Catalysis Letters Vol. 95, Nos. 1–2, May 2004 (© 2004)

Characterization of palladium nanoparticles adsorpt on polyacrylic acid particles as hydrogenation catalyst

Lothar Gröschel*, Rami Haidar, Andreas Beyer, Karl-Heinz Reichert, and Reinhard Schomäcker

Technische Universität.Berlin, Institut für Chemie, Straße des 17.Juni 124, D-10623 Berlin

Received 11 March 2003; accepted 11 March 2004

Palladium particles can be prepared in sizes of a few nanometers from $Pd(OAc)_2$ in the presence of a block copolymer in aromatic unpolar solvents with suitable reducing agents like $NaBH_4$ or $LiAlH_4$. After mixing the organic metal solution with a polyacrylic acid (PAA) dispersion of defined concentration and following a crosslinking process with an epoxide, reactive membranes with a well-defined pore diameter were obtained. The catalytic activity of the prepared palladium particles incorporated in the crosslinked PAA network has been proven by the gas phase hydrogenation of propyne in a special membrane reactor.

KEY WORDS: propyne hydrogenation; palladium nanoparticles; polyacrylic acid; membrane-reactor.

List of abbreviations and symbols

PAA:	polyacrylic acid
PS:	polystyrene
PEO:	polyethyleneoxyd
atm.:	Atmosphere
mg:	milligramm
vol%:	volume percent
wt%:	weight percent
ε:	porosity
τ:	time of residence
nm:	nanometers
K:	kelvin
s:	second

1. Introduction

In recent years, new approaches of using metal particles in the field of catalysis were reported in physics, chemistry and biology [1,2]. It is possible to prepare metal particles in sizes of a few nanometers by various methods including deposition of metal vapour, pulsed electroposition, noble gas condensation and severe plastic deformation [3].

The predominant chemical preparation method is the formation of nanoparticles by reduction of metal salt solutions with suitable reducing agents. A protective colloid or polymer is required generally to receive stable metal particles during the reduction process. Otherwise, the particles agglomerate and precipitate from the solution after a certain time.

Many methods of stabilizing metal particles with polymers are described in literature. Accordingly the application of poly(itaconic acid) and poly(butadiene-co-maleic acid) for the stabilization of platinum nanoparticles was proved feasible [4]. KBH_4 served as reducing agent. It is reported that gold particles can be stabilized with the Sokolan type copolymer (a mixture of polymaleic acid-co-olefin, sodium salt; polystyrene–maleic acid, sodium salt; polyacrylic acid (PPA)-co-maleic acid and poly C_{12} olefin-co-maleic acid anhydride) in an ethanolic solution [5]. Also stable palladium nanoclusters were synthesized within microphase-separated diblock copolymer films of $[MTD]_{113}[Pd(Cp^N)PA]$ [6]. No reducing agent was necessary. Monometallic palladium and bimetallic palladium/gold colloids were prepared using the methods described in [7] in micelles of the block copolymer polystyrene-b-poly-4-vinylpyridine in toluene. Pd nanoparticles were synthesized as is described in [8] by reduction of palladium acetate by ethanol in systems containing THF as the dispersion medium and tetradodecylammonium bromide in the role of surfactant. Pd nanoparticles have also been prepared as a monolayer adsorbed onto solid pillared clays [9] and on suspended SiO_2-particles in ethanol–toluene mixtures [10]. Nanocrystals in ranges of 5–15 nm were prepared using clay minerals as supported by immobilizing palladium in the interlammelar space of montmorillonite and saponite by pillaring with aluminium hydroxide cations [11]. In the referred literature the TEM, SEM and adsorption analyzing methods were cited as those the most commonly used for this task. More information about the reduction of precious metal cations and their stabilizing in aqueous or organic solutions can be found in [12–20].

---

*To whom correspondence should be addressed.
E-mail: L.Groeschel@chem.tu-berlin.de

1011-372X/04/0500–0067/0 © 2004 Plenum Publishing Corporation

In this paper, we present Pd nanoparticles synthesized in the presence of PAA particles. The result is a dispersion of mixed polymer and metal particles. This dispersion was used for the formation of porous polymer membranes by using a chemical crosslinking procedure. The resulting polymer gels were dried and investigated as catalytically active membranes.

With a defined pore diameter, a defined amount of catalyst and a convective gas flow through the porous membrane, consecutive reactions can be controlled better than in fixed bed reactors due to a minimized back mixing behaviour and improved adjustment of residence times.

2. Experimental

2.1. Chemicals

1,2,4-Trimethylbenzene (99%), toluene (99%), acrylic acid (99%), $NaBH_4$ (0.5 M solution in 2-methoxyethylether), $LiAlH_4$ (0.5 M solution in THF) and the catalysts; 0.15 wt% Pd on SiO_2; 0.5 wt% Pd on active carbon and 0.15 wt% Pd on Al_2O_3 were obtained from Aldrich.

2,2′-azobis(2,4-dimethylvaleronitrile) initiator was obtained from Wako Pure Chemicals. A block copolymer PS-b-PEO (M(polystyrene) = 3000, M(polyethylenoxide) = 1000) was purchased from Goldschmidt AG, Germany. Propyne (98%) and palladium(II)acetate were obtained from Merck and hexanediol-diglycidylether (66%) from Witco, Germany. Hydrogen and nitrogen were received from Linde.

