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Enantioselective hydrogenation of isophorone over Pd catalysts in the presence of (–)-dihydroapovincaminic acid ethyl ester The effect of reduction method of Pd blacks on the enantiomeric excess

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Abstract

The enantioselective heterogeneous catalytic hydrogenation of isophorone in the presence of apovincaminic acid ethyl ester was investigated. Various Pd black catalysts differing in their preparation method were studied. The catalysts were characterized by different methods such as physical adsorption and chemisorption, SEM and XPS. An explanation was created for the different enantioselectivity of the catalysts being precipitated by different reducing agents. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Pd black catalysts; Enantioselective hydrogenation; Isophorone

1. Introduction

In earlier publications we reported about the enantioselective hydrogenation of the C=C double bond of isophorone [1–4]. The best results were achieved in the system that consists of (–)-dihydroapovincaminic acid ethyl ester as chiral modifier and Pd black catalyst reduced with sodium-formate [1]. This reaction was studied in detail for understanding the catalyst-modifier-substrate-interactions occurring during the reaction. The effect of the structure of the modifier on the enantioselectivity was studied, which

parts of the molecule are crucial for the selective reaction [2]. The other aspect of the investigations was how does the structure of the catalyst influence the enantioselectivity of the reaction. The enantioselectivity of supported Pd catalysts (Pd/C and Pd/TiO₂) depended on the support used, it turned out that lower surface area of the support and smaller dispersion of the active metal are advantageous [4].

Enantioselectivity is very sensitive to the method of catalyst preparation, this is valid for the most effective modified catalytic systems: Pt/chinonidine and Raney-Ni/tartaric acid [5,6].

Previously we reported that the preparation method of Pd black catalyst affects the enantioselectivity in the hydrogenation of isophorone [4], but the correlation between enantioselectivity and the structure or

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the state of the catalyst surface itself has not been reported yet. The objective of this study was to explore with the characterization of the catalysts the relation between the surface properties of the Pd black catalysts and their enantioselectivity, how to prepare the best Pd black catalyst by different reduction methods, and to determine the effect of drying on air.

2. Experimental

2.1. Materials

Pd black catalysts were prepared according to the following procedure: 18 mmol (6.0 g) K_2PdCl_4 was dissolved in 100 ml water and reduced at boiling point with different reducing agents dissolved in 20 ml water. In the case of catalyst 1, the pH of the solution during the preparation was basic, and the whole amount of the reducing agent (HCOONa) was added at the beginning of the reaction. For type 2 catalyst, an equimolar amount of HCOONa was used, and at the end of the reduction the pH was acidic. For type 3 catalyst, the solution was basic like type 1, but the HCOONa was added drop by drop. Type 4 catalyst was reduced with $NaBH_4$, type 5 with hydrazine. The other method comprised, after similar preparation steps, the reduction of $Pd(OH)_2$ precursor with H_2 in water on 5 bar in a stainless autoclave with magnetic stirrer (type 6). All six catalysts were filtered and washed several times with distilled water until the water became neutral, and divided into two parts: A type catalysts were dried in air, B type catalysts were stored under water, and added wet to the reaction mixture. Apovincaminic acid ethyl ester was supplied by Richter Gedeon Co.

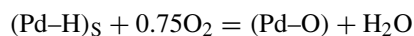
2.2. Catalysts characterizations

Adsorption measurements were made in an atmospheric flow system [10,11] in order to determine the number of surface sites on the Pd black samples. Four types of measurements were made: O_2 titration, H_2 titration, O_2 titration again and direct CO adsorption in H_2 carrier gas. Prior to the first adsorption of O_2 , the sample was treated in 1.2% H_2/Ar for 15 min and then in Ar gas to remove β -PdH, in order to avoid hydrogen absorption into the bulk phase of the metal.

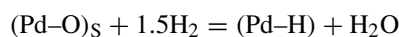
$(Pd-H)_S$ was titrated with O_2 injections via a calibrated loop (0.1 ml each). Next $(Pd-O)_S$ was titrated with H_2 . After decomposition of β -PdH O_2 was adsorbed again. Finally, Ar stream was replaced with H_2 and CO adsorption was recorded. The number of surface sites was calculated considering the accepted stoichiometry of these surface reactions.

