# Enantioselective hydrogenation of isophorone with titania supported Pd catalysts modified by (−)-dihydroapovincaminic acid ethyl ester effect of the support and the reduction method

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## Abstract

Enantioselective hydrogenation of isophorone was investigated over Pd/TiO$_2$ catalysts in the presence of (−)-dihydroapovincaminic acid ethyl ester. The used supports were different in crystalline form and in surface area. The influence of the catalyst preparation method on the optical purity was studied. The catalysts were characterized by H$_2$ adsorption and SEM. © 2002 Elsevier Science B.V. All rights reserved.

## 1. Introduction

The enantioselective hydrogenation of the C=C double bond of isophorone over Pd catalysts modified with (−)-dihydroapovincaminic acid ethyl ester has been studied in our laboratory and published in the literature [1–6]. The effect of different catalyst supports (C, TiO$_2$, SiO$_2$, Al$_2$O$_3$, BaSO$_4$) on the enantiomeric excess was investigated and it turned out that the enantioselectivity strongly depended on the type and specific surface area of the support [1,2]. Hydrogenation with Pd black catalyst afforded the best enantioselectivities (up to 55%). A correlation was found between the valence state of the catalyst surface and the enantioselectivity, the

catalyst having more oxidized species on its surface gave higher enantiomeric excess. The Pd black with lower surface area was more stereoselective [6].

In the first series of investigation the Pd on carbon catalyst gave poor enantiomeric excess (ee), in order to find out the reason of this phenomenon, Pd on different types of carbon supports have been screened [5]. The surface chemistry of carbon did not affect much the enantioselectivity. The surface area of the used carbon supports were quite different, those with much lower surface area were better with respect to the optical yield. The preparation method of the catalyst, as it influenced the dispersion of the metal, affected also the enantiomeric excess.

Enantioselectivity is very sensitive to the method of catalyst preparation, this is valid for the most effective modified catalytic systems: Pt/chinconidine and Raney-Ni/tartaric acid [7,8].

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The best enantioselectivity among supported catalysts was given by Pd/TiO$_2$ catalyst (40%) [1]. In this paper, the influence of titania support and the deposition method of Pd on enantioselectivity was investigated. Rutile and anatase form of TiO$_2$ as support materials were used, the latter with different BET surface area.

## 2. Experimental

### 2.1. Materials

The catalysts were prepared using anatase and rutile form of TiO$_2$ as the support materials. The XRD analysis showed, that starting TiO$_2$ (P25 Degussa and Aldrich) was anatase form. The rutile form was prepared by heat-treating of Aldrich TiO$_2$ at 1100 °C for half an hour.

An amount of 5 wt.% Pd on Aldrich anatase ($S_{BET} = 8 \, m^2/g$) and on rutile, 10 wt.% Pd on P25 Degussa anatase (Fig. 1) ($S_{BET} = 50 \, m^2/g$) were prepared as follows. The calculated amount of the K$_2$PdCl$_4$ 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) and NaBH$_4$ (type 2))

was added to the boiling mixture. After half an hour, the suspension was cooled, the catalyst was filtered and washed with distilled water. Half of all catalyst samples (marked with "t") were heat treated for 2 h in 10 l/h hydrogen stream at 200 °C in a glass reactor. The other method comprised, after similar preparation steps, the reduction of Pd(OH)$_2$ precursor with H$_2$ gas at 200 °C over a period of 4 h (type 3).

Apovincaminic acid ethyl ester was supplied by Gedeon Richter Co., (−)-dihydroapovincaminic acid ethyl ester was prepared according to the procedure described in [9]. Isophorone was supplied by Merck.

