

Enantioselective hydrogenations with highly mesoporous carbon supported Pd catalysts

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Abstract

Highly mesoporous carbon supported Pd catalysts were prepared using sodium formate and hydrogen for the reduction of the catalyst precursors. These catalysts were tested in the enantioselective hydrogenation of isophorone and of 2-benzylidene-1-benzosuberone. The support and the catalysts were characterized by different methods such as nitrogen adsorption, hydrogen chemisorption, SEM, XPS, and TPD. © 2003 Elsevier B.V. All rights reserved.

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1. Introduction

The type of catalyst strongly influences the enantioselectivity of heterogeneous catalytic hydrogenations [1]. In the enantioselective saturation of the C=C bond of isophorone over (–)-dihydroapovincaminic acid ethyl ester [(–)-DHVIN] modified Pd catalysts (Scheme 1) the optical purity strongly depended on the type of the support used [2]. In order to reveal the support effect in detail, carbon supports with different specific surface area and different surface chemistry [3], and titania supports differing in their crystalline form and in surface area [4], were used. In both cases, supports of low specific surface area proved advantageous for the enantioselectivity. The crystalline forms of the titania had only a small effect [4]. The surface chemistry of the carbon affected the enantiomeric excesses (e.e.) [3]: the optical purity increased from 10% [2] to 20% [3] upon modification of the properties of the carbon.

In the most effective, chirally modified catalytic systems: Pt/cinchonidine and Raney-Ni/tartaric acid, the enantioselectivity was also sensitive to the method of catalyst preparation [5,6].

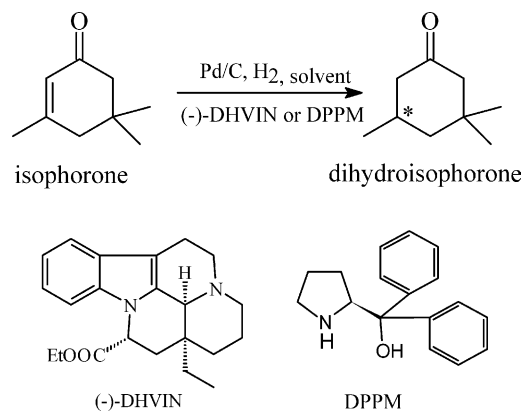
In the enantioselective hydrogenation of isophorone in the presence of (–)-DHVIN modifier the best optical purity

was afforded by small dispersion (<0.05) Pd black catalyst (enantiomeric excesses up to 55%) [7]. The influence of the preparation method of Pd black on the optical yield was reported [8]. A correlation was found between the oxidation state of the metal surface and the enantioselectivity, the catalyst having more oxidized species on its surface giving higher enantiomeric excess, while the Pd black with lower surface area was more enantioselective.

The Pd black catalyst was found to be most effective in the hydrogenation of isophorone (modifier (*S*)- α,α -diphenyl-2-pyrrolidinemethanol (DPPM), Scheme 1, e.e. up to 42%) [9] and that of 2-benzyl-1-benzosuberone (modifier cinchonidine (CD), Scheme 2, e.e. up to 54%) [10] also.

The objective of the present study was to use improved supported catalysts in the enantioselective hydrogenation of isophorone and 2-benzylidene-1-benzosuberone, which could compete with the Pd black catalyst. Carbon materials are common supports, their surface properties can be modified easily and it is possible to prepare carbons with different proportion of micro-, meso- and macropores, which can be key factors responsible for their extraordinary performances. A highly mesoporous carbon was synthesized and used as support of Pd catalysts. The catalysts were tested in the enantioselective hydrogenation of isophorone and 2-benzylidene-1-benzosuberone. To our knowledge this is the first report on the use of highly mesoporous carbon for the preparation of Pd catalysts.

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Scheme 1. Hydrogenation of isophorone.