The stoichiometry calculations were based on the following:

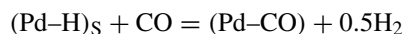
for titration with O_2



for titration with H_2



for CO adsorption



XPS tests were conducted in order to determine the surface chemical composition of Pd black catalysts.

The tests were performed with a VG Scientific ESCALAB 200 A spectrometer utilizing a non-monochromatized Mg K α radiation (1253.6 eV). The vacuum in the analysis chamber was always $<1 \times 10^{-7}$ Pa. The catalysts were observed by SEM (JEOL JSM 6301 F) to determine the particle size and the morphology of the catalysts.

The BET surface areas were determined by N_2 adsorption at 77 K with an equipment Coulter Omnisorp 100 CX by continuous flow techniques.

2.3. Hydrogenation

The hydrogenation of isophorone was carried out at 25°C and under 50 bar hydrogen pressure in a Büchi Bep 280 autoclave equipped with a magnetically driven turbine stirrer and a gas-flow controlling and measuring unit. Before hydrogenation, the reaction mixtures were stirred under nitrogen for 15 min in the reaction vessel. The water content of methanol was optimized because in the absence of water isophorone diacetal formation was observed, the reaction rate decreased and the ee moderated. The optimal water content of the methanol for this reaction was found to be between 3 and 10 vol.%.

The reaction mixtures were analyzed with a gas chromatograph equipped with a β -cyclodextrin capil-

Table 1
Characterization of the catalyst by XPS, SEM and N₂ adsorption

Pd black catalysts	Reducing agent	Atomic ratio (%)			Particle size (nm)	S _{BET} (m ² /g)
		Pd	PdO	PdCl ₂		
1	HCOONa in excess	50.0	34.5	15.5	50–100	5.7
2	HCOONa stoichiometric	50.0	30.0	20.0	100–150	6.0
3	HCOONa drop by drop	50.1	32.9	16.2	≤50	14.4
4	NaBH ₄	51.0	34.9	14.0	≤50	6.0
5	NH ₂ NH ₂	54.8	33.5	11.6	70–100	7.0
6	H ₂	78.1	14.5	7.3	230–450	1.7

lary column (analysis temperature: dihydroisophorone at 110°C) and FID. The chromatograms were recorded and peak areas were calculated with Chromatography Station for Windows V1.6 (DataApex Ltd., Prague).

The enantiomeric excess was defined as

$$ee (\%) = \left(\frac{[R] - [S]}{[R] + [S]} \right) \times 100$$

3. Results and discussion

3.1. Characterization of Pd blacks

The reduction method of precious metal precursors influence the surface area, the particle size and the chemical composition of the catalysts. The results of XPS, SEM and N₂ adsorption measurements are summarized in Table 1.

As the XPS measurements indicate, catalyst 6 (reduced with H₂) has the highest ratio of metallic Pd phase on its surface (Table 1). It means that most of the active sites were formed during the catalyst preparation, not during in situ reduction, in the enantioselective

reaction. The results of adsorption measurements are summarized in Table 2.

The dispersion data were calculated from the CO gas adsorption measurements. As expected, the values were rather small and uniform. Only the dispersion of catalyst 3 was twice that of the others, and the dispersion of catalyst 6 was much smaller.

The amounts of different gases adsorbed on the catalysts were similar, and there was no important difference in the number of active sites on the catalyst surfaces (see Table 2) determined by these small molecules.

The S_{ads} surfaces were calculated from the titration data and are in good agreement with the S_{BET} measurements.

The number of active sites of a used catalyst was measured in order to compare the active surface area, and there was no significant difference from the original catalyst.

