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Hydrogenation of 2-Butyn-1,4-diol in the Presence of Functional Crosslinked Resin Supported Pd Catalyst. The Role of Polymer Properties in Activity/Selectivity Pattern

**Anna Knapik · Alicja Drelinkiewicz ·
Anna Waksmundzka-Góra · Agnieszka Bukowska ·
Wiktor Bukowski · Jaroslaw Noworól**

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Abstract Functional gel type resins of various crosslinking degrees (3–20%) with C=O and carboxylic groups were used as the supports for Pd catalysts (0.5–2 wt% Pd). The role of polymer properties was studied in the hydrogenation of 2-Butyne-1,4-diol (B3-D) to alkene (B2-D) and alkane (B1-D). Hydrogenation was studied at atmospheric pressure of hydrogen using THF, H_2O and THF + H_2O mixtures as the solvents. Systematic studies were carried out to determine the role of the type of solvent, crosslinking degree of polymer, the content of Pd in catalysts, initial B3-D concentration and the procedure of catalyst reduction in activity/selectivity behaviour of catalysts. Swelling degree of polymer matrix under the catalytic run exhibits crucial role in the activity and selectivity to alkene, B2-D. In the presence of highly expanded catalyst (THF solvent, 3% crosslinking degree, 1 wt% Pd) the alkyne, B3-D, is hydrogenated to alkene, B2-D, with selectivity ca. 85% up to high B3-D conversion (90%). The suppression of alkene to alkane hydrogenation in the stage of B3-D is ascribed to high ability of Pd centres in the Pd/OFP catalysts to strong adsorption of alkyne substrate. It may also be related to steric hindrances of polymer in the vicinity of active Pd centres. At small content of added water (5% by vol.) to THF the catalysts offer very attractive performance in terms of activity and 98% selectivity to alkene. Water facilitates interactions of B3-D with functional groups of polymer that leads to better expansion of polymer matrix and more effective suppression of alkene hydrogenation in the alkyne stage.

Keywords Palladium · Functional resin · 2-Butyne-1,4-diol · Hydrogenation

1 Introduction

Recently, a great deal of interest has been directed in the design and use of cross-linked functional resins (OFP) as the catalysts in industrial synthesis of MTBE, methylvinyl ketone, hydratation of alkenes and synthesis of peptides [1, 2, 3]. These materials are also successfully used for dispersing metal nano-crystallites (Pd, Pt) and palladium catalyst of this type is currently applied for the removal of oxygen to the ppb level from water. Specific features of crosslinked functional resins like hydrophobic/hydrophilic character, swelling in contact with reaction medium, and high ability for the stabilization of finely dispersed metal nano-particles make gel type resins very attractive from the catalytic point of view and they are considered as "innovative supports for catalytically active metal particles" [4]. The role of such properties in catalytic performance of metal–resin systems and especially in successful preparation of highly dispersed catalysts has been reviewed in number of recently published papers [5–8]. However, to the best of our knowledge, no systematic study with respect to the role of specific properties of gel type matrix in activity/selectivity pattern of alkyne to alkene and alkane hydrogenation has yet been systematically studied. The hydrogenation of alkynes is of considerable industrial and academic interest and the main objective is to achieve the highest possible alkene selectivity. Generally, specificity of the interaction of catalytic centres with carbon—carbon

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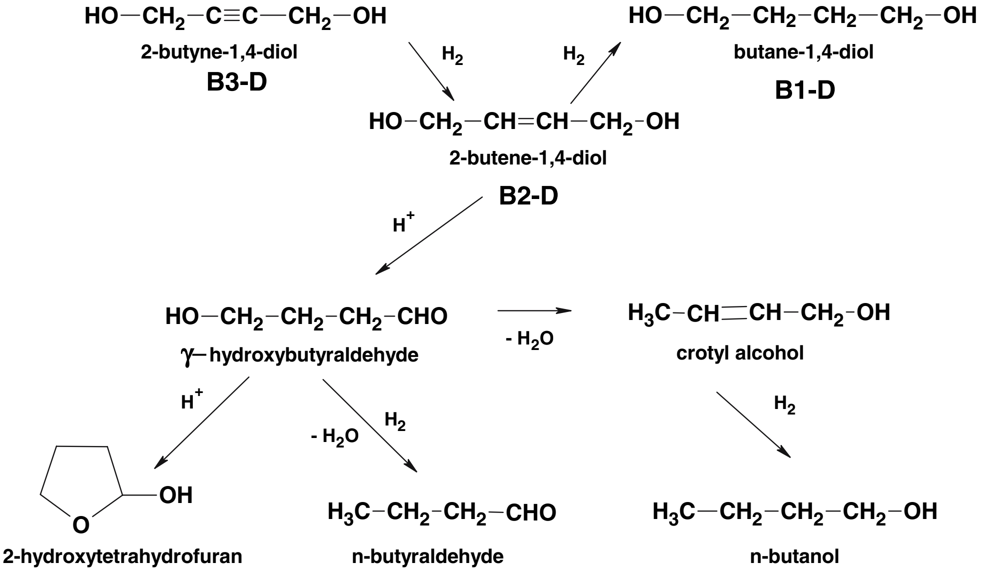
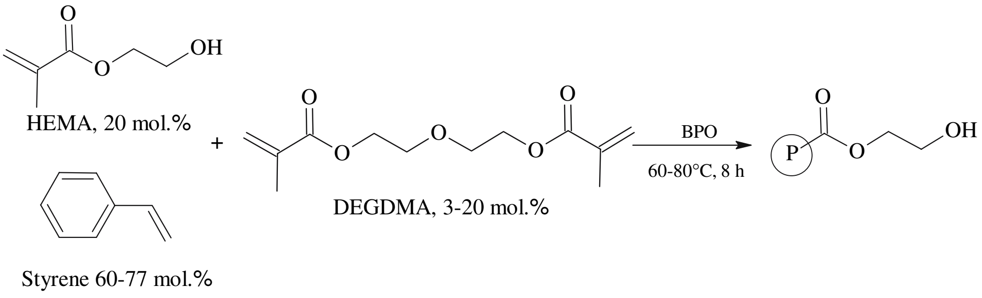
A. Knapik · A. Drelinkiewicz (✉) · A. Waksmundzka-Góra
Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Niezapominajek 8, 30-239 Krakow, Poland
e-mail: ncdrelin@cyf-kr.edu.pl