2. Experimental

2.1. Materials

A highly mesoporous carbon xerogel was synthesized by the condensation of resorcinol and formaldehyde in molar ratio of 1:2. An aqueous solution of sodium carbonate was used as a base catalyst, in a molar ratio 1:200 with resorcinol. The clear solution obtained was cured by employing [1,1,1] cycle keeping at room temperature, and 50 and 90 °C for one day each, respectively. The gel was exchanged with acetic acid, and it was further exposed to successive extractions of acetone and cyclohexane, to remove the solvent from the pores. The gel was first dried at ambient temperature and then it was further exposed to warm air at 50 °C for 2–3 h. Carbonisation of the gel was carried out in nitrogen atmosphere by heating it to 800 °C at a heating rate of 10 °C/min and further keeping it at this temperature for 6 h. The surface of the carbon material was modified by treatment with 5% oxygen in nitrogen at 400 °C for 10 h to reach a burn-off of 14% (referred as CX-14). Prior to surface acti-

vation the carbon was subjected to extraction with 2 M HCl in a Soxhlet apparatus for 6 h, in order to remove sodium and washed copiously with water till neutral pH.

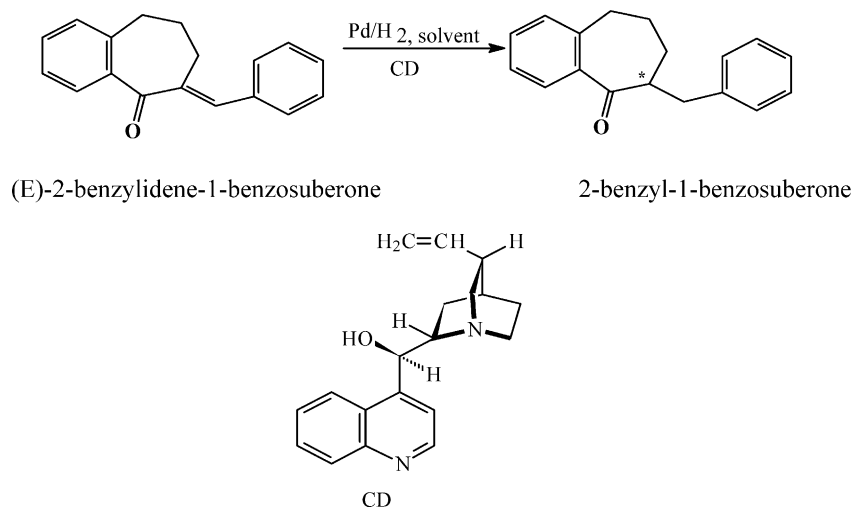
Catalysts with 10 wt.% Pd on highly mesoporous carbon xerogel CX-14 were prepared as follows. The calculated amount of the K₂PdCl₄ precursor was added to the aqueous suspension of the support. The pH value was adjusted to 11 by addition of KOH. The suspension was boiled for 1 h, then the reducing agent (HCOONa, three times the stoichiometric amount) (type 1) was added to the boiling mixture. After half an hour the suspension was cooled, the catalyst was filtered and washed with distilled water. The other method comprised, after similar preparation steps, the reduction of the Pd(OH)₂ precursor with H₂ gas in water at atmospheric pressure (type 2).

Apovincaminic acid ethylester was supplied by Richter Gedeon Co., (-)-dihydroapovincaminic acid ethyl ester was prepared according to the procedure described in [11]. (S)- α,α -diphenyl-2-pyrrolidinemethanol was synthesized as described [12]. 2-Benzylidene-1-benzosuberone was prepared as described in [13]. Isophorone was supplied by Merck. Cinchonidine was purchased from Fluka.

2.2. Catalysts characterization

The support and the catalysts were characterized by means of nitrogen adsorption, XPS, TPD and SEM. The nitrogen adsorption isotherms were determined at 77 K in a Coulter Omnisorp 1000 CX equipment, and were analyzed by the BET equation (S_{BET}), and by the *t*-plot for mesopore surface area (S_{meso}) and micropore volume (V_{micro}), using the standard isotherm for carbon materials. The catalyst samples were previously outgassed at 120 °C.

The dispersion of the catalyst was measured by hydrogen chemisorption at 27 °C in the Coulter Omnisorp 100 CX equipment. The catalysts were subjected to an in situ reduction under hydrogen at 350 °C for 1 h before chemisorption



Scheme 2. Hydrogenation of 2-benzylidene-1-benzosuberone.

analysis. The palladium dispersion were calculated by assuming a stoichiometry of 1:1 (H: Pd).