3.2. SEM measurements

Figs. 2–5 show the SEM pictures of some of the Pd black catalysts. The structure of the different catalysts

Table 2
Number of the active sites on the catalysts surface and the calculated surface area

Sample	(Pd–H) _S O ₂ (T)	(Pd–O) _S H ₂ (T) mol (Pd–X)/g	(Pd–H) _S O ₂ (T) Pd black	(Pd–CO) _S CO (A)	D	S _{ads} (m ² /g)
1	1.36 × 10 ⁻⁴	1.37 × 10 ⁻⁴	1.30 × 10 ⁻⁴	n.m.	0.014	6.7
2	1.07 × 10 ⁻⁴	1.23 × 10 ⁻⁴	1.11 × 10 ⁻⁴	8.57 × 10 ⁻⁵	0.009	6.0
3	2.24 × 10 ⁻⁴	1.97 × 10 ⁻⁴	2.24 × 10 ⁻⁴	2.15 × 10 ⁻⁴	0.022	11.3
4	1.08 × 10 ⁻⁴	1.23 × 10 ⁻⁴	1.19 × 10 ⁻⁴	1.23 × 10 ⁻⁴	0.013	6.0
5	1.41 × 10 ⁻⁴	1.53 × 10 ⁻⁴	1.41 × 10 ⁻⁴	1.32 × 10 ⁻⁴	0.014	7.0
6	8.3 × 10 ⁻⁶	1.56 × 10 ⁻⁵	1.50 × 10 ⁻⁵	8.5 × 10 ⁻⁶	0.0009	0.6
After reaction	1.11 × 10 ⁻⁴	1.20 × 10 ⁻⁴	1.05 × 10 ⁻⁴	1.01 × 10 ⁻⁴	0.011	–

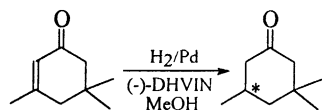


Fig. 1. Hydrogenation of isophorone.

is rather uniform. The elementary palladium particles are stuck together to a big grain forming a structure like a sponge. The elementary particle sizes are different, as can be seen in the figures, in the case of catalyst 1 the particle size diameter is approx. 50 nm, in the case of catalyst 5 approx. 270 nm.

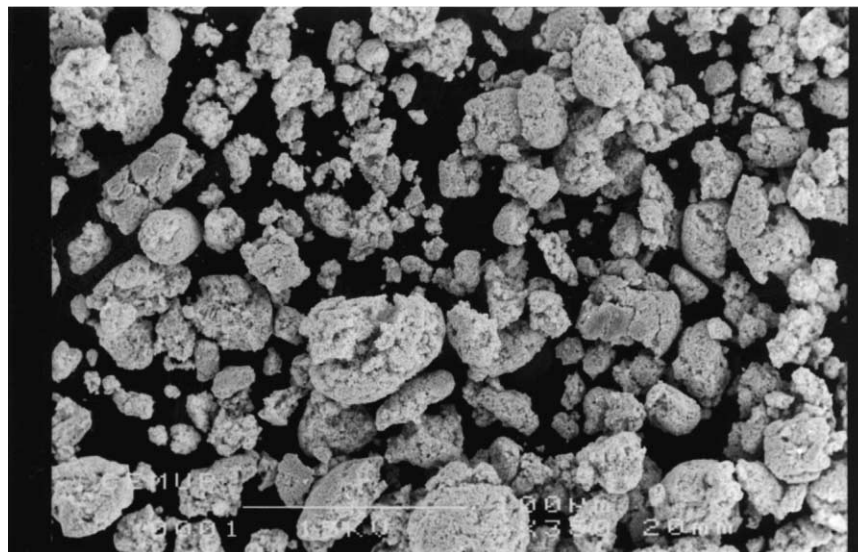


Fig. 2. The SEM picture of catalyst 3.

