Carbon-based monolithic supports for palladium catalysts: The role of the porosity in the gas-phase total combustion of *m*-xylene

A.F. Pérez-Cadenas(1)*, S. Morales-Torres(1), F. Kapteijn(2), F.J. Maldonado-Hódar(1),
F. Carrasco-Marín(1), C. Moreno-Castilla(1), J.A. Moulijn(2)

[1] *Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada, 18071 Granada, Spain*
[2] *Catalysis Engineering, DelftChemTech, Faculty of Applied Sciences, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands*

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*Corresponding author. Tel.: +34-958243235; fax: +34-958248526.

E-mail address: afperez@ugr.es (A.F. Pérez-Cadenas)

Abstract

Three different carbon based monoliths have been studied in their performance as Pd-catalyst supports in the total gas-phase combustion of *m*-xylene at low temperatures. The first monolithic support (HPM) was a classical square channel cordierite modified with α-Al_2O_3, blocking the macroporosity of the cordierite and rounding the channel cross section, on which a carbon layer was applied by carbonization of a polyfurfuryl alcohol coating obtained by dipcoating. The other two monolithic supports were composite carbon/ceramic monoliths (MeadWestvaco Corporation, USA), micro- (WA) and a mesoporous (WB) sample.

All the catalysts have a comparable total Pd loading and very similar Pd particle size (around 5 - 6 nm). In sample Pd/WA the Pd is situated only in the macropores, while in the case of Pd/WB the Pd is distributed throughout the mesoporous texture. In the case of Pd/HPM, Pd particles are clearly situated at the external surface of the carbon layer.

The catalytic activities of the samples were very different, decreasing in the order: Pd/WB > Pd/WA > Pd/HPM. These results show that the carbon external surface area, the macro and mainly mesopores, play an important role in this kind of gas phase reactions, improving the contact between the Pd particles and the *m*-xylene molecules. The catalytic activity of the Pd supported on carbon based monoliths correlates with the surface area developed in macro and mesopores of the monolithic support.

1. Introduction

Carbon based monoliths are being considered as catalyst support for industrial applications [1-4] due to their mechanical resistance, easy handling and good chemical and textural properties of carbon materials (versatility in surface area, pore texture and surface chemistry [5]), as well as, due to the other properties showed by the ceramic monoliths in catalysis, as low pressure drop, short diffusion distance and the lack of attrition by vibrations and thermal shock resistance [6].

Within gas-phase reactions, carbon coated monoliths have been recently used as Pt and Pd catalyst supports in the low temperature total combustion of xylenes, as example for Volatile Organic Compounds (VOC) abatement [4]. It is known, that VOC are major air pollutants, and aromatic compounds inhalation represents a serious risk to the health [7,8]. Thus, one of the more important reasons of the carbon use as catalyst support in this kind of reaction was the hydrophobicity of carbon materials [9-12].

It is well-known that the porosity plays an important role in catalytic processes [13]. If internal transport problems (diffusion limitations) of reactants and products are important [13], both activity and selectivity can be improved, using well developed porous material as catalyst supports. In this way, depending on the kind of reaction, reactants and products, the use of micro-, meso- or macroporous carbon based monoliths as catalyst supports can be attractive.

In this work the catalytic behaviour of Pd catalysts supported on three different porous carbon based monoliths was studied in the total gas-phase combustion of *m*-xylene at low temperature. The aim of this work is to elucidate the role of the macro- and mesopores in the above mentioned gas-phase reaction.

2. Experimental

2.1. Preparation of the monolithic supports and catalysts

For the HPM catalyst support preparation [2], cordierite monolithic substrates have been coated with an α-Al_2O_3 layer using a dipcoating method, in order to block the macroporosity and to prevent deposition of catalytic material in the wall of this monolith substrate, as well as to round the channel cross section [14]. The monolithic substrates had square cells, a cell density of 62 cells cm^{-2} (400 cpsi), a wall thickness of 0.18 mm, a length of 1.5 cm and a diameter of 1 cm. In a second step a thin carbon layer of uniform thickness (14 μm, determined by SEM) has been formed on the α-Al_2O_3 layer [2], which serves as a support for the active catalytic phase. The total carbon content of HPM was 6.3 wt.% (Table 1).