The amount and type of surface functional groups of the carbon support were studied by temperature programmed desorption (TPD) in helium atmosphere. The analyses were carried out in a custom built set-up consisting of an U-shaped quartz tubular 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 CO₂ (m/z 44) products from the samples. XPS analysis was carried out in a VG Scientific ESCALAB 200A spectrometer using non-monochromatized Mg K α radiation (1253.6 eV) to determine the surface chemical composition of Pd catalyst on carbon. Basically, the Pd 3d⁵, 3d³ high-resolution spectrum was analysed for Pd oxidation states by deconvoluting the peaks with mixed Lorentzian–Gaussian functions.

The surface analysis for morphology and average particle size was carried out with JEOL JSM 6301 F scanning electron microscope (SEM). The micrographs of the samples were observed at different magnifications under different detection modes (secondary or back-scattered electrons).

2.3. Hydrogenation

The hydrogenations were carried out in a stainless steel autoclave with magnetic stirrer at room temperature and 50 bar hydrogen pressure. Before the hydrogenation, the reaction mixtures were stirred under nitrogen (2–3 bar) for 10 min in the reaction vessel.

The reaction mixtures of isophorone were analyzed with a gas chromatograph.

The working-up procedure of the reaction mixtures of the 2-benzyl-1-benzosuberone was the catalyst filtration and the removal of the solvent in vacuum. The residue was dissolved in dichloromethane and extracted with 5% HCl and

distilled water. The organic phase was separated and dried over Na₂SO₄. After filtration, the solvent was removed in vacuum. The product was analyzed by HPLC.

2.4. Analysis

The GC analyses were carried out with gas chromatograph equipped with a β -cyclodextrine capillary column (analysis temperature: dihydroisophorone at 110 °C) and FID. The chromatograms were recorded and peak areas were calculated with Chromatography Station for Windows CSW32[®] version 1.2 (DataApex Ltd. 2001, Prague).

The HPLC analyses were carried out on a Chiralcel OJ column (0.46 × 25 cm). The column contains silica-gel as packing material coated with a cellulose derivative. The eluent was hexan/2-propanol (90:10, v/v), the flow rate was 1.0 ml/min and the column pressure was 50 kg/cm². The UV-absorbance was measured at 249 nm.

Enantiomeric excesses (e.e.) were calculated according to the following equation:

$$\text{e.e. (\%)} = \frac{[A] - [B]}{[A] + [B]} \times 100$$

where [A] is the concentration of the major enantiomer and [B] is the concentration of the minor enantiomer.

3. Results and discussion

3.1. Characterization of the carbon and the Pd/C catalysts

Table 1 gives the textural properties of the support and catalyst samples. As expected the pore volumes and the surface areas of the catalysts are smaller than those of the support. This indicates that the palladium blocks some part of the surface of carbon.

The catalysts surface area and pore volume are similar, differences are within the experimental error.