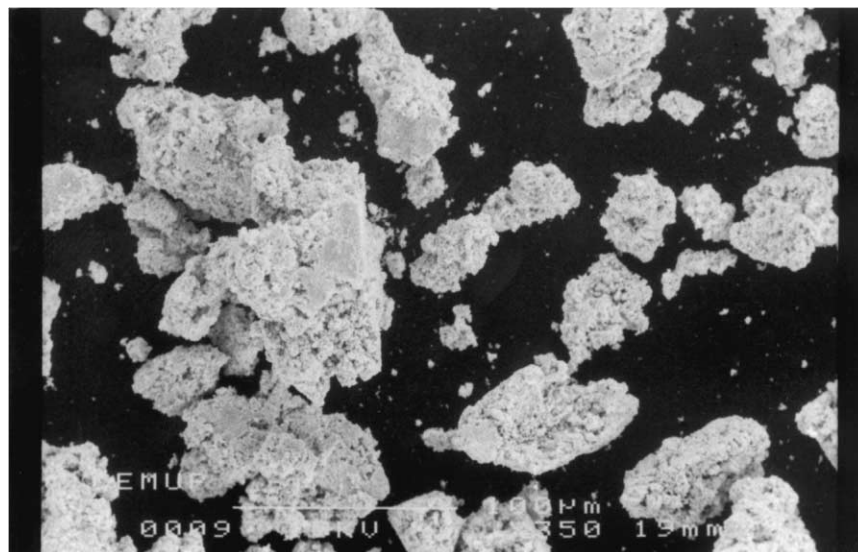


Fig. 3. The SEM picture of catalyst 4.

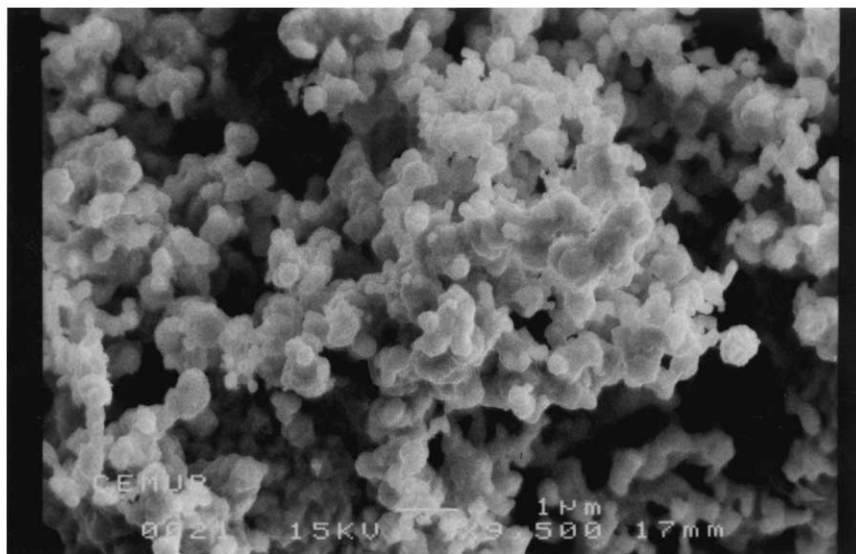


Fig. 4. The SEM picture of catalyst 6.

3.3. Catalytic tests

The Pd black catalysts prepared with different reduction methods were tested in the enantioselective hydrogenation of isophorone (Fig. 1).

The enantioselectivities of the catalyst prepared with different methods are summarized in Table 3. The reaction conditions were optimized earlier [1].

Catalyst 1 gives the best enantioselectivity, 50% of R-(–)-dihydroisophorone. Therefore, it seems that the