A. Bukowska · W. Bukowski · J. Noworól
Faculty of Chemistry, Technical University, ul. W. Pola 22, 35-059 Rzeszow, Poland

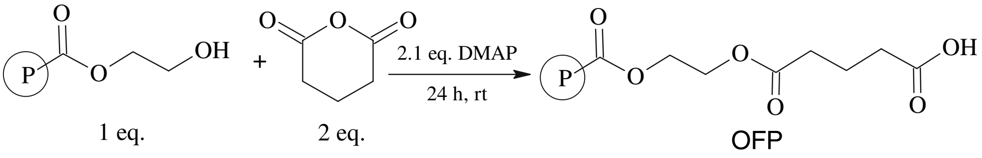
multiple bonds as well as electronic and/or morphological properties of metal particles have been considered to explain the activity/selectivity behaviour of Pd catalysts in hydrogenation of alkynes [9, 10]. High selectivity to alkene is related to the increased Pd electron density that leads to the decreased alkene adsorption. In numerous studies various attempts have been made to modify the morphological and/or electronic properties of the Pd catalysts in order to improve the selectivity to alkene formation. Thus, greater selectivity to alkene has been achieved by employing electron donor compounds, like *N*-bases (quinoline, pyridine, ammonia) or by pre-impregnating the additives like metals (Pb, Zn) onto the Pd catalyst. Very promising results have also been reported for polymer supported catalysts. Their advantageous performance has been related to the geometric—electronic modification of Pd centres caused by the presence of *N*-bases as the constitutional units of polymers. For example, Pd-heterocyclic polyamides exhibited high selectivity in hydrogenation of alkadienes and alkynes to monoenes [11], Pd-oligomeric aramides in hydrogenation of phenylacetylene to styrene [12], Pd and Rh species—copolymers containing amino and heterocyclic ligands in the hydrogenation of number of dienes and alkynes to monoenes [13]. Moreover, the advantageous role of polymer has also been related to the steric hindrances of polymer in the vicinity of catalytically active centres [13, 14]. In the present work crosslinked functional gel type resins are used as the support for palladium catalysts and the hydrogenation of 2-butyne-1,4-diol (B3-D) is selected as the test reaction (Scheme 1). Polymer used in the present work exhibits hydrophobic character due to the presence of styrene and it contains C=O and carboxylic groups (Schemes 2, 3). Hydrogenation of B3-D represents a class of reactions that are of interest to the pharmaceutical and fine chemical industries [15, 16]. The olefinic diol, 2-butene-1,4-diol (B2-D) and final



Scheme 1 Reaction pattern for 2-butyne-1,4-diol hydrogenation



Scheme 2 First stage of resin preparation (HEMA, 2-hydroxyethyl methacrylate; DEGDMA, diethylene glycol dimethacrylate; BPO, benzoyl peroxide)



Scheme 3 Chemical modification by glutaric anhydride (DMAP, 4-(dimethylamino)pyridine)