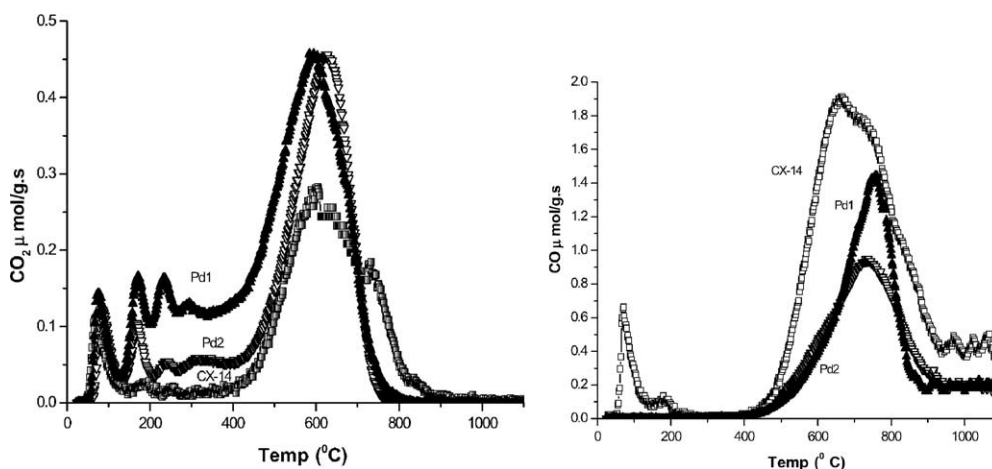


Fig. 1. Gas evolution profiles (CO₂ and CO) of support and catalysts (Pd1 is for Pd/C type 1, Pd2 is for Pd/C type 2).

Table 1
Textural properties of the samples

Sample	$S_{\text{BET}}^{\text{a}}$ (m ² /g)	$S_{\text{meso}}^{\text{b}}$ (m ² /g)	$V_{\text{micro}}^{\text{b}}$ (cm ³ /g)
CX-14	954	601	0.14
Pd/C type 1	797	496	0.12
Pd/C type 2	805	510	0.11

^a Calculated from the BET equation.

^b Calculated from the *t*-plot.

Table 2
Surface properties of the samples

Sample	CO (μmol/g)	CO ₂ (μmol/g)	ΔCO	ΔCO ₂
CX-14	6784	1023		
Pd/C type 1	3126	1606	−3658	+583
Pd/C type 2	2953	1155	−3821	+132

The adsorptive behavior of a carbon, as well as its catalytic and electrical properties, strongly depend on the nature and concentration of the oxygen-containing surface complexes [14]. The main characteristic of the TPD profiles (Fig. 1) of the catalyst can be a decrease or increase of the amount of surface oxygen-containing groups of the support oxidized in gas phase, expressed by ΔCO and ΔCO₂, the difference between the CO and CO₂ values of the support and those of corresponding catalysts (Table 2).

The TPD profiles indicate that the nature of the CO₂ and CO-generating groups are the same on the support and on the catalysts. All spectra exhibit a broad peak between 550 and 850 °C, assigned to anhydride and lactone type linkages generating CO₂, above 800 °C in case of CO assigned to quinone and ether groups.

The amount of the CO-yielding complexes decreased on the catalyst surface compared to the carbon support. It indi-

Table 3
Characterization of the catalysts by SEM and H₂ chemisorption

Pd/C catalyst	Reducing agent	Average particle size (nm)	Dispersion (%)
Type 1	HCOONa	≈500	8.40
Type 2	H ₂	≈50	30.58

cates that the palladium is attached to CO-generating groups. The increased concentration of CO₂-containing complexes on the catalysts surfaces can be explained by the preparation method.

In the preparation method, the support is put in suspension in water together with the Pd precursor and boiled. The anhydride groups suffer hydrolysis and are converted into carboxylic acids. During TPD, the anhydrides give one CO and one CO₂ peak, while the carboxylic acids give CO₂. Therefore, there will be an increase in CO₂ and the corresponding decrease in CO. Moreover, in the TPD spectra (Fig. 1 and Table 2) it can be observed that type 1 releases more CO₂ than type 2. This may be due to the use of HCOONa as a reducing agent (perhaps some formate remains on the carbon).

The reduction methods of precious metal precursors influence the particle size, the dispersion and the chemical composition of the catalyst. The results of SEM and H₂ chemisorption measurements are summarized in Table 3. The reduction of catalyst precursor with sodium formate resulted in a catalyst with lower dispersion than the one prepared by hydrogen reduction.

The XPS spectra display Pd 3d_{5/2} single peaks at 335.4 eV for catalyst type 1 and at 335.5 eV for type 2, corresponding to Pd(0). The surface composition of both the catalysts are identical in spite of their different reduction methods.