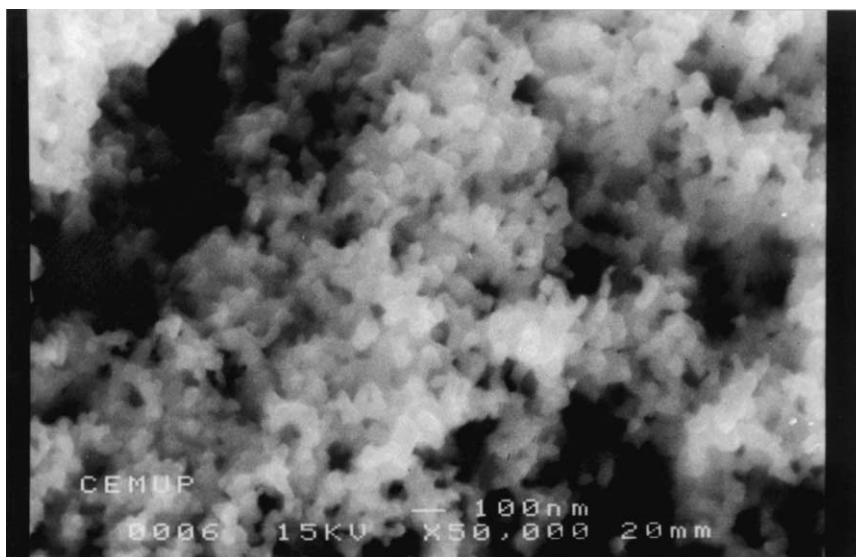


Fig. 5. The SEM picture of catalyst 1.

Table 3
The enantiomeric excess on different Pd black catalysts^a

Pd black catalyst (reducing agent)	Type	Reaction time (h)	Conversion (%)	Enantiomeric excess (%)
1 (HCOONa) low S_{BET}	A	6	100	50
	B	7	100	23
2 (HCOONa) acidic	A	7.5	100	25
	B	8	100	20
3 (HCOONa) high S_{BET}	A	8	81	24
	B	6	–	–
4 (NaBH ₄)	A	5	100	30
	B	6	75	23
5 (NH ₂ NH ₂)	A	6.5	100	40
	B	7	33	28
6 (H ₂)	A	7	80	24

^a Conditions: 0.05 mol isophorone, 0.02 g (–)-DHVIN, 0.2 g AcOH, 50 ml methanol, 50 bar, 25°C.

best reducing agent is the HCOONa. With respect to the other reduction methods, the catalyst made with hydrazine gave also a proper ee, but the catalyst prepared with hydrogen in the liquid phase showed reduced activity and enantioselectivity.

However, the reducing agent is not the only factor, since the catalysts types 2 and 3 were prepared also with Na-formate and the optical purity in this case was only half of the former catalyst. Types 1 and 3 catalysts were prepared with the same stoichiometry of the reactants, but according to the preparation method catalyst type 1 has much lower surface area and dispersion, so the enantioselectivity depends on the surface area, and in this reaction surface area and dispersion do not influence much the catalyst activity. In the case of the catalysts 1 and 3, the catalyst with low surface area gave better enantioselectivity. It seems that a surface area around 6–7 m²/g is advantageous for enantioselectivity. Much higher and much lower surface areas do not influence the enantioselectivity in the right way. Our earlier investigations with the Pd/C catalyst in isophorone hydrogenation gave the same results, namely the lower dispersion is advantageous for the ee, or the dispersion has an optimal extent [4].

In the often studied enantioselective hydrogenation of α -ketoesters using cinchona modified platinum catalyst, Wells and co-workers found that an elaborate aerobic modification procedure of the catalyst with the modifier molecule in ethanol led to much better enantioselectivity than the anaerobic one [7]. Additional explanations were offered for the role of oxygen [8,9]. In our experiments we used the prepared Pd black cat-

alyst in two ways: dried in air atmosphere, and stored under water to exclude air. The results indicate that dried catalysts give higher enantioselectivity and have better activity. This observation is significant for all types of catalyst. In this case, when the catalyst is dried in air, the surface is oxidized and the catalyst become active during the reaction by the presence of hydrogen. As the air was excluded from the catalysts type B, there was no oxidation and reduction step in the presence of the reactants. In our earlier paper we reported that the in situ reduction of the catalysts in the presence of the substrate and the modifier is advantageous for the ee.

4. Conclusion

The methods used for the preparation of Pd black catalysts have strong influence on the enantiomeric excess. Among the catalysts prepared with the same reducing agent, the catalyst with lower surface area was more effective. The surface chemistry affected the optical yield also. The results show unequivocally that the in situ reduction of the catalysts by the presence of the substrate and the modifier is crucial for the enantiodifferentiation process.

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