2.2. Preparation of the Pd/polyacrylic acid (Pd-PAA) dispersions

Pd/PAA dispersions with a polymer content of 0.1, 10, and 20 wt% were produced as described in [21]. A solution of 10 wt% acrylic acid in 1,2,4-trimethylbenzene was polymerized by radical starter addition to form polymer particles with sizes between 80 and 120 nm. The preparation of metal colloids in different polymeric dispersions and the crosslinking of the polymer–metal dispersions with hexanediol-diglycidylether were performed as described in [22]. The procedure involves the solution of palladium(II)acetate in the PAA dispersion or in the solvent, with subsequent reduction by $LiAlH_4$ or $NaBH_4$ to form Pd particles with sizes of 3–6 nm.

The membranes were prepared by crosslinking the Pd–PAA dispersions with hexanediol–diglycidylether at 80 °C during a reaction time of 24 h. After exchange of the solvent against cyclohexane and a freeze drying process a porous catalytically active membrane with well-defined pore diameters is obtained.

2.3. Characterization

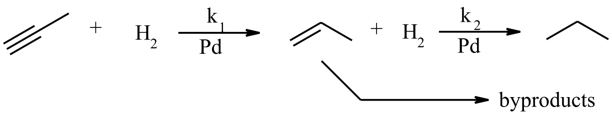
Surface fragments of the prepared reactive membranes were characterized by means of a scanning electron microscope, using a HITACHI S 4000 at 20 kV and a Quantacrome hydrogen adsorption apparatus to determine the active surface of the membranes.

Transmission electron microscopy was performed with a JEOL-JTSEM 200B electron microscope operating at 150 kV. The liquid dispersion samples were diluted with Toluene (1/120) and afterwards treated in an ultrasonic bath to prevent agglomerations of the polymer particles. The well mixed dispersion was evenly distributed on a copper sample grid and afterwards the solvent was evaporated. The size of the polymer particles was determined with dynamic light scattering (apparatus 4600 of Firma Malvern).

Samples of Pd–PAA dispersions were analysed with a Optima XLA/XLI analytical ultracentrifuge (Firma Beckmann).

2.4. Catalytic tests

To determine the catalytic activity and selectivity of the produced membranes with regard to Pd particles with different amounts of block copolymer, the gas phase hydrogenation of propyne to propene was chosen:



In the experiments the concentration of propyne, propene, propane and the by products were measured after the reaction using gas chromatography. Thus, the conversion X of propyne and the selectivity S to propene were calculated with the following formulas:

$$X = \frac{c_{ino} - c_{in}}{c_{ino}}, \quad S = \frac{c_{en}}{c_{ino} - c_{in}},$$

c_{ino} = concentration propyne before reaction [mol/L]
c_{in} = concentration propyne after reaction [mol/L]
c_{en} = concentration propene after reaction [mol/L]

Further details of the catalysis can be taken from [21].

The thickness and the diameter of the membranes were about 1 mm and 6.5 cm. The flow rate of the reactants was adjusted to be 20 up to 80 mL/min. All measurements were carried out under ambient conditions with a stoichiometric ratio between hydrogen and propyne.

3. Results and discussion

3.1. Light scattering characterization

Dynamic light scattering was used for the determination of the particle size of the PAA dispersion. The following figure 1 shows the size distribution of PAA particles from a 10 wt% acrylic acid dispersion stabilized by 1.6 g SE3010 polymerized in 1,2,4-trimethylbenzene at 50 °C.

This figure shows a narrow particle size distribution. Half of the number of particles are in a range between 70 and 100 nm.

3.2. Scanning microscopic characterization

A standard analytical method for the characterization of the surfaces of membranes is the SEM technique. With this method a network structure of the PAA membrane can be visualized. In figures 2 and 3 REM and an electron dispersed micrograph are shown of a membrane containing 5 mg Pd in 1 g PAA (enlargement: 100,000×). The porosity of the membrane is about 60%, as obtained from density measurements. As a result of the higher electron density of the metal compared to polymer, the electron backscattering is a most suitable method for the identification of palladium in such systems:

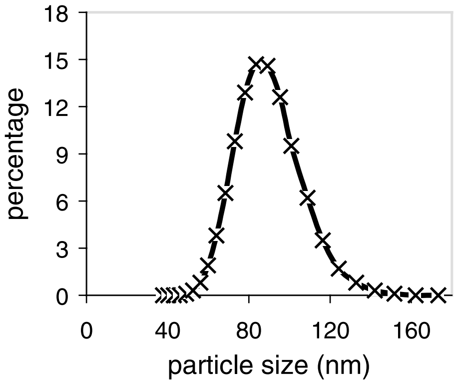


Figure 1. Sizes of PAA particles formed by polymerization at 50 °C.

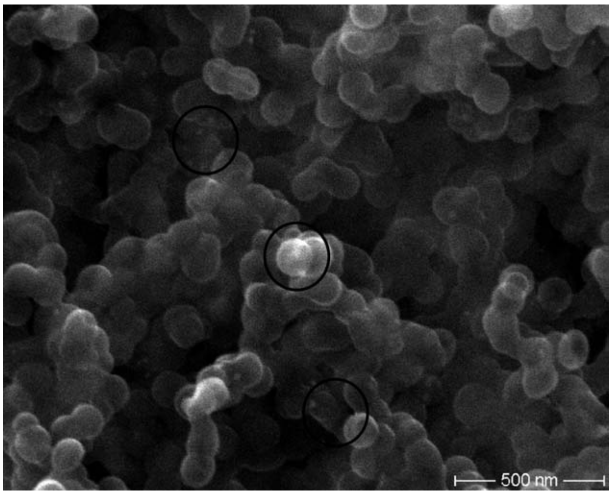


Figure 2. REM of a PAA-membrane (surface).

