

# Highly Selective Mono-hydrogenation of Dicyclopentadiene with Pd-nanoparticles

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Received: 30 October 2012 / Accepted: 10 January 2013 / Published online: 24 January 2013  
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**Abstract** In this paper, we present a new protocol to synthesize dihydrodicyclopentadienes (DHDCP), via mono hydrogenation of dicyclopentadiene. With the use of Pd-nanoparticles as catalysts the products are formed highly selective under mild conditions. The ratio between the DHDCP and the tetrahydrodicyclopentadiene (THDCP) can be shifted by variation of the hydrogen pressure from 7:1 to 1:8, with high conversions of over 85 %. The product DHDCP is an essential building block in co-polymerizations. Also we show an easy recycling concept for the nanocatalyst by phase separation. With simple filtration the solid products DHDCP and THDCP can be isolated and the liquid catalyst phase can directly be reused. Over all recycling runs a steady high conversion of about 75 % was observed.

**Keywords** Dicyclopentadiene · Homogeneous catalysis · Hydrogenation · Nanoparticles · Palladium

## 1 Introduction

Dicyclopentadiene (**1**), which is an important component of the C<sub>5</sub>-fraction of the steamcracker [1–3], can be hydrogenated to valuable products, the two dihydrodicyclopentadienes (**2a** + **2b**) and tetrahydrodicyclopentadiene (**3**) (Fig. 1).

**Electronic supplementary material** The online version of this article (doi:10.1007/s10562-013-0960-3) contains supplementary material, which is available to authorized users.

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There are already different applications for these products in the market. THDCP is used for the synthesis of aircraft fuels [4, 5]. Another application is the skeletal isomerization with strong Lewis acids to adamantane [6]. DHDCP can be a starting material for flavors and can be used as comonomer in polymerization reactions, for example in the production of a low density ethylene copolymer [7]. Using DHDCP in ring-opening metathesis polymerization, linear polymers with a well-controlled linearity can be synthesized [8].

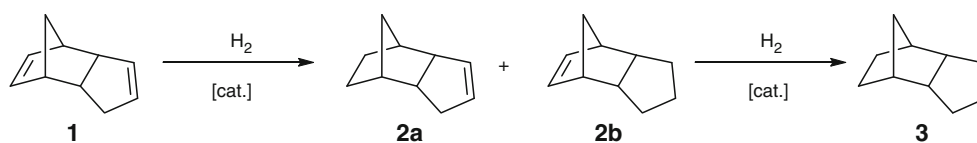
Until now there are only a few publications describing the synthesis of **2a** and **2b**. In 1983 Degenhardt et al. [9, 10] investigated the selective synthesis of compound **2b**. Normally the formation of **2a** is preferred because the ring-tension of the norbornene double bond is more energy-rich. Therefore Degenhardt protected the norbornene double bond with an iron-complex. After the hydrogenation, the protection group was removed by acetone and sodium iodide.

However, reaction sequences with protecting groups are not favorable for industrial processes.

In a patent by Lyondell [7], palladium is applied as a catalyst at temperatures of 50–150 °C. Approximately 80 weight-% of dicyclopentadiene was converted to DHDCP and 20 % to THDCP. A differentiation between the two products **2a** and **2b** is not given.

Antonova et al. [11] tested Pd, Pt, Rh and Ru catalysts in different solvents to hydrogenate dicyclopentadiene. They announced yields of DHDCP of 80 % and THDCP of 7 % and trace amounts of dicyclopentadiene. Also in this publication the authors did not differ between **2a** and **2b**.

In the hydrogenation of dicyclopentadiene to THDCP transition metals like Pd [12, 13], Rh [14] and Ni [4] can be used. Palladium is one of the best catalytic metals for hydrogenation [15, 16]. We decided to use palladium



**Fig. 1** Synthesis of dihydrodicyclopentadienes (DHDCP, **2a** and **2b**) and tetrahydrodicyclopentadiene (THDCP, **3**)

nanoparticles because colloidal palladium can absorb hydrogen, at room temperature, up to 3,000 times of its own volume [17]. The use of different kinds of nanoparticles for hydrogenations with remarkable selectivity effects have already been described [13, 18–25]. Behr et al. [26, 27] obtained interesting results in the selective hydrogenation of alkynes and dienes. We investigated the hydrogenation of dicyclopentadiene with nanocatalysts with the aim to proceed this reaction with high selectivity for mono-hydrogenation. The main aim of this investigation was the selective synthesis of mixtures of **2a** and **2b**, without formation of greater amounts of product **3**.