Two composite carbon/ceramic monoliths, WA and WB samples (MeadWestvaco Corporation, USA), have also been selected as catalyst supports. Both monoliths have a cell density of 400 cpsi, length 1.5 cm, diameter 1 cm, and a total carbon content of 34.7 and 30.9 wt.% for WA and WB, respectively. The ceramic % weight composition of SiO_2/Al_2O_3/other amounted to 62.7/29.8/7.5.

The three monoliths (HPM, WA and WB) were subjected to an oxidation treatment of the carbon with an aqueous solution of H_2O_2 9.8 M for 24 h at room temperature to create anchoring sites on the carbon for metal deposition. Pd was deposited by equilibrium impregnation of the monolithic supports with an aqueous solution of tetraammine palladium (II) nitrate.

2.2. Characterization of the monolithic supports

Textural characterization of the samples was carried out by CO_2 and N_2 adsorption at 0 ºC and –196 ºC, respectively, and by mercury porosimetry. The BET [15] equation was used for analysis of N_2 adsorption isotherms, and the Dubinin-Raduskevich and Stoeckli [16] relations for analysis of CO_2 adsorption data. The liquid density of CO_2 at 0 ºC was taken as 1.03 g cm^{-3} and the molecular area of N_2 at -196 ºC as 0.162 nm^2. Mercury porosimetry was performed up to a pressure of 4200 kg cm^{-2} using Quantachrome Autoscan 60 equipment. With this technique, the following parameters were obtained: pore volume corresponding to pores with diameter between 3.7 and 50 nm, V_{MESO}, referred to as mesopore volume (note that mesopore volume range [17] is classically defined as 2-50 nm); pore volume of pores with diameter greater than 50 nm, or macropore volume, V_{MACRO}; external porous surface area (surface area of macro and mainly mesopores), S_{EXT}.

The surface chemistry of the carbon-based monoliths was characterised by temperature-programmed desorption (TPD). TPD experiments were carried out by heating the samples to 1000 ºC in He flow (60 $cm^3 min^{-1}$) at a heating rate of 50 ºC min^{-1}. The amount of evolved gases was recorded as a function of temperature using a quadrupole mass spectrometer (Balzers, model Thermocube), as described elsewhere [18]. The oxygen content (O_{TPD}) was calculated from the amounts of CO and CO_2 evolved during the TPD experiments.

2.3. Characterization of the monolithic catalysts

The Pd loading of the monolithic catalysts was analyzed by neutron activation analysis (NAA) using a Germanium semiconductor as detector. The palladium dispersion, *D*, and its average particle size were obtained by CO-chemisorption at 40 ºC assuming a CO:Pd = 1:1 stoichiometry, and that the average particle size = 1.12/*D* (nm). CO-chemisorption isotherms were measured in conventional volumetric equipment made of Pyrex glass and free of mercury and grease, which reached a dynamic vacuum better than 10^{-6} mbar at the sample location. Equilibrium pressure was measured with a Baratron transducer from MKS. All catalysts were pretreated at 300 ºC in H_2 flow (purity of 99.999 %) for 2 h., both prior to the characterization by CO-chemisorption and for the *m*-xylene combustion reaction.

XPS measurements of the pretreated catalysts were made with an Escalab 200R system (VG Scientific Co.) equipped with MgKα X-ray source (hν = 1253.6 eV) and hemispherical electron analyzer. Prior to the analysis, the samples were crushed and evacuated at high vacuum and then introduced into the analysis chamber. A base pressure of 10^{-9} mbar was maintained during data acquisition.

TPR was carried out in a tubular quartz reactor (5 mm inner diameter) coupled to a TCD analyzer for monitoring H_2 consumption. Crushed monolith samples (150mg) were heated at 2 ºC min^{-1} from room temperature to 1000 ºC in an Ar flow (30 cm^3 min^{-1}) containing 8 % of H_2.