The PAA particles are clearly visible in figure 2. The spherical nature of the particles and a mesoscopical porous pore system is observed. Also the size of the PAA particles can be estimated from the micrograph to be 80 nm.

The markings show catalytically active palladium nanoparticles adsorbed on the surface of the polymer particles. They are distributed homogenously. From the EDM-micrograph the Pd-particles can be seen as white spots with a diameter of approximately 15 nm.

From the same membrane fragment analysed with SEM, an energy dispersed X-ray-analysis was carried out. From this method figure 4 it could be proven that the visible particles adsorbed at the surface of the polymer are definitely palladium.

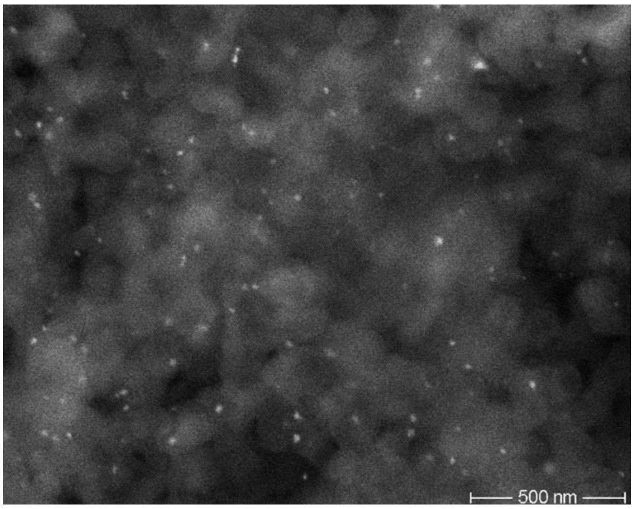


Figure 3. EDM belonging to figure 2.

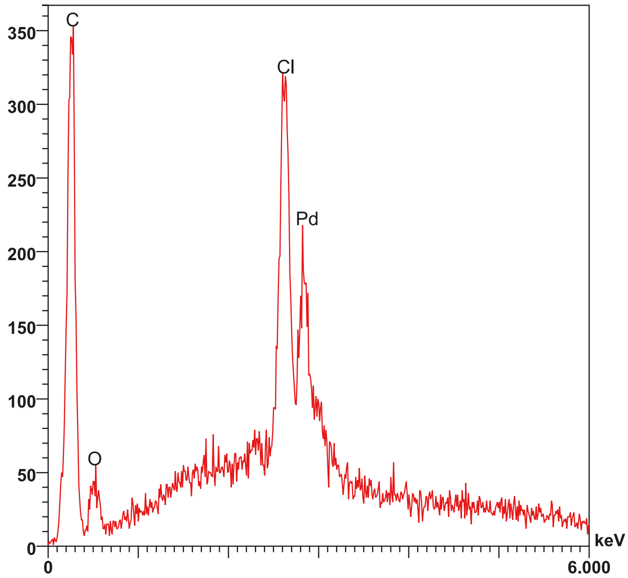


Figure 4. EDX-analysis of the reactive membrane surface.

The high concentration of chlorine is a result of the manufacturing of the crosslinker via the chlorohydrine route and represents in this case a contamination.

3.3. Preparation of samples to indicate the influence of block copolymer on particle size

As previously discussed, palladium particles – prepared by reduction with suitable reducing agents in organic solvents – can only be stabilized by addition of a block copolymer. It can be expected that metal particles of sizes between 3 and 5 nm and a defined amount of block copolymer molecules will form a micellar system with a metal core in the organic solvent. The following figure 5 illustrates this effect.

In this model the hydrophilic polyethylene oxide chain adsorbs onto the electropositive surface of the Pd particle and the lipophilic polystyrene section orients towards the organic solvent.

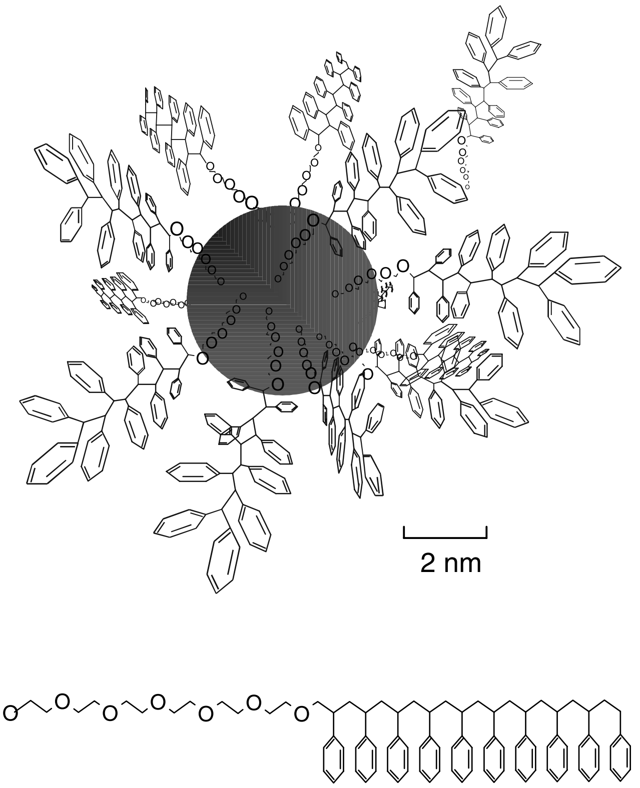


Figure 5. Stabilizing effect of a palladium nanoparticle due to adsorbed block copolymer.