product, butane-1,4-diol (B1-D), both reagents are important raw materials, B2-D is used in the preparation of pharmaceuticals, like endosulfan and pyridoxine (vitamin B_6) and several insecticides, fully saturated B1-D is major raw material in plastics and tetrahydrofuran manufacture. The reaction network shows that the target product, olefinic diol, (B2-D) can also transform to various by-products (γ-hydroxybutyraldehyde, *n*-butyraldehyde, *n*-butanol, crotyl alcohol and 2-hydroxytetrahydrofuran) by acid catalyzed isomerization and hydrogenolysis reactions [17]. For conventional catalysts such as Pd/C, Pd/Al_2O_3, Pd/TiO_2 high selectivity to B2-D is achieved by using various modifiers [15, 16] and $1\%Pd/CaCO_3–NH_3$ is the best catalyst system [18]. Recently, advantageous performance of metal nano-particles stabilized by various polymers in highly selective formation of B2-D has also been reported [19]. Highly active and selective catalyst for the B3-D hydrogenation was also obtained using Pd-nano-particles stabilized in micellar core of poly(ethyleneoxide)-block-poly-2-vinylpyridine in unsupported and supported on γ-Al_2O_3 carrier [20]. However, to attain high selectivity strongly alkaline reaction medium (KOH added, hydrogenated solution of $pH = 13.4$) was necessary [20]. In view of these results the functional resins supported Pd seems to be promising catalyst for the hydrogenation of B3-D and the objective of the present research is to examine the role of specific properties of crosslinked functional resin supported Pd catalysts in activity/selectivity pattern in the course of B3-D hydrogenation. Main attention is paid to conditions enabling highly selective formation of target product, olefinic diol, B2-D.

2 Experimental

2.1 Synthesis of Resin (OFP)

Monomers 2-hydroxyethyl methacrylate (HEMA), styrene (S) and diethylene glycol dimethacrylate (DEGDMA) were purchased from Aldrich. 2-hydroxyethyl methacrylate (HEMA) was distilled under reduced pressure before use. Styrene and DEGDMA were purified by extraction with 5 wt% NaOH in 20 wt% NaCl solution. Other regents and solvents were used as received.

The functional gel-type resin (OFP) in the form of spherical grains was prepared by two stage procedure (Schemes 2, 3). In the first stage (Scheme 2) co-polymer of HEMA in the form of spherically shaped beads was prepared by suspension polymerization technique using 2-hydroxyethyl methacrylate (HEMA) styrene (S) and diethylene glycol dimethacrylate (DEGDMA) as the crosslinking reagent [21]. Sample with 3% crosslinking degree was prepared using 20 mol% of HEMA, 77 mol% of styrene and 3 mol% of DEGDMA, the crosslinking reagent. To prepare highly 10% and 20% crosslinked materials, polymerization was carried out using 20 mol% of 2-hydroxyethyl methacrylate, and 10 mol% or 20 mol% of crosslinking reagent at the expense of styrene. Polymerization of HEMA with styrene and cross-linker, (DEGDMA) was carried out under nitrogen atmosphere in 800 cm^3 cylindrical reactor equipped with a heating coat, mechanical stirrer, reflux condenser and addition funnel. The dispersion medium was prepared by dissolving 1 wt% polivinylpyrrolidone in water. The obtained beads of HEMA co-polymers (3, 10 and 20% crosslinked samples) were sieved and two fractions of diameter $d = 75–150$ µm and $d = 150–250$ µm were used in the second stage in which functionalization by glutaric anhydride was performed (Scheme 3). The functionalization was carried out in the following way: a dry resin (1 equiv.) was left to swell in CH_2Cl_2 and a mixture of glutaric anhydride (2 equiv.) and *N,N*-dimethylaminopyridine (2.1 equiv.) was added. The mixture was shaken for 24 h at room temperature and then an excess of acetic acid was added. The obtained resin was filtered off and washed several times with CH_2Cl_2 and CH_3OH by turns and dried at 400 °C under reduced pressure.

The samples of final polymers contain ca. 1.1. mmol COOH groups per 1 g [21, 22]. Three samples of functionalized resins of 3, 10 and 20% crosslinkiing degree, OFP-3, OFP-10, OFP-20, respectively, and two sieve fractions of 3% crosslinked sample of beads diameter $d_p = 75–150$ µm and $d_p = 150–250$ µm were used to prepare the catalysts.

2.2 Preparation of Catalysts

The catalysts were prepared by reacting starting OFP resin with $Pd(OAc)_2$ solution in THF (4.73×10^{-3} mol/dm^3 of $Pd(OAc)_2$). An appropriate volume of precursor solution to obtained 0.5–2 wt% Pd in the final catalysts was used. The suspension was gently stirred at room temperature when all of Pd ions reacted (ca. 24 h). Then, the catalyst was filtered off, washed with THF (5×20 cm^3) and dried in air.

Prior to reduction, the Pd^{2+}—containing yellow samples were left to swell in THF. Reduction was performed with 10 times excess of NaBH4 solution (0.05 mol/dm^3) in THF: CH_3OH (9:1 volume ratio) under vigorous stirring using a shaker. Then, the catalysts were decanted, washed several times with THF and THF–H_2O mixture and dried under vacuum to constant weight (1 h at 500 °C).

Reduction of pre-swollen catalyst was also performed using the THF–H_2O solution of $N_2H_4 \times H_2O$. After the reduction the catalyst was washed with THF and water up to neutral pH and dried under vacuum to constant weight (1 h at 500 °C).