## 2 Experimental

### 2.1 Preparation of the Pd Nanocatalyst Solution

For generating the Pd nanocatalyst solution 19.1 mg (0.085 mmol) Pd(OAc)<sub>2</sub> was dissolved in 86.77 g (0.85 mol) propylene carbonate, after that the solution was transferred in a 300 mL stainless steel autoclave and charged with 5 bar hydrogen pressure. The solution was stirred at 500 rpm and 80 °C for 2 h, after cooling and venting surplus hydrogen the now black solution of Pd nanoparticles is ready to use. Using this protocol we generated a solution of 100 ppm Pd nanoparticles in propylene

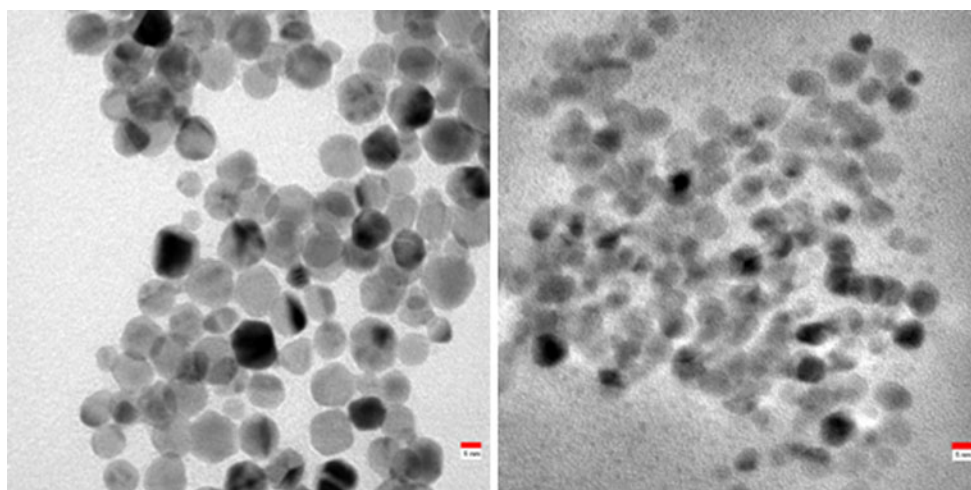
carbonate. Nanocatalyst solutions of other solvents like cyclopentanone are generated on an equal way.

TEM images (see Fig. 2) show that there are Pd particles of about 7 nm for Pd in propylene carbonate and of about 5 nm for Pd in cyclopentanone.

In dynamic light scattering (DLS) experiments we see for the Pd/PC nanoparticles a relatively small size distribution of about 6.5–11.5 nm (see Fig. 3). The main size is 8.7 nm with 25.5 % of the particles. In comparison the Pd/cyclopentanone nanoparticles have a little bit expanded size distribution from 2.9 to 10.2 nm. The main size here is 4.5 nm with 28.8 % of the particles.

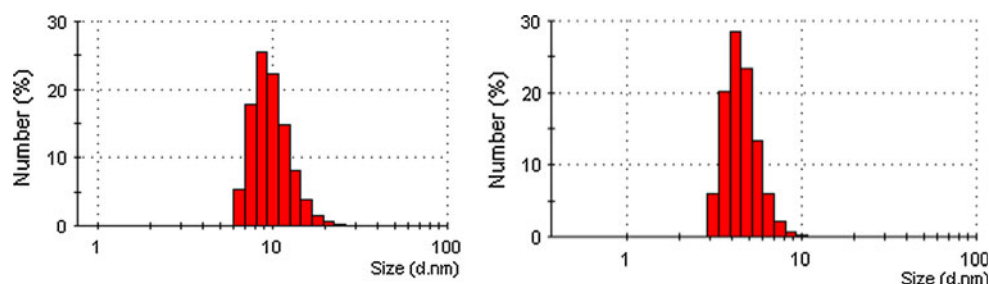
### 2.2 Typical Hydrogenation Experiment