Without any surfactant, no formation of nanoparticles will occur. Accordingly the formation of nanoparticles is strongly influenced by the concentration of the surfactant. To observe the influence of surfactant concentration on the growth and formation of Pd nanoparticles and to further determine their catalytic behaviour, different palladium – surfactant-dispersions were prepared. Each solution, 5 cm^3 in volume contained 8.5 mg $Pd(OAc)_2$ and a different amounts of surfactant, except for one sample which contained none. These dispersions were then reduced with $NaBH_4$. Afterwards, an equal volume of PAA dispersion was added to each solution. Table 1 gives an overview of the amounts of surfactant in the investigated membranes.

3.3.1. Transmission microscopic characterization of the dispersions

After the block copolymer and the Pd salt was completely dissolved, $Pd(OAc)_2$ was reduced in all dispersions with a stoichiometric amount of $NaBH_4$. As the reduction was completed and the mixture turned black in colour, the dispersions were analysed using the TEM-technique. The result showed that the sizes of the reduced Pd particles depends strongly on the amount of added surfactant.

In the reduced dispersion with 20 mg surfactant the Pd particles are in a size range of 3–5 nm. The TEM micrograph in figure 6 shows a one layered PAA particle film in a hexagonal gasket where the Pd particles can be seen to have a nearly homogeneous distribution. They are almost isolated from each other. The three white dots are areas where no material has adsorbed to the grid. The TEM figure 6b shows a Pd–PAA dispersion in which 9.6 mg of surfactant were added. In this case the PAA particles are obvious in lower contrast to the metal particles. It is ascertainable that in this dispersion the reduced metal particles seem to be bigger than those in the dispersion with the higher content of surfactant. The distribution of the particle sizes is broader, being between 3 and 20 nm. They are also distributed homogeneously and are isolated from each other. All Pd particles have contact to the polymer particles. In the white areas where no polymer is present accordingly Pd is absent. This leads to the assumption that particles are adsorbed at the surface of the polymer particles.

Pd particles formed in a solution stabilized with 4 mg block copolymer have nearly the same appearance. The size of the metal is between 3 and 20 nm. In figure 6c it is also sure to say that the palladium particles are fixed

Table 1
Amounts of surfactant in the dispersions

Sample	1	2	3	4	5	6	7
Amount SE 3010 mg (wt%)	20 (3.6)	17 (3.1)	13.2 (2.4)	9.6 (1.7)	7.4 (1.3)	4 (0.7)	0 (0)