### 2.2. Catalysts characterization

Most of samples were characterized by H$_2$ adsorption at room temperature. In these tests, the sample was placed in the sample holder of the TPD system and was subjected to H$_2$ injections via a calibrated loop, following a degassing under a flow of He. The purity of H$_2$ was 99.9995%. Data were acquired by mass spectrometry. In adsorption experiments, a He flow-rate of 20 ml/min was used. The stoichiometry of the adsorption and the dispersion calculations were based on the following reaction:

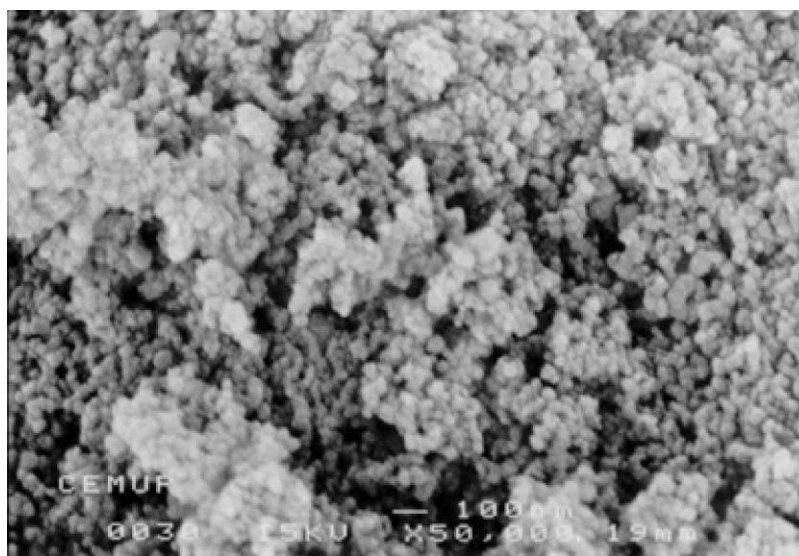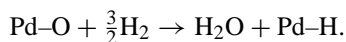$$Pd-O + \tfrac{3}{2}H_2 \rightarrow H_2O + Pd-H.$$



Fig. 1. The SEM picture of the catalyst on P25 Degussa anatase support.

The catalysts were observed by SEM (JEOL JSM 6301 F) to determine the morphology of the catalysts.

### 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 the hydrogenation, the reaction mixtures were stirred under nitrogen for 15 min in the reaction vessel.

The reaction mixtures were analyzed with a gas chromatograph equipped with a 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 V1.6 (DataApex Ltd., Prague). Enantiomeric excess (%) was defined as

$$ee = \frac{[R] - [S]}{[R] + [S]} \times 100.$$

## 3. Results and discussion

### 3.1. Characterization of Pd/TiO$_2$ catalysts

The results of H$_2$ adsorption measurements are summarized in Table 1. The preparation of catalysts with good dispersion on Aldrich anatase and rutile supports was not possible because of the very small specific surface area of these supports. The size of Pd particles on low surface area supports is much bigger than the size of catalyst particles prepared on support with higher specific surface area. The heat treatment decreased the catalyst dispersion, in the case of the rutile support more than in the case of P25 Degussa support. The catalyst with best dispersion was prepared by H$_2$ reduction on the anatase support with higher specific surface area. There is no important difference between the dispersion values of catalysts prepared by formate and boronhydride reduction. The structure of the supports and the catalysts was determined by SEM.

Fig. 2 shows the Aldrich anatase support in 50,000× magnification. The distribution of the particle size is even. Fig. 3 shows the catalyst on rutile support prepared by H$_2$ reduction. The magnification is here 10,000×. It is observable that the particle size of rutile is bigger than that of anatase and the form of the particles are uneven.

The surface of the rutile support is not covered evenly by the Pd (Fig. 3), but the metal are attached to the support particles like a mixture of the support and the metal, as Pd black. It is not possible to speak about supported catalyst in this case.

Figure 1 shows the 10% Pd/TiO$_2$ catalyst prepared on the support with higher specific surface area (50 m$^2$) in 50,000× magnification. The particle size of support is much smaller in this case and the particle size distribution is even. The active metal covers really the support surface, it does not form an other phase.