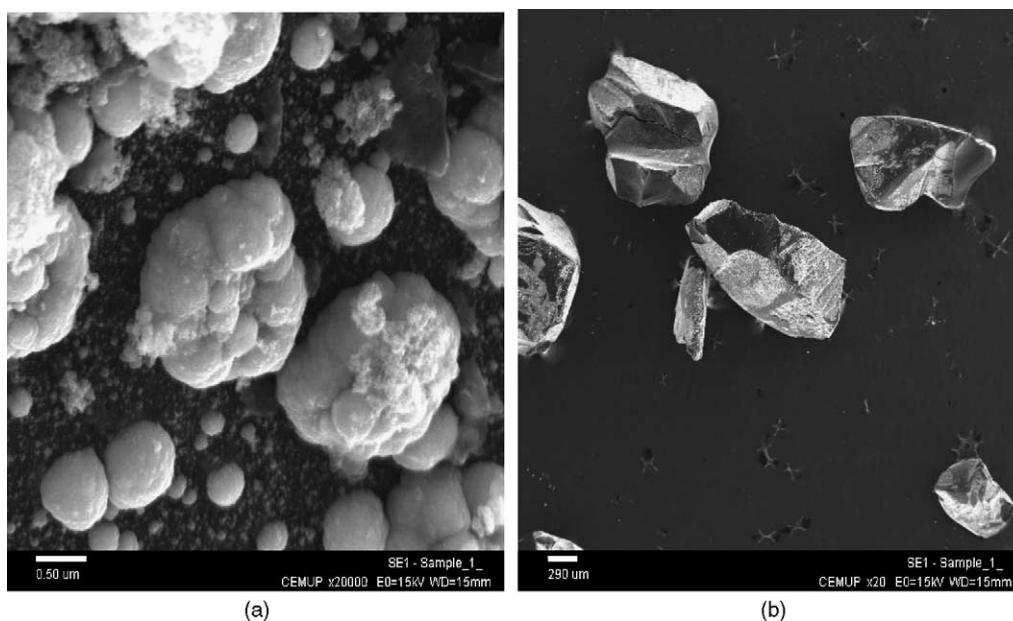


Fig. 2. The SEM pictures of Pd/C type 1 catalyst: (a) secondary mode, (b) back-scattered electron.

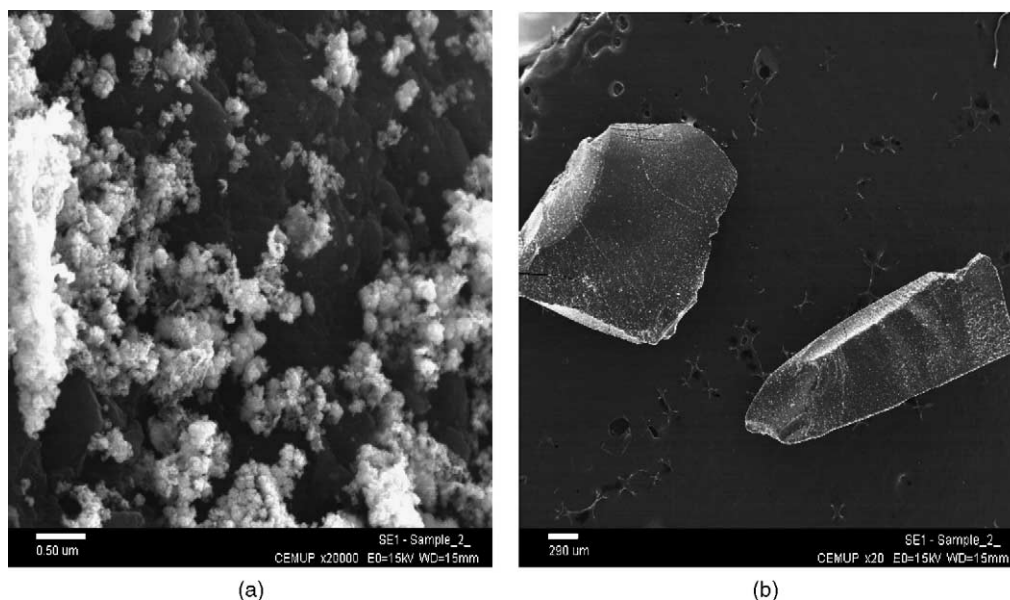


Fig. 3. The SEM pictures of Pd/C type 2 catalyst: (a) secondary mode, (b) back-scattered electron.