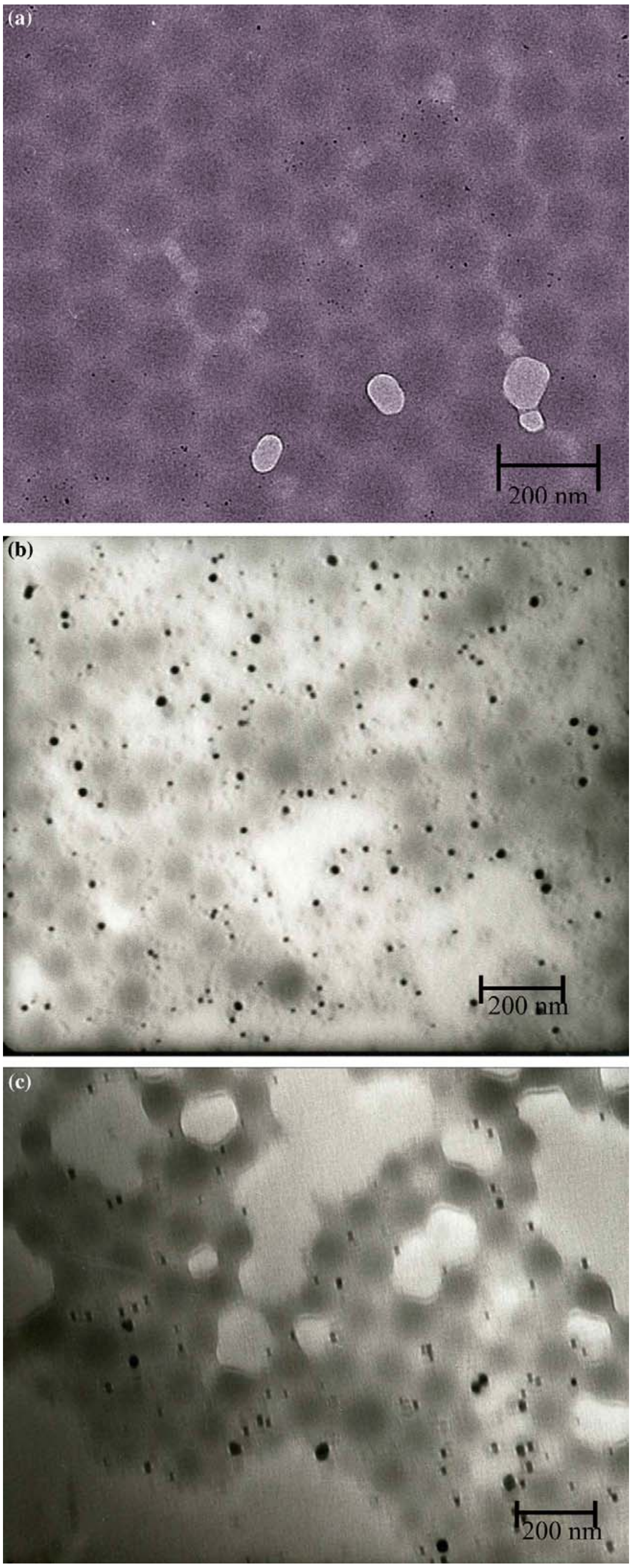


Figure 6. a, b and c: TEM micrographs of a 10 wt% Pd–PAA dispersion with 209.6and 4 mg amount SE3010.

onto the surface of the PAA particles because they are located only in limited areas and spaces between the polymer particles.

It was observed using the TEM method that without any addition of surfactant to the $Pd(OAc)_2$–PAA dispersion, no isolated spherical palladium particles were obtained. Also no homogeneous distribution of metal was obtained. The results were agglomerated and amorphous Pd clusters with a non-consistent structure.

3.4. Analytic ultracentrifugation characterization

From the TEM pictures it is obvious that the Pd particles are on the surface of the polymer particles. In order to investigate the interactions between Pd and PAA particles, experiments with the analytic ultracentrifuge (AU) were performed. In this method the palladium was detected by light absorption and the PAA was determined from the refraction index difference to the solvent. AU-investigations of PAA – dispersions with an allotment of 10 wt% PAA and 2.7 mg Pd (0.6 wt%) as well as a much lower concentration of 0.1 wt% PAA and 0.027 mg Pd (0.06 wt%) – to broadly eliminate any interaction between free metal particles and polymer – were performed. The results of the sedimentation profiles show that in both dispersions the palladium cannot be separated under centrifugation of 15,000 × g. From these sedimentation profiles and the calculated sedimentation coefficients it is obvious that in dispersions of such concentrations unbound Pd particles are not present (figures 7 and 8).

In these figures the solid line represents the adsorption of Pd and the dashed line represents the interference of PAA with the solvent. The parallel course of the two curves as a function of time and the cell distance show strong bonded Pd–PAA dispersion.

3.5. Hydrogen adsorption on PAA–Pd membranes

A titration with carbon monoxide or hydrogen on a dispersion of polymer and metal is a suitable method to specify the catalytically active metal surface incorporated in any support. The method was used to determine the intrinsic active surface of the palladium particles bonded by the PAA particles. For these experiments, four samples of membranes with different palladium contents and a corresponding amount of surfactant were chosen. For the calculation of the overall metal surface, an average Pd-particle of diameter 5 nm was assumed due to TEM micrographs. The hydrogen adsorption measurements were accomplished with an Autosorb 1C Quantacrome – chemisorption apparatus. The results were gained with the interpolation method and have an error of about 5%. The following table shows the composition of the samples and the adsorption results.

It can be seen from table 2 that the catalytically active surface of the Palladium is between 7% and 18% of the existing surface. From this result,it can be concluded that the main part of the metal surface is covered with

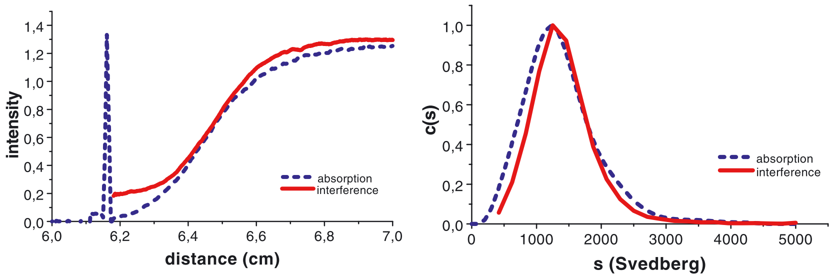


Figure 7. Sedimentation profile and coefficients of a Pd–PAA dispersion (10wt% PAA).

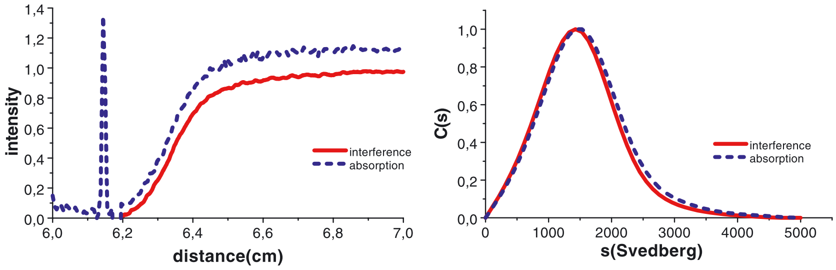


Figure 8. Sedimentation profile and coefficients of a Pd–PAA dispersion (0.1wt% PAA).