2.3 Charcterization of Catalysts

Swelling of starting polymer and reduced catalysts was evaluated by measurement the bulk expanded volumes in THF, H_2O and THF–H_2O mixtures as well as in the solutions of B3-D and B2-D regents of the same composition as that used in the hydrogenation experiments. As the measure of swelling ability the ratio of V_S/V_0 was assumed, where V_S is the volume of swollen samples and V_0 is the initial volume of dry, powdered samples. Scanning electron microscopic investigations (SEM) were performed using a Philips XL-30 electron microscope. The microscope was equipped with a Kevex energy-dispersive X-ray analyser. X-ray microprobe analysis was performed for the assessment of Pd and Na distribution throughout the grains of reduced catalyst. In order to perform X-ray microprobe analysis over the cross-section of catalyst grains they were resin-bonded and cut by rotary microtome.

TEM investigations were carried out by means of Philips CM-20 instrument operated at 200 kV. HRTEM analysis was performed using TECNAI G2 high-resolution microscope. Samples for TEM and HRTEM studies were prepared by placing a drop of the suspension of sample in ethanol or THF onto a carbon-coated copper grid, followed by evaporating the solvent.

2.4 Hydrogenation Experiments

Hydrogenation experiments were carried out in an agitated batch glass reactor at constant atmospheric pressure of hydrogen at temperature 22 °C following the methodology previously described [22]. THF, H_2O and THF–H_2O mixtures were used as the solvent. Before the hydrogenation experiment (in typical procedure) the catalyst was allowed to swell "in situ"—inside the reactor by wetting it with an excess of THF (or THF–H_2O mixtures). Nitrogen (15 min) and subsequently hydrogen (30 min) was passed through the reactor. Since the expansion of catalyst proceeded very quickly (1–2 min) as showed swelling experiments, the time period used for passing nitrogen was enough to reach the complete expansion of the catalyst grains. Pre-swollen catalyst was contacted with the hydrogenated solution and after 2–3 min the experiment was started. The progress of the hydrogenation was monitored by measuring the volume of hydrogen consumed against reaction time. The reactor was connected with system of gas-burettes and electronic device for registration the volume of hydrogen consumed in the reaction. Samples of solutions were withdrawn from the reactor via a sampling tube at appropriate intervals of time and they were analysed by GC.

Products analysis was performed with a gas chromatograph PE Clarus 500 equipped with a flame ionisation detector in conditions: capillary column Elite-5 MS (30 m × 0.25 mm × 0.25 μm coating) with helium as a carrier gas (flow rate 1 ml/min) and injection temperature 250 °C. Product separation was obtained using temperature ramp 80°C for 1 min, 15 °C/min to 220 °C, hold for 3 min. Octan-2-ol was used as the standard. The analytical standards of reagents B3-D, B2-D (mixture of cis—trans isomers 1;1), B1-D, *n*-butyraldehyde, crotyl alcohol and *n*-butanol (Fluka) were used in chromatographic analysis. Other side product, 2-hydroxytetrahydrofuran was identified using GC-MS. The analysis was carried out using Auto system XL (PE) instrument in conditions : capillary column PE-5 MS (30 m × 0.25 mm × 0.25 μm coating) temperature ramp 15 °C/min from 70 °C to 150 °C, injection temperature 250 °C with He as a carrier gas (flow rate 1 ml/min). The cumulative content of by-products (termed P) was calculated from the mass balance.

As a measure of catalyst activity the initial rate of B3-D hydrogenation expressed as number of B3-D moles reacted per minute and per gram of Pd in the catalyst (mol min^{-1} g Pd^{-1}) is assumed. The selectivity towards B2-D is calculated at 90% B3-D conversion form the formula

$$S\ [\%] = \text{number of B2} - \text{D moles formed/number of B3} - \text{D moles reacted.}$$

Typically the hydrogenation test was carried out at 22 °C using 40 cm^3 of B3-D solution in THF of c° B3-D = 0.052 mol/dm^3 and catalyst concentration 3 g/dm^3. The hydrogenation was carried out up to the moment when the hydrogen uptake was cased. Shaking of the reactor was carried out at such a speed to ensure that the reaction rate does not depend on agitation speed.

3 Results and Discussion

3.1 Characterization of Catalysts

During the reduction of catalyst with $NaBH_4$ the colour of the samples changes from yellow to black.

The observations performed by means of optical microscope indicate that the whole volume of polymer grains becomes black upon $NaBH_4$ treatment. The X-ray microprobe analysis (Pd map) shows very homogeneously distributed Pd throughout the grains of reduced catalyst (Fig. 1). This observation is also confirmed by the analysis of Pd content determined by X-ray microprobe analysis over the cross-section of reduced 2%Pd-3 catalyst (Fig. 2). The content of Pd is determined in 3 points (1, 2 and 3 marked in Fig. 2) that are localized near to the outer surface and inside the catalyst particle. The content expressed as the intensity of Pd signal (arb. units) is also plotted in Fig. 2.