In a typical experiment, a Pd nanocatalyst solution (2.98 g, containing 0.31 mg Pd) and dicyclopentadiene (28 mmol, 3.70 g) were diluted and dispersed in propylene carbonate (36.12 g). The reaction mixture was transferred into an evacuated 300 mL stainless steel autoclave (Parr Instrument Company, USA). The autoclave was pressurized with the desired pressure of hydrogen. After reaching the reaction temperature, the reaction was left for the desired reaction time with a stirrer velocity of 500 rpm. The reaction was stopped by cooling the reaction mixture to room temperature. The hydrogen was vented and the solid products were separated by filtration. Samples of both



**Fig. 2** TEM-Images of Pd nanoparticles in PC (*left*) and in cyclopentanone (*right*)

**Fig. 3** Size distribution of Pd nanoparticles in propylene carbonate (*left*) and cyclopentanone (*right*), measured by DLS



phases were analyzed by gas chromatography using 1-octene as an internal standard. The catalyst leaching was determined by ICP analysis.

### 3 Results and Discussions

#### 3.1 Hydrogenations

The hydrogenation of dicyclopentadiene was performed at 50 °C and 5 bar hydrogen at a reaction time of two hours. By using cyclopentanone as a solvent, only the formation of **3** was observed, while with propylene carbonate the monoolefins **2** could be synthesized with a selectivity of 87 % (Table 1, entry 1.1). Therefore all the following parameter variations were performed with propylene carbonate as the solvent.

First the influence of the hydrogen pressure at 50 °C was investigated (see table 1). In two hours high conversions (X) of 86–88 % were observed at mild hydrogen pressures. The conversion was calculated by the consumption of hydrogen and checked by the addition of the yields of **2** and **3**. We see a quit clear dependency between pressure and selectivity. With higher pressure a change between the selectivity's of product **2** and **3** is observed. At low pressures (5 bar and 7.5 bar) high amounts of product **2** (S > 80 %) are achieved, and at pressures from 10 bar and more product **3** yielded with high selectivity of 88 %. Only with a minor change in pressure a strong shift can be observed.

In a next step the influence of the reaction time was investigated at the lower temperature of 25 °C (see table 2).

First the hydrogenation of dicyclopentadiene was carried out at 25 °C with a pressure of 10 bar to increase the

**Table 1** Variation of hydrogen pressure

Entry	p (bar)	X <b>1</b> (%)	Y <b>2</b> (%)	Y <b>3</b> (%)	S <b>2</b> (%)
1.1	5	88	77	11	87
1.2	7.5	86	69	17	80
1.3	10	86	10	76	12

Reaction conditions: 50 °C, 2 h

X conversion, Y yield, S selectivity

**Table 2** Optimization of reaction time at different hydrogen pressures at 25 °C

Entry	t (h)	p (bar)	X <b>1</b> (%)	Y <b>2</b> (%)	Y <b>3</b> (%)	S <b>2</b> (%)
2.1	2	10	4	4	0	100
2.2	7	10	84	71	13	84
2.3	19	10	83	59	25	71
2.4	3	15	42	40	2	95
2.5	8	15	100	59	41	59

selectivity to **2**. After the standard reaction time of 2 h, however, the conversion of dicyclopentadiene is very low with 4 % (Table 2, entry 2.1) compared to 86 % after 2 h at 50 °C (Table 1, entry 1.3).

To enhance the conversion of dicyclopentadiene and the yield of **2** the reaction time was increased. After 7 h a conversion of 84 % and a yield of **2** of 71 % could be achieved (Table 2, entry 2.2). At even longer reaction time (19 h) the selectivity decreases, while the conversion stays almost constant. Although a high selectivity could be obtained under these mild reaction conditions, reaction time of 7 h is too long for an industrial application. Therefore the pressure was increased to 15 bar while the reaction time was reduced to 3 h and the temperature was kept at 25 °C. Using these reaction parameters (Table 2, entry 2.4) a very high selectivity to **2** could be obtained with 95 %. If the reaction time is enhanced up to 8 h full conversion can be achieved, but the selectivity to product **2** breaks down to 59 % (Table 2, entry 2.5).

Further investigations should increase the conversion of dicyclopentadiene again, for which reason the reaction temperature was raised to 60 °C and the reaction time was varied between 0.5 h and 24 h (Table 3).