Table 2
Overview of the hydrogen adsorption experiments

Weight of sample/g	Amount of Pd/mg	Amount of surfactant/mg	Surface of pd-particles (r = 2.5 nm)/m^2 g	Determined surface of Pd/m^{2}g	% catalytic active surface
(1) 0.1417	2.44	20	1.719	0.12	7
(2) 0.1653	4.57	37	2.760	0.25	9
(3) 0.1435	7.14	58	4.967	0.85	17
(4) 0.162	21.42	175	15.809	2.12	16

surfactant and polymer is presumably catalytically inactive.

3.6. Catalytic activity of membranes

In all experiments a gas mixture of 50 vol% hydrogen and 50 vol% propyne has been led through the membrane and analysed by gas chromatography. The flow rate of the reactants was adjusted with 20 up to 80 mL/min. Membranes with a defined porosity of about 50% were used. The reaction temperature was 298 K in each experiment.

3.6.1. Influence of the reducing agent

It was mentioned earlier [1] that the heterogeneous catalysis in reactive membranes depends on the reducing agent which was used to prepare the metal particles. Furthermore, it is known that in PAA dispersions containing Pd^{2+}-Ions, the reduction is initiated without adding a reducing agent. This process is obtained for a long time, in contrast to processes involving the use of reducing agents. Within the scope of the present work three different membranes with a porosity of 50% and 2 mg Pd content were prepared with $NaBH_4$ and $LiAlH_4$ and one membrane without adding any reducing agent. The results of hydrogenation at 298 K and a residence time of 4 s are shown in figure 9.

The highest catalytic activity was found with metal particles produced with $LiAlH_4$. The reduction with $NaBH_4$ leads to membranes with less acticity. The lowest activity is displayed by metal particles formed without adding a reducing agent. These results lead to the assumption that metal particles of higher specific surface are formed by stronger reducing agents and show higher activities. In the following work only $NaBH_4$ was used as reducing agent for palladium acetate due to easier handling.

3.6.2. Effect of the surfactant

As described above, the concentration of the surfactant has great influence on the formation process of the Pd particles. After the characterization of the PAA–Pd dispersions with different contents of surfactant (de-

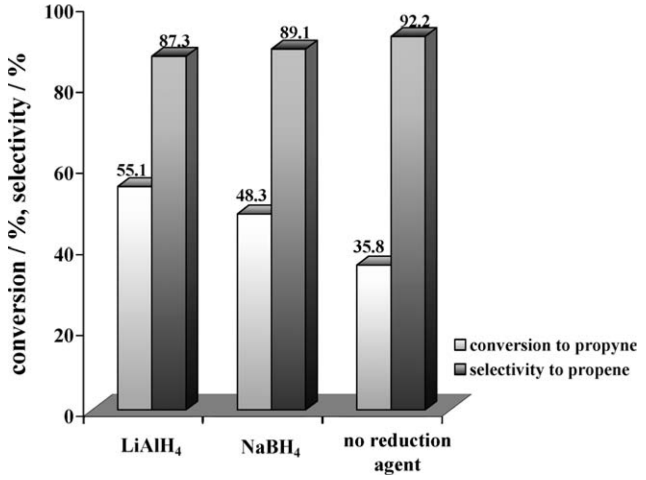


Figure 9. Dependency of the catalytic activity to the reducing agent.

scribed in 3.3), membranes were prepared from them via interparticle crosslinking of the polymer dispersions.

In these membranes the selective partial hydrogenation of propyne to propene as a model reaction was studied. An equimolar ratio and a partial pressure of 0.5 atm of the reactants were used at a temperature of 298 K with a residence time of 4 s. The dependence of the catalytic activity of 2 mg Pd on the amount of surfactant is illustrated in figure 10.

It is obvious that the conversion of hydrogenation passes through a maximum at a surfactant amount between 10 and 13 mg within the standard recipe. An increasing or decreasing content of surfactant leads to decreasing activity of the membranes and consequently to a decreasing yield of propene.

This unusual catalytic behaviour of the PAA-membranes can only be interpreted together with the microscopic analysis of the dispersions referred in figure 5. From other publications it is well known that the hydrogenation of propyne proceeds according to the Langmuir–Hinshelwood mechanism which requires the adsorption of two reactive species. A high concentration of surfactant in the dispersion leads to palladium particles more covered with SE 3010. Accordingly, the gases can only adsorb on less adsorption sites. With decreasing amount of surfactant the yield of propene increases to a maximum of nearly 47%. This behaviour can be explained by the increase of adsorption sites for the gases on the palladium surface as a result of lower adsorption of the surfactant.

From the TEM micrographs, it was shown that with lower surfactant amount the Pd particles grow up to sizes of 20 nm. Due to the particle growth the specific surface area of palladium decreases as does the number of available adsorption sites. The catalytic experiments also show this behaviour in that the yield of propene decreases in membranes with a content of surfactant of less than 10 mg. The lowest conversion of 22.4% is observed for a membrane containing no surfactant. In this case, the palladium is not present in spherical particles but in amorphous non-stabilized thick agglomerates with less specific surface.