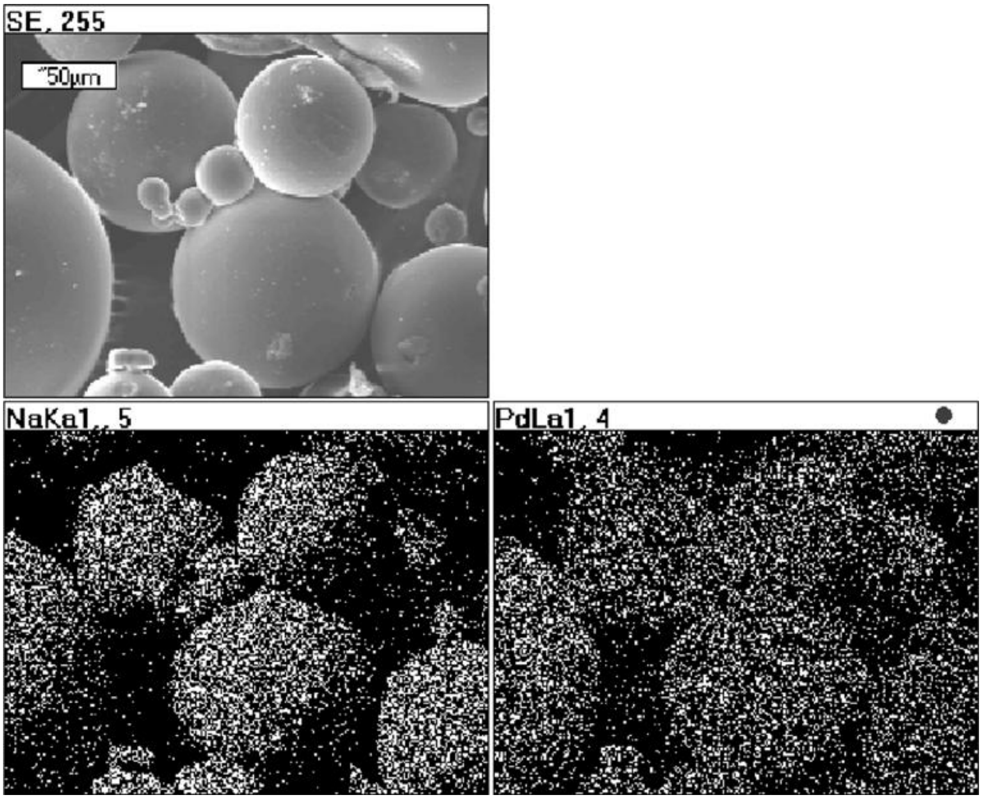


Fig. 1 The SEM micrograph of reduced 2%Pd-3 catalyst and X-ray microprobe analysis of Pd and Na distribution (magnification 10000)

In reduced catalyst the presence of sodium is also revealed by the X-ray microprobe analysis (Fig. 1). This indicates a replacement of H^+ ions in carboxylic acids of polymer by Na^+ ions during the reduction of catalysts by $NaBH_4$ [23]. Our previous studies showed practically the same values of Na/Pd ratio for 1%Pd-3 and 2%Pd-3 catalysts [22]. No change in the Na/Pd ratio appears for the catalysts after the hydrogenation reaction performed in THF or H_2O solvents indicating no removing of sodium under the catalytic test.

The TEM images registered for number of reduced catalysts are displayed in Fig. 3a–d. For these studies the catalysts with 1 wt% Pd and 2 wt% Pd as well as the sample reduced by hydrazine are selected. In all the catalysts, Pd particles of sizes in nano-scale can be seen and no appreciable differences in the distribution or in the metal nano-particles sizes are observed from one catalyst to the other. Hence, polymer used in the present studies exhibits high ability for the stabilisation highly dispersed Pd nanoparticless.

The results of swelling measurement for starting polymer and $NaBH_4$ reduced catalysts are reported in Fig. 4. Owing to hydrophobic character, the OFP resin exhibits no volume expansion in polar solvent like methanol, H_2O whereas it swells remarkably in the THF medium. The samples swell very quickly when contacted with THF and after 1–2 min their expansion becomes complete. It is observed that 3% crosslinked OFP-3 swells remarkably in THF ($V_S/V_0 = 5.2$) whereas expansion of highly 10% and 20% crosslinked polymer gradually decreases attaining $V_S/V_0 = 3.02$ and 2.25, respectively. Hence, similarly to the observation of other authors the degree of crosslinking has a direct effect on the resin swelling, when there is an increase of the crosslinking degree, the structure becomes more rigid and the resin swells to evidently lower extent.

Insertion of palladium followed by reduction of catalysts with $NaBH_4$ also reduces swelling ability of polymer and as Fig. 4 shows the expansion of $NaBH_4$ reduced catalysts gradually decreases with a rise in Pd content. These effects were ascribed in our previous work to some changes in the polymer backbone under treatment by $NaBH_4$. Reduction of carbonyl groups present in the polymer was evidenced by FT-IR spectra [23]. The X-ray microprobe analysis reveals the replacement of H^+ ions in carboxylic groups by Na^+ ions (Fig. 1).