The monolithic catalysts were analyzed by immersion calorimetry. The immersion enthalpies into *m*-xylene of the previously outgassed samples (110 ºC for 12 h) were measured at 30 ºC with an isothermal calorimeter of the Tian-Calvet type, Setaram C-

80. Corrections corresponding to the bulb breaking energy and to the liquid vaporization energy have been made.

The thermal stability of the catalysts in the reaction conditions was studied in a thermogravimetric analyser (TGA, Mettler Toledo, TGA/SDTA851e). Oxidation experiments were carried out by heating the catalysts at 2 ºC min^{-1} up to 800 ºC in 100 cm^3 min^{-1} air flow, and also with the same conditions up to 190 ºC for 12 h.

2.4. *m*-Xylene catalytic combustion

Samples were tested in the *m*-xylene catalytic combustion. Experiments were carried out in a glass reactor, operating in continuous mode at atmospheric pressure. In all cases, a piece of 1.5 cm of monolithic catalyst was used. The total flow of the reactant mixture (*m*-xylene/O_2/He = 0.1/20.0/79.9 %) was tuned to a space velocity of 2000 $m^3_{gas}h^{-1}m^{-3}_{monolith}$. The reaction was performed at temperatures ranging from 120 to 180 ºC, and always from high to low temperature.

Prior to the catalytic activity measurements, the monolithic catalysts were pre-treated in H_2 flow as described above. Reaction products were analysed online by gas chromatography using a Perkin-Elmer gas chromatograph, model 8500, with a thermal conductivity detector and Paraplot Q capillary column. The only reaction products found were CO_2 and H_2O. Other products were not detected under the experimental conditions used. In all the cases, the same conversion was obtained on the basis of both *m*-xylene consumption and CO_2 formation. Catalytic activity (r) was calculated using:

$$r = F \cdot C / W$$

Where F is the *m*-xylene flow through the monolithic catalyst in moles per second, C is the conversion to CO_2 and W is the weight (g) of palladium in the sample.

3. Results and discussion

3.1 Characterization of the monolithic supports

Surface areas are compiled in Table 2. Results show that the carbon layer in sample HPM has a S_{BET} much lower than S_{CO2}, which is indicative of small micropores or pore constrictions at the entrance of the micropores, making the microporosity almost inaccessible to the N_2 molecules at –196 ºC. The N_2 adsorption isotherm of WA was of type I, indicative of a microporous material. The N_2 adsorption isotherm of WB, however, showed a progressive increase in volume adsorbed over a wide pressure range, suggesting a broad distribution of mesopores.

Both samples, WA and WB, show similar S_{BET} value which was higher than S_{CO2}, indicative of a heterogeneous micropore size distribution. In addition, whereas WA has only macropores, WB has meso and macropores, which makes its S_{EXT} greater than that of sample WA.

In Table 3 are collected the amounts of CO and CO_2 evolved up 1000 ºC during the TPD experiments, as well as the oxygen content (O_{TPD}) of the monoliths after the oxidation treatment. The HPM carbon component has the highest total oxygen content due to the low carbonization temperature of its coating (Polyfurfuryl Alcohol), while in the case of the WA and WB monolithic supports, the amounts of CO and CO_2 evolved up to 1000 ºC are very similar.

3.2. Characterization of the monolithic catalysts

All catalysts showed intense hydrogen consumption in TPR below 300 ºC, indicating the reduction of the Pd particles during the pre-treatment [19,20], as indicated in Figure 1 for catalyst WB as example. The hydrogen consumption at higher temperatures is ascribed to hydrogenation of the carbon and possible methane formation.

Pd loading, dispersion and particle size of the catalysts are presented in Table 4. All catalysts have a comparable Pd loading based on the total sample mass, and although sample Pd/WA showed a slightly lower dispersion we consider that all catalysts have a similar Pd particle size. The Pd XPS-signal was negligible in samples Pd/WA and Pd/WB, whereas that in sample Pd/HPM indicated a high Pd concentration. As we have crushed the samples for XPS analysis this indicates that in the Pd/WA and Pd/WB samples the Pd is distributed homogeneously throughout the sample whereas for the HPM sample significant surface enrichment has taken place.