3.6.3. *Effect of Pd content in membranes*

For studying the effect of Pd content, membranes with 1.5, 2, 2.7, 4 and 5.5 mg Pd were prepared. The stabilizer SE 3010 and $NaBH_4$ were added in stoichiometric amount with increasing $Pd(OAc)_2$ addition. The mass ratio between metal and surfactant in the membranes was chosen to be 1–5, which has shown the highest activities earlier, see figure 10. The residence time of the reactants in the membrane were about 4 s in each measurement.

From figure 11 it is obvious that the amount of catalyst influences the activities of the membranes substantially.

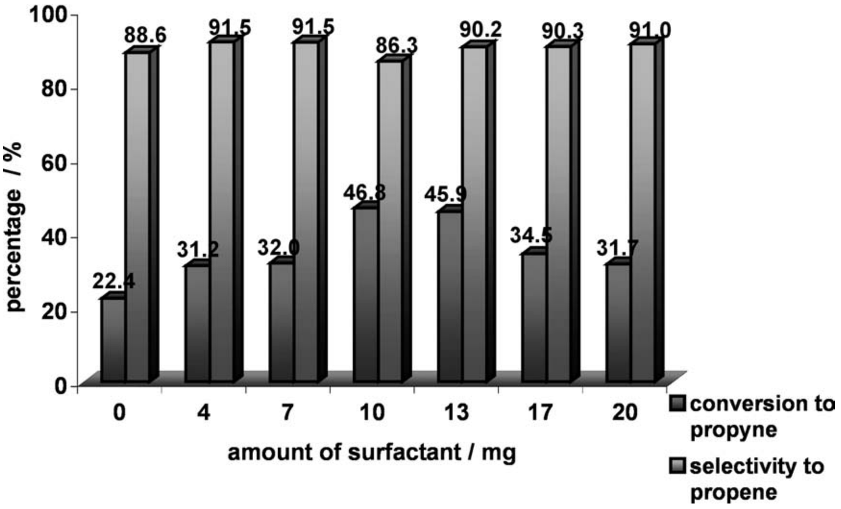


Figure 10. Dependency of the catalytic activity versus amount of stabilizing surfactant (reduced with $NaBH_4$).

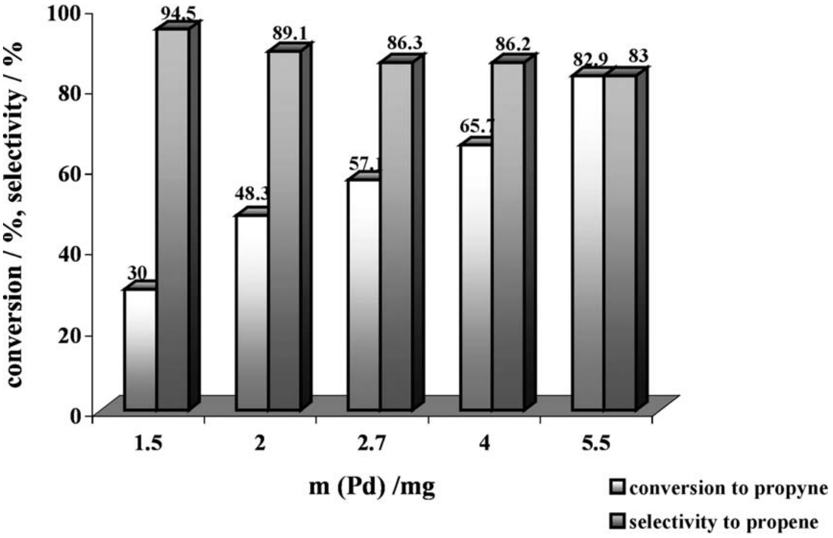


Figure 11. Conversion and selectivity subject to catalyst amount of PAA membranes, $T = 298$ K, $p = 1$ atm, $\tau = 4.6$ s.

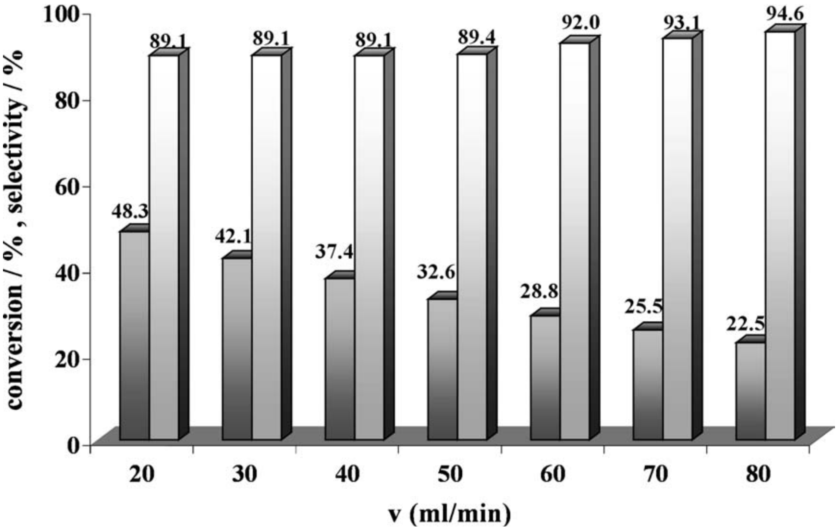


Figure 12. Conversion and selectivity *versus* flow rate of gas phase $T = 298$ K, $p = 1$ atm, m(Pd) = 2 mg.