### 3.2. Catalytic tests

The catalysts prepared on the different TiO$_2$ supports with different reduction methods were tested

Table 1
Characterization of the catalysts by H$_2$ adsorption

| Type of reduction | Support | Dispersion | $S_M$ (m$^2$/g)[a] | $d_l$ (nm)[a] |
|---|---|---|---|---|
| 10% Pd/TiO$_2$ catalysts | | | | |
| 1 (NaOOCH) | P25 Degussa anatase ($S_{BET} = 50$ m$^2$/g) | 0.41 | 18.7 | 2.7 |
| 1 + t | P25 Degussa anatase ($S_{BET} = 50$ m$^2$/g) | 0.31 | 13.9 | 3.6 |
| 2 (NaBH$_4$) | P25 Degussa anatase ($S_{BET} = 50$ m$^2$/g) | 0.34 | 15.1 | 3.3 |
| 2 + t | P25 Degussa anatase ($S_{BET} = 50$ m$^2$/g) | 0.31 | 13.9 | 3.6 |
| 3 (H$_2$) | P25 Degussa anatase ($S_{BET} = 50$ m$^2$/g) | 0.58 | 25.9 | 1.9 |
| 5% Pd/TiO$_2$ catalysts | | | | |
| 1 | Aldrich anatase ($S_{BET} = 8$ m$^2$/g) | 0.15 | 3.4 | 7.1 |
| 1 + t | Aldrich anatase ($S_{BET} = 8$ m$^2$/g) | 0.024 | 0.8 | 31.1 |
| 3 | Rutile | 0.063 | 1.4 | 17.8 |

[a] $S_M$: metal specific surface area, $d_l$: average particle size of the catalyst.
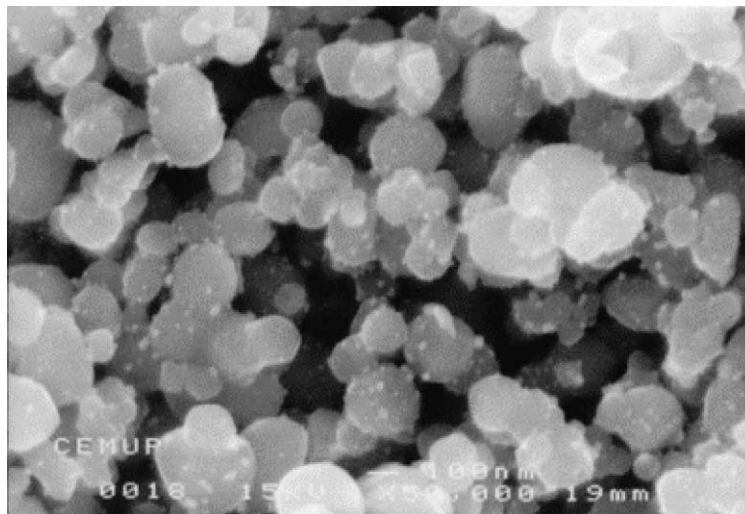
Fig. 2. The SEM picture of the Aldrich anatase support.

in the enantioselective hydrogenation of isophorone (Scheme 1). The enantioselectivities are listed in Table 2.

The reactions were followed with pressure drop measurements and were stopped when no hydrogen consumption could be observed.

The 10% Pd/TiO$_2$ catalysts are more active catalysts in the hydrogenation of isophorone than Pd black
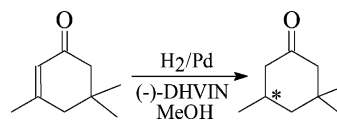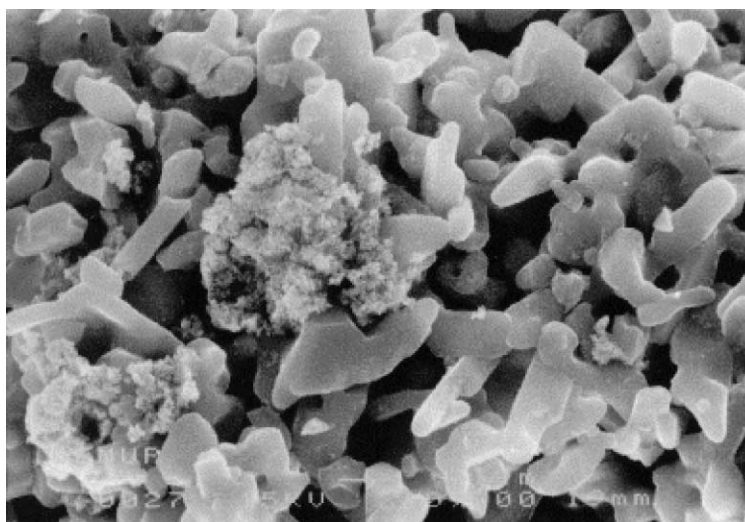


Scheme 1. Hydrogenation of isophorone.