3.2 Hydrogenation of B3-D

All the hydrogenation experiments (except the runs described in Sect. 3.2.3) are performed using the solution of initial B3-D concentration of 0.052 mol/dm^3 and the

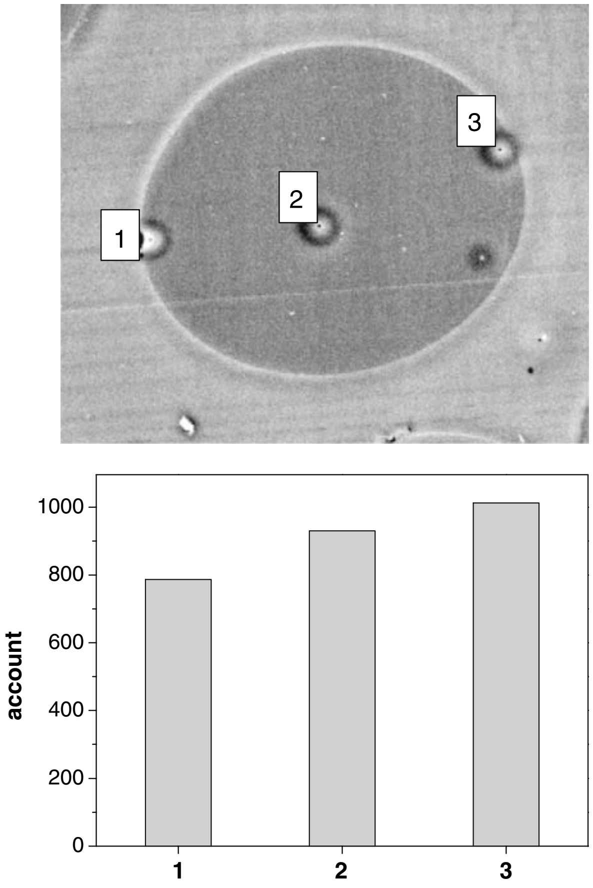


Fig. 2 X-ray microprobe analysis for Pd distribution over the cross-section of reduced 1%Pd-3. The data of analyses performed in points 1, 2 and 3 are plotted in the graph

catalyst concentration of 3 g/dm^3. Catalytic tests indicate that activity/selectivity behaviour of Pd/OFP catalysts extremely varies depending on the swelling efficiency of solvent with respect to the polymer matrix (Figs. 5 and 6). Two solvents of extremely different polarity, water and THF are used. A difference in catalytic performance of Pd/OFP in these two solvents is evidenced by the shape of hydrogen uptake curves and the graphs showing the change in reagents concentrations (B3-D, B2-D and B1-D) against the time of hydrogenation. The first extreme case is represented by water which is no swelling solvent for the polymeric matrix (Fig. 5). In these conditions the outer surface of catalyst mostly participates in the hydrogenation because the active centres located deeper, inside the polymer are practically not accessible to the reactants. In aqueous conditions the rate of B3-D hydrogenation is low. In these conditions, from the very beginning of reaction not only the triple bond of alkyne, B3-D, is hydrogenated to the double one but also the alkene, B2-D, is hydrogenated to alkane, B1-D. As the consequence, the selectivity towards the target product, B2-D, is low, ca. 25%.

Second extreme case is represented by hydrogenation in THF solvent, i.e., in conditions resulting in remarkable expansion of catalyst grains (Fig. 6). In these conditions the rate of B3-D hydrogenation dramatically increases compared to aqueous system and the reaction proceeds through two well separated stages clearly observable on the hydrogen uptake curve (Fig. 6). In the initial stage lasting until 1 molar equivalent of hydrogen had been consumed, the half-hydrogenation of B3-D to B2-D ($C\equiv C$ to $C{=}C$) is the main reaction. The second stage started after 1 equiv. of hydrogen had been consumed. It has been generally observed that in swollen state of catalysts induced by THF medium below 80–85% B3-D conversion range, olefinic diol B2-D is the major product with selectivity 90–95%. At the stage of complete conversion of B3-D, the selectivity to B2-D is in a range 80–85%, the remaining product being B1-D. The hydrogenation of B2-D to alkane, B1-D and to other by-products starts only at almost complete conversion of alkyne, B3-D. The supposed side products, butyraldehyde, crotyl and butyl alcohols are not found during the present experiments probably due to their low concentrations. Only one by-product is detected in the presence of Pd/OFP catalyst and this product is identified by GC-MS analysis as γ-hydroxybutyraldehyde.

Hence, in swollen sate of catalyst grains, the hydrogenation of intermediate olefinic diol, B2-D, to the saturated one, B1-D, is almost completely suppressed in the stage of triple, $C\equiv C$ bond in the B3-D, hydrogenation. For a better understanding the role of polymer matrix, the systematic studies are performed in THF solvent using wide range of operating conditions. The aim is to determine the influence of crosslinking degree of the polymer support, loading of palladium in catalysts and initial B3-D concentration on activity/selectivity behaviour of Pd/OFP catalyst.

3.2.1 *The Effect of Crosslinking Degree of Polymer*

The hydrogenation of B3-D is performed in the presence of catalysts with 1 wt% Pd supported by 3, 10 and 20% crosslinked polymers (1%Pd-3, 1%Pd-10 and 1%Pd-20 respectively). The obtained data (Table 1) indicate that crosslinking degree of polymer matrix has an effect on activity and selectivity to alkene. It is observed that with rise in crosslinking degree of polymer the rate of B3-D hydrogenation gradually decreases. On highly, 10% and 20% crosslinked polymers, a suppression of B2-D to B1-D hydrogenation during the B3-D stage becomes less effective giving lower selectivity (ca. 80%) to the target product, B2-D. In the presence of all three catalysts the content of by-products determined in the final solution is very similar and amounted to 21.2–27%.