Already after half an hour a conversion of 33 % was achieved with a good selectivity to **2** of about 70 %. Rising up the reaction time to one hour the conversion rises to 63 % but the selectivity to **2** decreases (Table 3, entry 3.2). Increasing the reaction time to 24 h increase the conversion of dicyclopentadiene as expected. But the selectivity to **2** decreased from 70 % to only 2 % (Table 3, entry 3.3) and the main product is now the full-hydrogenated product **3**. At a lower pressure of five bar (Table 3, entries 3.4 and 3.5) the same effect can be observed.

**Table 3** Reactions at 60 °C and 10 bar or 5 bar, respectively

Entry	t (h)	p (bar)	X <b>1</b> (%)	Y <b>2</b> (%)	Y <b>3</b> (%)	S <b>2</b> (%)
3.1	0,5	10	33	23	10	70
3.2	1	10	63	34	29	54
3.3	24	10	83	2	81	2
3.4	1	5	71	41	30	58
3.5	3	5	68	4	64	6

Comparing the results (Fig. 4) of the conversion-time-experiments at 25 and 60 °C it can be shown, that a similar distribution of conversions and yields is achieved. For this plot every 30 min (60 °C, 5 bar) respectively every 2 h (25 °C, 10 bar) a sample is taken from the reaction mixture and analyzed by gas chromatography. It seems that the influence of temperature is obvious higher than the influence of the reaction pressure. With higher temperature the maximum yield can already be achieved after a much shorter reaction time of about one hour. At a lower temperature and even higher pressure the maximum conversion is achieved not until about 8 h. At this maximum there is also the maximum yield of product **2** generated. After this, it seems that now only the product **2** is further on hydrogenated to the product **3**.

### 3.1.1 Summing Up

It can be noticed that either by the change of pressure or by variation of temperature a shift in selectivity is possible. Even at mild conditions (up to 60 °C and 15 bar hydrogen pressure) both products (**2** and **3**) are accessible.

For example a conversion of 89 % with a selectivity of 84 % to **2** is available (Table 2, entry 2.2) or with 88 % selectivity to **3** at 86 % conversion (Table 1, entry 1.3).

In all experiments the catalyst leaching was analyzed by inductively coupled plasma (ICP-OES) measurement, yielding a low value of only 2–4 ppm Pd.

It seems that the normal leaching of the weak stabilized nanoparticles during the reaction is reversible. The atoms or atom cluster reagglomerated on the mother nanoparticle at the end of the reaction, as well as presented in literature [28].

Alongside this, a comparative experiment with a supported catalyst system of 1 mol % Pd on activated carbon was performed, which is a ten times higher catalyst to reactant ratio as used in the experiment with the nano catalyst solution. The influence of a potentially mass transfer limitation in this heterogeneous reaction was checked by doing various experiments with different educt or Pd concentrations. There was no influence observable.

At 50 °C, 10 bar hydrogen and 2 h reaction time a conversion of 35 % was obtained, yielding 3 % of product **2** and 32 % of product **3**. Under similar mild reaction conditions a much better selectivity could be obtained with the Pd nanoparticle solution as catalysts. A problem of the supported catalyst system is that under these reaction conditions the solid product can precipitate during the reaction and deactivates the supported catalyst by choking up the pores. This is another advantage of nanocatalysts dispersed in solution that the catalyst can not easily be deactivated by solids.

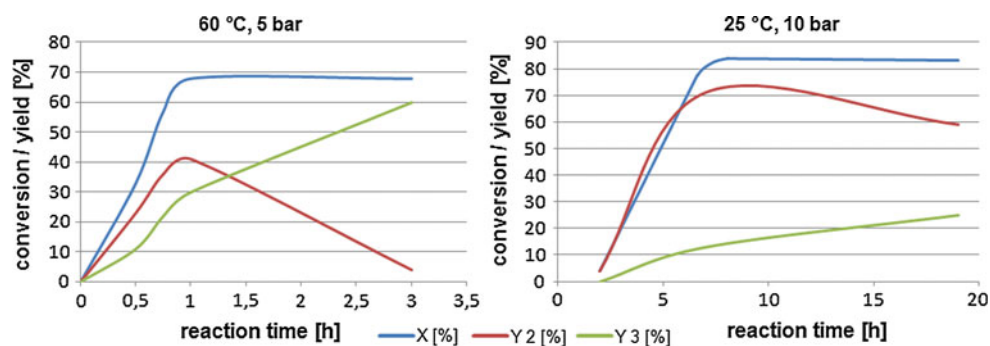
### 3.2 Catalyst Recycling and Suggested Flow Scheme

In addition a recycling of the catalyst solution proved to be possible. In Table 4 a recycling experiment over four runs is presented.