Fig. 3. The SEM picture of the catalyst on rutile support.

Table 2
The enantiomeric excess on different Pd/TiO$_2$ catalysts[a]

| Support | Type of reduction | Reaction time (h) | Conversion (%) | Enantiomeric excess (%) |
|---|---|---|---|---|
| P25 Degussa anatase ($S_{BET} = 50\,m^2/g$) | 1 (NaOOCH) | 1.5 | 100 | 25 |
| | 1 + t | 2 | 100 | 27 |
| | 2 (NaBH$_4$) | 2 | 100 | 20 |
| | 2 + t | 3 | 100 | 17 |
| | 3 (H$_2$) | 1.5 | 100 | 14 |
| Aldrich anatase | 1 | 10 | 94 | 23 |
| | 1 + t | 5.5 | 93 | 16 |
| | 2 | 5 | 64 | 27 |
| | 2 + t | 5 | 48 | 26 |
| | 3 | 8 | 58 | 31 |
| Rutile from Aldrich anatase | 1 | 8 | 50 | 29 |
| | 1 + t | 8 | 37 | 15 |
| | 2 | 5.5 | 62 | 31 |
| | 2 + t | 6 | 18 | 24 |
| | 3 | 4 | 70 | 21 |

[a] Reaction conditions: 0.025 mol isophorone, 0.5 g Pd/TiO$_2$, 0.25 g AcOH, 0.05 g (−)-DHVIN, 30 ml methanol, 25 °C, 50 bar.

catalysts [6], but they have lower activity than the Pd/C catalysts [5]. Among the 10% Pd/TiO$_2$ catalysts the best enantioselectivity was achieved on the heat treated catalyst, reduced with NaOOCH (1 + t). The heat treatment did not influence significantly the enantioselectivity, but it decreased the activity. The catalyst made by H$_2$ reduction gave the lowest optical purity.

The activity of 5% Pd catalysts prepared on the supports with low surface area was small. The optical purity depended mainly on the preparation method, but was not dependent on the structure of the support. The catalyst on anatase support reduced with H$_2$ and on rutile support reduced with NaBH$_4$ afforded the best enantioselectivities (31%), however the differences between the non-heat treated catalysts are not significant.

## 4. Conclusion

The preparation methods of Pd/TiO$_2$ catalysts influenced the dispersion of the metal and the enantiomeric excess. The crystal forms of the support had not much effect. The low specific surface area of the support was advantageous with respect to the opti-

cal yield. The SEM measurements proved that these catalysts are like a mechanical mixture of the Pd and the support, so the metal has a structure which is similar to that of Pd black.

## References

[1] T. Tarnai, A. Tungler, T. Máthé, J. Petró, R.A. Sheldon, G. Tóth, J. Mol. Catal. 102 (1995) 41.
[2] A. Tungler, T. Máthé, K. Fodor, R.A. Sheldon, P. Gallezott, J. Mol. Catal. A 108 (1996) 145.

[3] G. Farkas, K. Fodor, A. Tungler, T. Máthé, G. Tóth, R.A. Sheldon, J. Mol. Catal. 138 (1999) 123.

[4] A. Tungler, Y. Nitta, K. Fodor, G. Farkas, T. Máthé, J. Mol. Catal. 149 (1999) 135.

[5] M.M.A. Freitas, J.L. Faria, G. Farkas, T. Máthé, J. Mol. Catal. 153 (2000) 215.

[6] G. Farkas, É. Sípos, A. Tungler, A. Sárkány, J.L. Figueiredo, J. Mol. Catal. A 2963 (2000) 1–7.

[7] Y. Nitta, F. Sekine, T. Imanaka, S. Teranishi, J. Catal. 74 (1982) 382.

[8] H.U. Blaser, H.P. Jalett, M. Müller, M. Struder, Catal. Today 37 (1997) 441.

[9] A. Tungler, T. Máthé, T. Tarnai, K. Fodor, G. Tóth, J. Kajtár, I. Kolossváry, B. Herényi, R.A. Sheldon, Tetrahedron: Asymmetry 6 (9) (1995) 2395–2402.