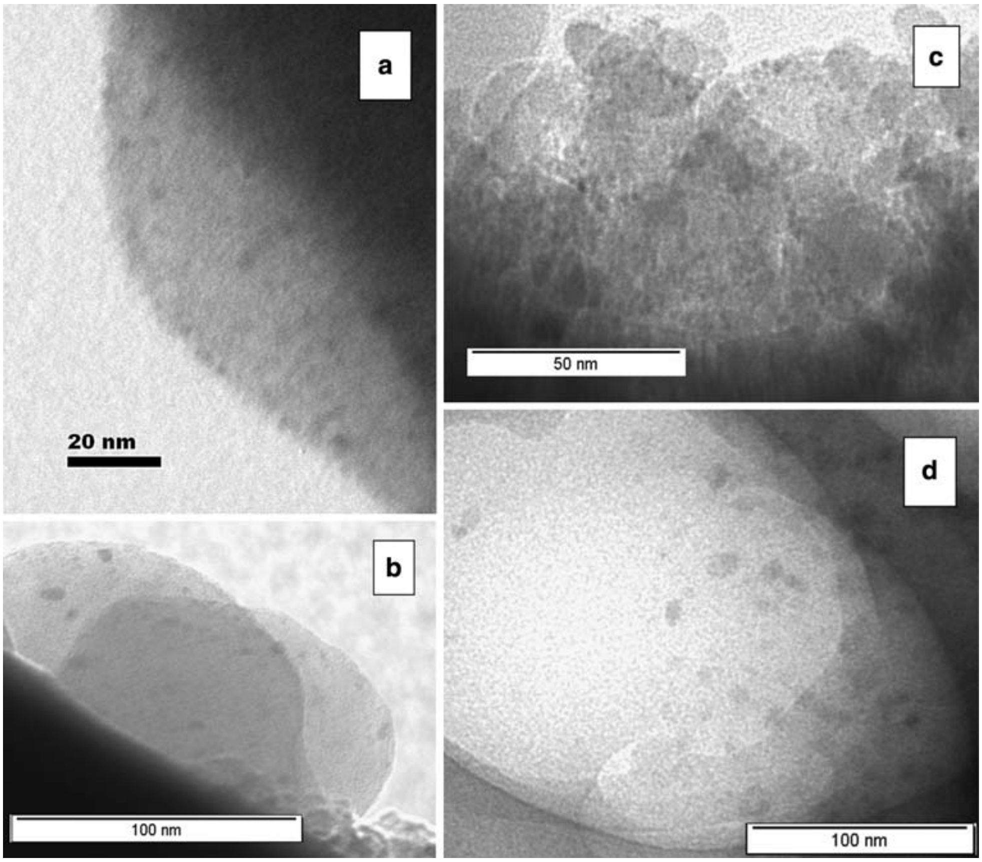


Fig. 3 TEM micrographs of $NaBH_4$ reduced catalysts 2%Pd-3 $d_p = 150–250$ µm, (**a**); 1%Pd-3, $d_p = 75–150$ µm, (**b**); 2%Pd-3, $d_p = 75–150$ µm, (**c**); and hydrazine reduced 1%Pd-3, $d_p = 75–150$ µm, (**d**)

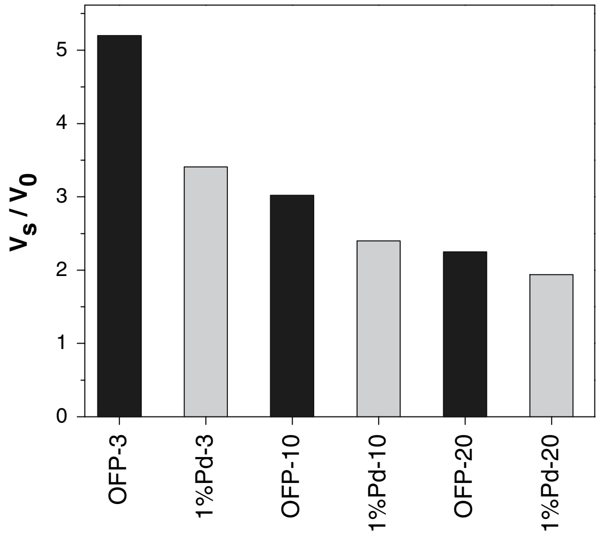


Fig. 4 Swelling ability in THF for 3, 10 and 20% crosslinked polymers and catalysts