Taking into account the mean Pd particle size of the samples (around 5-6 nm), the catalyst preparation method (equilibration from an aqueous solution), the XPS results and the type of porosity of the supports, it is concluded that the Pd crystallites are located at the external non–porous surface of the carbon layer in the Pd/HPM sample. In the case of the Pd/WA sample the Pd is located in the macropores, while in sample

Pd/WB the Pd is distributed throughout the meso and macropore space. In view of their size the Pd particles will not be located in the micropores of the samples. Therefore, the microporosity will not affect the activity of the Pd catalysts.

Figure 2 shows schematic cross sectional views of the monolithic channels for the three catalysts, indicating the effective surface area of the monolithic supports accessible to Pd particles in each sample (micropores are not drawn).

In order to investigate the *m*-xylene-support interaction, the samples were studied by *m*-xylene immersion calorimetry. Due to the fact that the samples have important inorganic contents (Table 1), immersion calorimetry experiments of these inorganic parts were carried out as well. The immersion enthalpy data are collected in Table 5. In this Table, it is observed that the "inorganic content" immersion enthalpies were much lower than those determined for the complete corresponding samples. So, the carbon content contribution to the immersion enthalpy values of the catalysts was the most important. In order to compare the carbon content contribution to the immersion enthalpies, the immersion enthalpies of the catalyst were corrected for the inorganic content contribution, taking in account the amount of inorganic content and the enthalpy per gram of inorganic content of each sample. In this way, we obtained for each catalyst the corresponding values of *m*-xylene immersion enthalpy per gram of carbon content which we will refer as "*corrected enthalpies*". In Table 5 we can see that the *corrected enthalpies* follow the sequence: Pd/WB = Pd/WA > Pd/HPM. That is, immersion enthalpies give information about the *m*-xylene accessible carbon surface areas which are qualitatively similar to the BET ones. In spite of the lower micropore surface area in sample WB, the contribution of its mesopores to the immersion enthalpy results in a similar enthalpy value as for WA.

The results show that *m*-xylene has access to the surface area of samples containing micropores where Pd particles are not deposited (due to their size). Sample HPM has the lowest interaction with *m*-xylene due to its smallest surface area than samples WA and WB.

A possible drawback of using carbon materials as a catalyst support is that they can be consumed during reaction under oxidizing conditions. For this reason, the oxidation resistance of the monolithic catalysts was studied by TGA. Results are depicted in Figure 3 and show that the burn-off of the support started between 230 and 280 ºC. This temperature range is much higher than that used to study the catalytic oxidation of m-xylene. In order to avoid any risk in a practical application, additional experiments at 190 ºC under a 3.6 Lh^{-1} air flow for 12 h were carried out, and no weight loss in the monolithic support was observed. Therefore, significant oxidation of the support is not expected to take place during the study of the deep oxidation of *m*-xylene. Thermal stability of the supported catalysts was also checked at reaction conditions (140-180 ºC). For this purpose, the xylene/O_2/He flow was switched to an air flow and no CO_2 was detected, confirming the stability of the support material.

3.3. *m*-Xylene catalytic combustion

The catalytic performance of the monoliths was evaluated by measuring for the oxidation of *m*-xylene conversion versus reaction temperature, as well as versus time on stream. All the catalysts were active in this reaction. The light-off curve (conversion as function of the temperature) for sample Pd/WB, the most active catalyst, is shown in Fig. 4 as an example. In this case complete *m*-xylene oxidation was reached at 170 ºC. In all experiments no variation of CO_2 conversion against reaction time was observed for 15 hours.