As expected, selectivity decreases with higher conversion. The membranes show conversions between 30% (1.5 mg content of Pd) and to 83% (5.5 mg Pd). The selectivity decreases from 94.5% to 83%. The reason for that is the formation of green oil and propane with a higher load of Pd-particles.

3.6.4. *Effect of flow rate on gas mixture*

The catalytic activity and selectivity of a membrane with a porosity of 50% and 2 mg Pd content was investigated concerning the flow rate of reactants. The interval of the flow rate from 20 to 80 mL/min corresponds to residence times between 1 and 4 s figure 12 show the results.

From figure 12 it can be seen that increasing flow rate (decreasing residence time) through the membrane causes a decreased conversion and increases selectivity. This behaviour was expected for this type of consecutive reaction. The quantitative evaluation of these data will be performed within a kinetic investigation of this reaction.

4. Summary

The present work gives information about the physical properties of a PAA dispersion where in Pd nanoparticles can be produced and stabilized by a block copolymer. The amount of the surfactant becomes essential for the formation process and the final quality of the Pd particles. It was shown by TEM micrographs that smallest Pd particles were obtained by addition of 20 mg surfactant (3.6 wt% of the solution) and that the particle diameter grows within reducing the amount of block copolymer. Amorphous agglomerations of palladium will be formed without addition of surfactant. This dependency could be proven in tests based on catalytic studies. The accessible catalytical surface of the palladium particles was determined by hydrogen titration. The results of these measurements show that only a low fraction of the metal surface is active and over 80% is covered with surfactant or polymer.

The reactivity of the nanoparticles is dependent on the reducing agent. By using stronger reducing agents ($LiAlH_4$) membranes with a higher catalytic activity can be prepared as by the use of softer ones ($NaBH_4$). It can be assumed that Pd particles with a higher specific surface are formed in presence of strong reducing agents.

The activity of the palladium nanoparticles is also governed by the concentration of the block copolymer which controls the particle growth and stability. Membranes with an amount of 2.7 mg Palladium (0.6 wt%) and 9.6 mg block copolymer (1.7 wt%) show in test series the highest activity for the hydrogenation. The reason for maximum activity is the optimized ratio between the palladium particle size and the adsorption of surfactant at the particle surface.

Acknowledgments

This project is a part of SFB 448 "Strukturierte Verbundsysteme" financed by the Deutsche Forschungsgemeinschaft. The authors acknowedge also the financial support provided by the Graduiertenkolleg "Polymerwerkstoffe" of the Deutsche Forschungsgemeinschaft. Thanks also to Duncan Pearse at Imperial College London, for help with proof-reading.

References

[1] G. Schmidt, *Clusters and Colloids* (VCH, Weinheim, 1994).

[2] P. Mulvancy, F. Grieser and D. Meisel, Surf. Sci. Ser. 38 (1991) 303.

[3] R. Hempelmann, Nanokristalline Metalle und Oxide mit kontrollierter Teilchengröße;Arbeitsbericht aus dem SFB 277.

[4] A. Mayer, J. Mark and S. Hausner, Angew. Makrom. Chem. 259 (1998) 45.

[5] A. Mayer and M. Antonietti, Colloid. Polym. Sci. 276 (1998) 769.

[6] J. Ciebien, R. Cohen and A. Duran, Mat. Sci. Eng. C7 (1999) 45.

[7] M.V. Seregina, L. Bronstein, O. Platonova, D. Chenyshov and P. Valetsky, Chem. Mater. 9 (1997) 923.

[8] S. Papp and I. Dékany, Colloid. Polym. Sci. 279 (2001) 449.

[9] A. Szucs, Z. Kiraly and F. Berger Colloid Surface 139 (1998) 109.

[10] A. Szucs, A. Beck and H. Horvath, Catal. Lett. 65 (2000) 33.

[11] A. Szucs, F. Berger, and I. Dekany, Colloid Surface 174 (2000) 387.

[12] K. Meguro, M. Torizuka and K. Esumi, Bull. Chem. Soc. Jpn. 61 (1988) 341.

[13] K. Esumi, M. Suzuki and T. Tano, Langmuir 7 (1991) 457.

[14] K. Esumi, M. Suzuki, T. Tano, K. Torngoe and K. Meguro, Colloid. Surface. A 55 (1991) 9.

[15] N. Aihara, K. Torigoe and K. Esumi, Langmuir 14 (1998) 4945.

[16] N. Toshima, M. Harada, T. Yonezawa and K. Kushihashi, J. Phys. Chem. 95 (1991) 7448.

[17] N. Toshima, M. Harada, T. Yonezawa and K. Asakura, J. Phys. Chem. 96 (1992) 9927.

[18] N. Toshima and T. Teranishi, Bull. Chem. Soc. Jpn. 65 (1992) 400.

[19] T. Teranishi and N.and Toshima, J. Chem. Soc. Dalton Trans. (1995) 979.

[20] T. Teranishi and H. Miyake, Chem. Mater. 10 (1998) pp. 594.

[21] U. Mähr, H. Purnama, R. Schomäcker and K.-H.-Reichert, J. Membr. Sci. 171 (2000) 285.

[22] A. Beyer, R. Schomäcker, K.-H. Reichert,*Synthesis and Characterisation of Palladium Containing Memberanes Based Upon Polyacrylic Acid,* in press.

[23] A. Henglein, Ber. Bunsenges. Phys. Chem. 101 (1997) 1562.