The micrographs of the samples Pd/C type 1 and Pd/C type 2 are shown in Figs. 2 and 3, respectively. The structure of the catalysts is rather uniform. The surface of the support is covered evenly by the palladium. The elementary palladium particles are stuck together to a big grain, their size is different, as can be seen in the figures, in the case of catalyst type 1 the particle size is 10× bigger than that of type 2.

3.2. Catalytic tests

The Pd catalysts on the highly mesoporous carbon support were tested in the enantioselective hydrogenation of isophorone (Scheme 1) and of 2-benzylidene-1-benzosuberone (Scheme 2). The enantioselectivities are summarized

in Table 4. The reaction conditions, the amount of modifiers, which were used in these experiments, were optimized earlier for Pd black catalyst [10,11,15].

The significant difference in the amount of (–)-DHVIN and DPPM chiral modifier is due to the fact that the optimal (–)-DHVIN/isophorone ratio was found to be 0.3 mol %, and for DPPM/isophorone this value was 1.4 mol %. For weighing the modifier calibrated solution was used. The results obtained at similar conversions for differently reduced catalysts and with a high dispersion ($D > 0.5$) Pd/C Selcat commercial catalyst are included in Table 4 for comparison. However the vinca alkaloid and the pyrrolidine derivative as modifiers ensured constant ee values in the total conversion range with all catalysts studied in this work and earlier also.

Table 4

The enantiomeric excesses in the enantioselective hydrogenation of isophorone and 2-benzyl-1-benzosuberone on highly mesoporous carbon supported Pd catalysts

Substrate	Modifier	Catalyst	Reaction time (h)	Conversion (%)	e.e. (%)
Isophorone ^a	(–)-DHVIN	Type 1	4	85	14 (R)
			6	100	14
		Type 2	2	89	10 (R)
		Pd/C selcat	7.5	87	10 (R) [2]
Isophorone ^b	DPPM	Type 1	6	100	33 (S)
		Type 2	6	100	14 (S)
		Pd/C selcat	4	100	10 (S) [9]
2-Benzyl-1-benzosuberone ^c	CD	Type 1	3	80	20 (S)
			5	100	20
		Type 2	5	82	27 (S)
		Pd/C selcat	5	100	0

^a Reaction conditions: 0.35 g isophorone, 0.02 g catalyst, 0.005 g AcOH, 0.001 g (–)-DHVIN, 3 ml MeOH.

^b Reaction conditions: 0.35 g isophorone, 0.02 g catalyst, 0.01 g DPPM, 1.5 ml MeOH, 1.5 ml water.

^c Reaction conditions: 0.25 g 2-benzyl-1-benzosuberone, 0.025 g catalyst, 0.00125 g cinchonidine, 10 ml toluene, 25 °C, 50 bar.

4. Conclusion

The smaller BET surface area values of the catalysts indicate that the palladium blocks some part of the surface of this mesoporous carbon.

The decreased amount of the CO-yielding complexes on the catalyst surface compared to that of the carbon support indicates that the palladium is attached to CO-generating groups.

The reduction of the catalyst precursor with sodium formate resulted in a lower Pd dispersion than the catalyst prepared by hydrogen reduction, the particle size of the former catalyst is 10× larger.

The highly mesoporous carbon supported Pd catalysts afforded higher e.e. than the more dispersed commercial Pd/C catalyst [2,9]. Even these enantioselectivities are about one half of the optical purities obtained with Pd black catalysts [4,15]. The mesoporous carbon supported Pd catalysts are near to those of Pd on titania with respect to their enantiodifferentiating ability, but not competitive with Pd black.

In the hydrogenation of isophorone the catalyst type 1 of smaller dispersion resulted in higher enantiomeric excesses especially with DPPM modifier. In the hydrogenation of 2-benzylidene-1-benzosuberone the catalyst type 2 of higher dispersion was more enantioselective. These reverse tendencies or smaller relative difference in e.e. for the latter reaction can be attributed to the use of modifiers with totally different structure and working mode. The interesting properties of the mesoporous carbon supported Pd needs further studies, among others because the reaction conditions were not optimized for these catalysts.

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