The activity of the monolithic catalysts (expressed per gram of Pd) versus temperature in the *m*-xylene oxidation reaction is shown in Figure 5. It is observed that Pd/WB catalyst was the most active, followed by Pd/WA and Pd/HPM being the least active one. That is, for similar Pd loading and Pd particle size, the larger the external porous surface area, the higher the activity. In Figure 6 the activity is plotted against the external surface area (from Hg porosimetry). A positive correlation is observed at all three temperatures. Therefore, there is a strong interplay between the carbon porosity, where Pd particles are located (the macro- and mesoporosity) and the catalytic activity in the total combustion of *m*-xylene. Results of this work show that the external surface area of carbon, that in meso and macropores, plays an important role in this kind of gas phase reactions, because although m-xylene can reach the micropores Pd was not deposited inside them. Therefore, it is proposed that the role of the carbon support is to improve the contact between the Pd and the *m*-xylene molecules. In this way, it is expected that mesopores could make easier the contact between reactants and catalyst particles than macropores.

4. Conclusions

The three carbon based monoliths, HPM, WA and WB, can be used as supports of Pd-catalysts in the total combustion of *m*-xylene at low temperature.

Complete *m*-xylene combustion was reached at 170 ºC with a total selectivity to CO_2 and H_2O.

For catalysts with similar Pd loading and Pd particle size, the larger the macro and mesoporous carbon surface area, the higher the activity.

Catalytic activity, external carbon surface areas and *m*-xylene immersion enthalpies show that there exists a strong interplay between the carbon porosity, macro- and mesopores, and its performance in the Pd catalyzed total combustion of *m*-xylene. These pores improve the contact between the Pd particles and the *m*-xylene molecules.

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Figure Captions:

Figure 1. TPR curves of WB (black line) and Pd/WB (grey line).

Figure 2. Scheme of the channel cross section of the monolithic catalysts. a) Pd/WB, b) Pd/WA, c) Pd/HPM.

Figure 3. Percentage of burn-off in air as a function of temperature for the monolithic catalysts.

Figure 4. Light-off curves for Pd/WB. Closed symbols: conversion calculated from the CO_2 concentration. Open symbols: conversion calculated from the m-xylene concentration.

Figure 5. Activity of the monolithic catalysts normalized per gram of Pd.

Figure 6. Activity of the three monolithic catalysts normalized per gram of Pd versus their external surface area.

Table 1. Inorganic and carbon contents of the monolithic supports.

Monolithic support	Total inorganic content (wt. %)	Total carbon content (wt. %)	Total carbon content (mg) (*)
WA	(1) (a) 65.3	(a) 34.7	114
WB	(1) (a) 69.1	(a) 30.9	87
HPM	(2) (a) 37.6 (3) (b) 56.1	(b) 6.3	74

(a) Structural part of the monolith

(b) Coating

(*) Per piece of 1.5 cm length.

(1) SiO_2/Al_2O_3/other: 62.7/29.8/7.5 (wt. %)

(2) Cordierite

(3) α-Al_2O_3

Table 2. Surface characteristics of the monolithic supports. Data in parenthesis are given per gram of carbon.

Monolithic support	(1)S_{CO2} (m^2 g^{-1})	S_{BET} (m^2 g^{-1})	(2)S_{EXT} (m^2 g^{-1})	(2)V_{MACRO} (cm^3 g^{-1})	(2)V_{MESO} (cm^3 g^{-1})
WA	329 (947)	474 (1366)	4 (12)	0.325 (0.937)	0
WB	242 (782)	460 (1489)	62 (199)	0.233 (0.754)	0.138 (0.447)
HPM	17 (269)	(2)	(< 1)	(n.d.)	(n.d.)

(1) By application of Dubinin-Radushkevich equation to CO_2 adsorption data

(2) By mercury porosimetry

n.d. = not detected

Table 3. Amounts of CO and CO_2 evolved up to 1000 ºC and oxygen content of the monoliths (TPD). Data are given per gram of carbon.

