C=O bond compared to other transition metals [6]. The changes of selectivity among transition metals have been explained in terms of d-band radial expansion: the larger the d-band is, the stronger repulsive interactions.

![Fig. 5. Correlation between the specific surface area of the supports and the Pd dispersion (from CO chemisorption).](image1)

![Fig. 6. Reaction pathway of the hydrogenation of cinnamaldehyde.](image2)

![Fig. 7. Cinnamaldehyde conversion profiles on the different catalysts at 423 K: (a) Pd/AC-A; (b) Pd/AC-B; (c) Pd/AC-C; (d) Pd/AC-D; (e) Pd/AC-E.](image3)
between C=Cs and the metal are, which leads to a poor HCAL selectivity [22].

The HCAL selectivities obtained on Pd/AC-X are mostly higher than those reported in the literature. For example, Giroir-Fendler et al. [7] observed a 55/45 HCAL/PP mixture by using 4% Pd/C catalyst prepared by ion exchange (size of Pd particles /C24 1.7 nm). Janowska et al. [9] found similar results to ours, but with very sophisticated catalysts since those are made of carbon nanotubes anchored on silica walls and further Pd deposited. This could facilitate products diffusion and therefore limit side reactions leading to poor selectivities. This low selectivity was explained by the restriction of HCAL diffusion caused by the highly microporous texture of the used activated carbon. The slowing down of HCAL diffusion out of the carbon grain makes the consecutive hydrogenation to PP easier. Zhang et al. [21] reported with a 5% Pd/C catalyst (solvent: n-heptane, T = 303 K, P H2 = 0.1 MPa) a 18/53 HCAL/PP mixture, balance with propylbenzene (29%); propylbenzene came from the hydrogenolysis of PP.

4. Conclusion

The use of the deposition/precipitation method for metal loading and activated carbons of different textual properties but similar surface chemistry, allowed elaborating a series of 4–5% Pd/AC catalysts. They differ by the Pd dispersion from 0.13 to 0.39, that is to say Pd particles from ca. 8.5 to 2.8 nm, respectively. The prime parameter which determines the Pd particle size is the extent of AC surface in the meso- and macro-pores. A large value favors the formation of Pd particles of small sizes (2–3 nm). These catalysts are highly selective in the hydrogenation of CAL to HCAL (90% selectivity at 90% CAL conversion), and exhibit similar turn over frequencies. Selectivities do not seem to be dependent on the texture of the materials even if particle dispersions are strongly influenced by this parameter. The choice of the catalytic test to evidence the influence of textural properties is therefore questionable and different catalytic tests are currently being tested to try to generalize the results obtained in this paper.

Acknowledgments

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References