The conversion in all 4 runs is almost equal and with about 75 % quite high. The activity of the catalyst solution remains high. The selectivity decreases drastically in run 2 and 3 compared to run 1. Therefore the catalyst was regenerated by stirring the catalyst solution for 2 h at 80 °C with hydrogen. Then this catalyst solution was reused again in the reaction. By this regeneration a shift in the selectivity could be achieved. In the fourth recycling run a selectivity of 67 % to product **2** could be obtained, which is even a better selectivity to **2** than in the first run.

The products are in the reaction mixture insoluble solids (m.p. of about 48–50 °C) and can therefore be separated by simple filtration and washing from the liquid educt and catalyst solution. After all runs the Pd nanoparticles are still stable in solution and can easily be reused in the reaction.

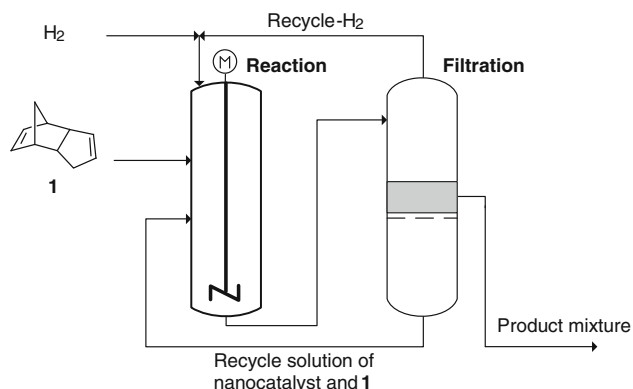
**Fig. 4** Conversion-time plots for different reactions at 60 °C at 5 bar (*left*) and 25 °C at 10 bar (*right*)



**Table 4** Results of the recycling experiments

Entry	X <b>1</b> (%)	Y <b>2</b> (%)	Y <b>3</b> (%)	S <b>2</b> (%)
4.1	71	41	30	58
4.2	81	31	50	38
4.3	70	19	51	27
4.4	75	50	25	67

(Reaction conditions: T = 60 °C, t = 1 h, p = 5 bar)

**Fig. 5** Flow diagram for the continuous mono-hydrogenation of dicyclopentadiene

A potential flow scheme for a continuous reaction in a technical scale is proposed in Fig. 5.

The diagram shows, that the surplus hydrogen, the unconverted starting compound (**1**) and the catalyst solution can easily be recycled. After washing and purification the solid products (**2a** and **2b**) can be isolated.

#### 4 Conclusion

In conclusion, we performed the first highly selective hydrogenation of dicyclopentadiene with Pd nanocatalysts. Already at room temperature the desired product is formed in high selectivity of up to 95 %. Best reaction conditions are 50 °C, 5 bar hydrogen and 2 h, yielding 77 % dihydrodicyclopentadienes (**2**) at 88 % conversion. By this we could show the great potential of Pd nanoparticles in the hydrogenation of the bulk chemical dicyclopentadiene to the more valuable product (**2**).

Even the tetrahydrodicyclopentadiene can be generated by changing the hydrogen pressure. At 50 °C and 10 bar hydrogen in 2 h we achieved 76 % (**3**) at 86 % conversion.

Referring to the flow scheme (shown in Fig. 4) an easy catalyst recycling is possible. The solid products can be separated with an easy filtration step and the liquid catalyst solution can directly be reused. With a reused catalyst solution we achieved similar results as with the original

catalyst solution: 70–81 % conversion and a selectivity to product **2** up to 67 %.

Although the nanoparticle stabilization is weak and certainly reversible, the ICP data show very low leaching of Pd. This is a very good advantage for industrial applications.

**Acknowledgments** We thank Iris Henkel for ICP-OES measurements and Monika Meuris (Group of Prof. Tiller) for TEM measurements and Jens Beneken (Group of Prof. Rehage) for supports in DLS measurements. This work was financially supported by the DFG (Deutsche Forschungsgemeinschaft).

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