Monolith	CO_2 (μmol g^{-1}_{CARBON})	CO (μmol g^{-1}_{CARBON})	O_{TPD} ($wt._{CARBON}$ %)
WA	409	1166	3.18
WB	377	1127	3.01
HPM	2620	7295	20.1

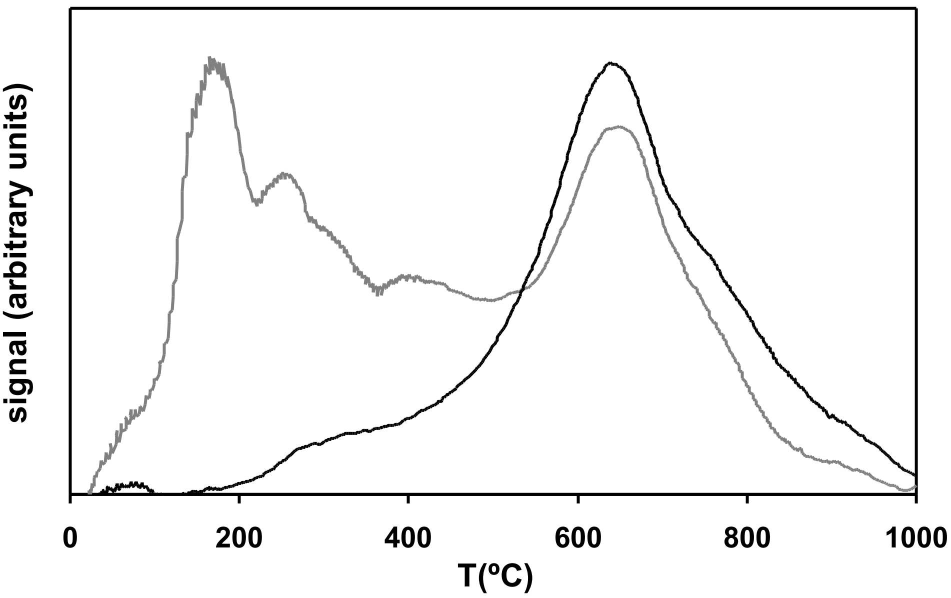
Table 4. Pd loading, dispersion and metal particle size of the catalysts

Monolithic catalyst	Pd (By XPS) (% wt)	Pd (% wt_{total})	Dispersion (%)	Particle size (nm)
Pd/WA	b.d.	0.42	18.2	6.1
Pd/WB	b.d.	0.49	23.0	4.9
Pd/HPM	2.56	0.30	23.1	4.8

b.d. = below detection limit

Table 5. Immersion calorimetry enthalpies of the samples in *m*-xylene.

Sample	Enthalpy ($J\ g^{-1}_{TOTAL}$)	Corrected Enthalpy ($J\ g^{-1}_{CARBON}$)
Pd/WB	49.8	154.6
Pd/WA	54.2	150.6
Pd/HPM	5.7	62.4
Inorganic content of Pd/WB	2.9	-
Inorganic content of Pd/WA	2.9	-
Inorganic content of Pd/HPM	1.9	-



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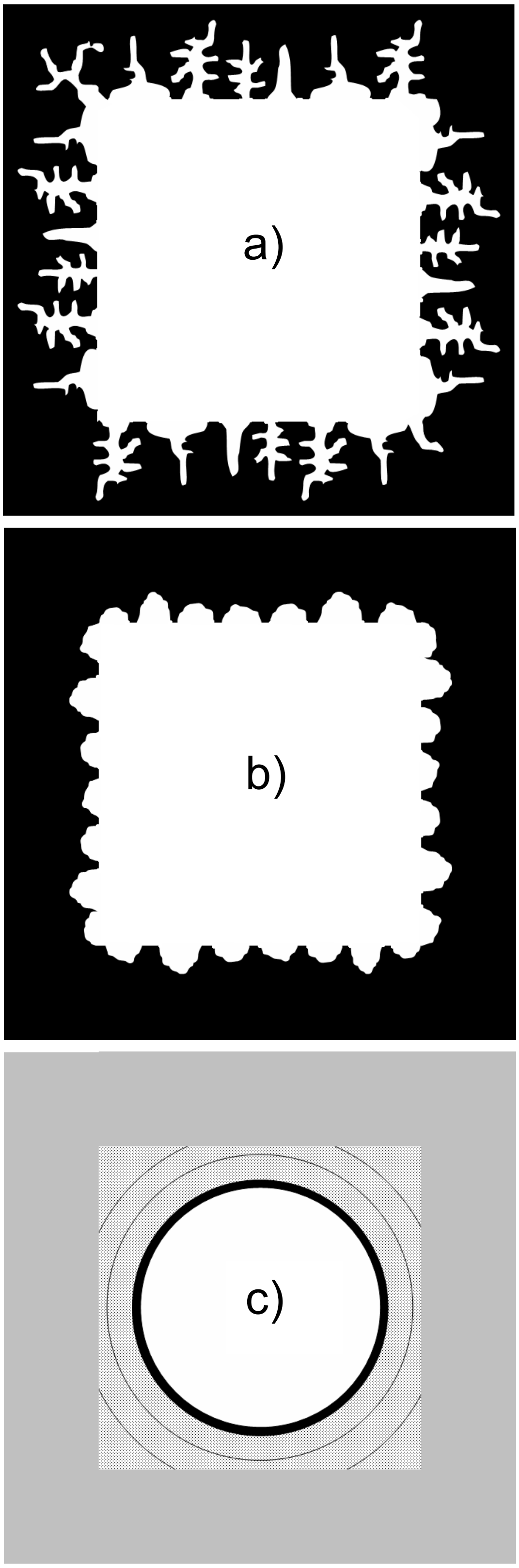

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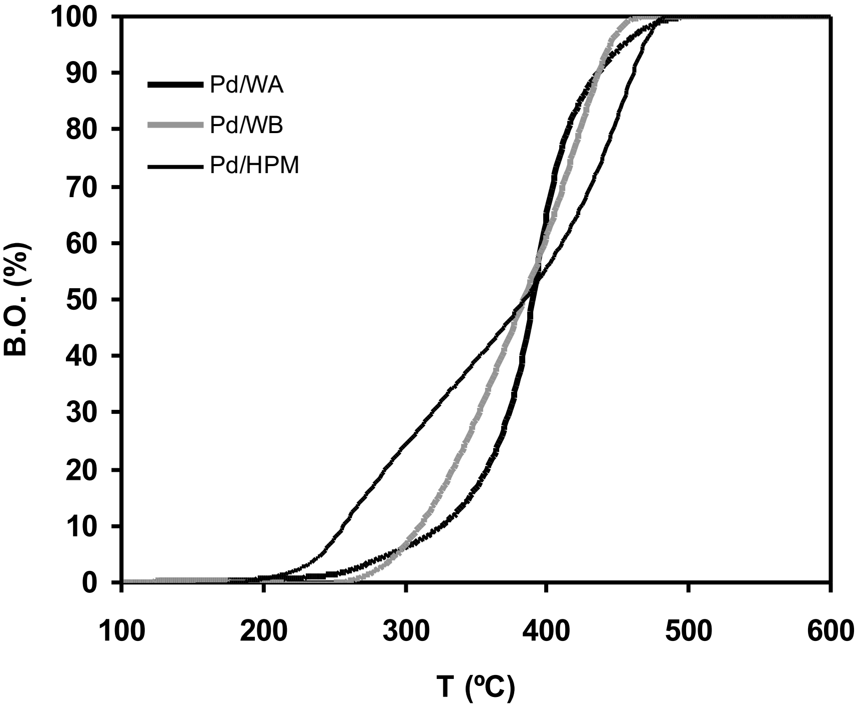

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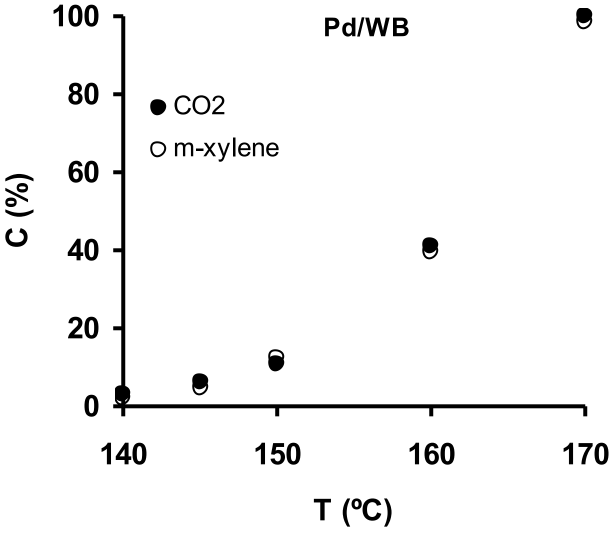

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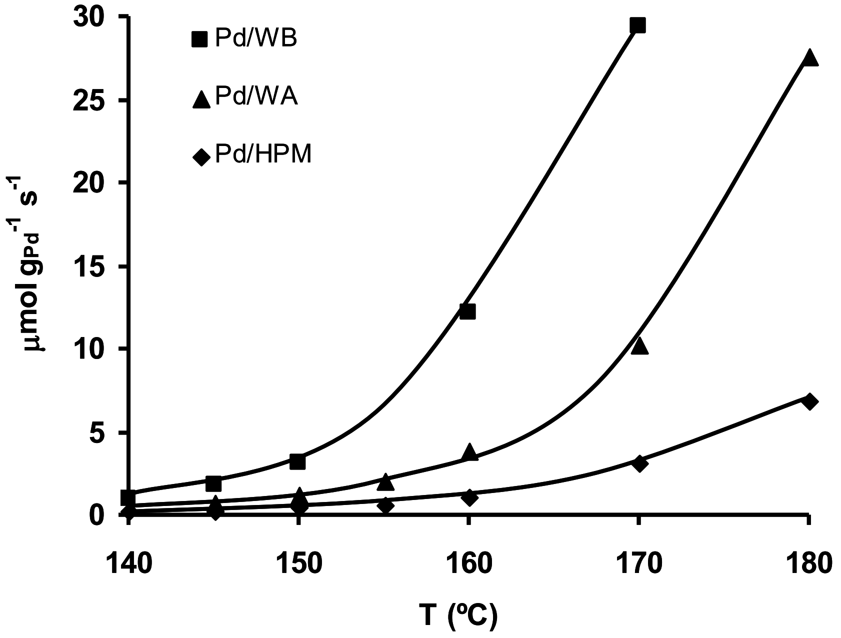

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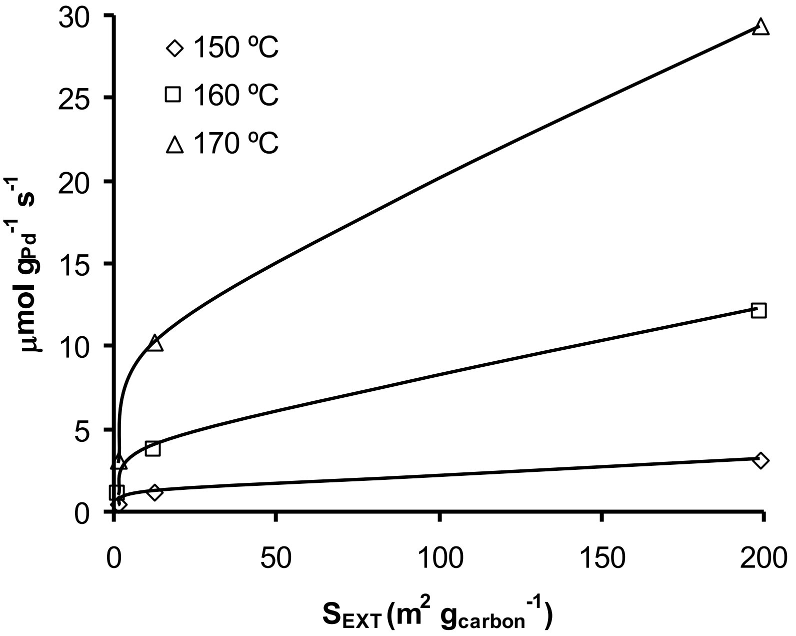

Figure 6.