Hence, less crosslinked 1%Pd-3 catalyst is more active and more selective than highly crosslinked samples. This “crosslinking effect” may be related to the influence of polymer network on the accessibility of catalytically active centres which depends on the expansion of polymer matrix induced by reaction medium. Literature information show that reactivity of metal particles (Rh, Pd, Pt) located throughout the polymer matrix depends critically on both, the steric hindrances (nano-environment) in the vicinity of active centres and the accessibility of particles for the reactants migrating through the polymer network. Swelling of the polymer results in the formation of nano-porosity and it can make a substantial fraction of the interior of resin particle available for the reactants molecules that migrate through the polymer matrix. Such swelling dependent nano-porosity depends on the degree of crosslinking of the polymer. It implies that in highly crosslinked polymer the migration of B3-D molecules to the active centres located in the pores (inside) becomes more hindered and as a consequence the rate of hydrogenation decreases. In these conditions the selectivity towards B2-D also decreases showing detrimental effect of microporous structure existing in highly crosslinked polymers. This observation is consistent with generally presented opinion, that in the course of alkyne hydrogenation, the selectivity towards olefin, an intermediate product, is reduced due to pore

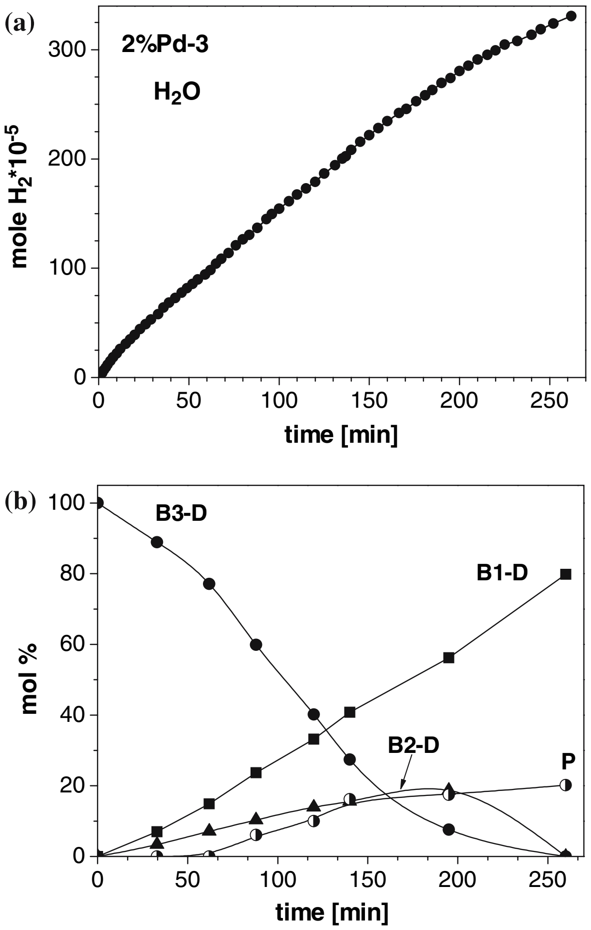


Fig. 5 Hydrogenation of B3-D in aqueous medium (**a**) hydrogen consumption and (**b**) reagents concentration as a function of reaction time. (c°(B3-D) = 0,052 mol/dm^3 catalyst concentration 3 g/dm^3)

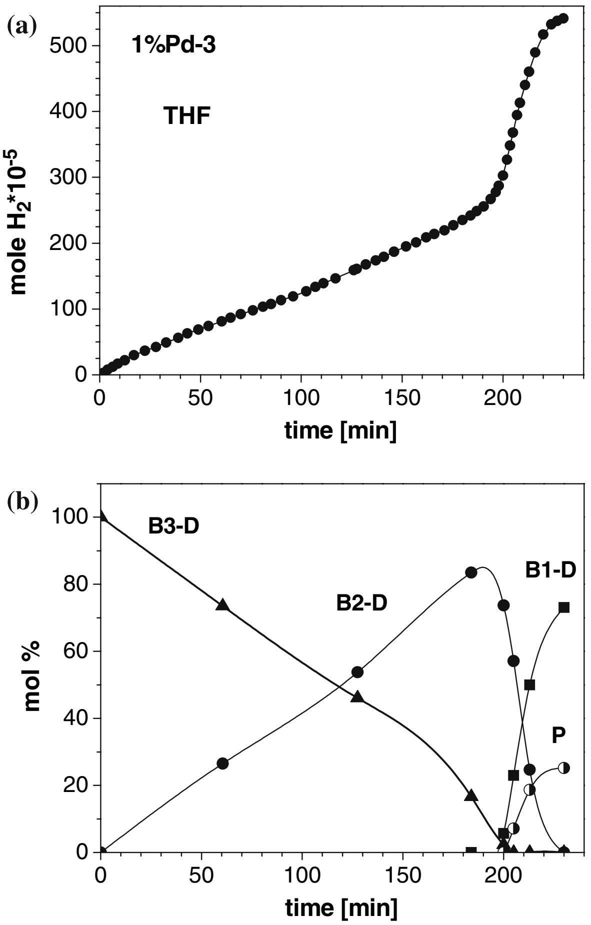


Fig. 6 Hydrogenation of B3-D in THF solvent (**a**) hydrogen consumption and (**b**) reagents concentration as a function of reaction time. (c°(B3-D) = 0.0835 mol/dm^3 catalyst concentration 3 g/dm^3)

diffusion limitation. Practice shows that the most selective palladium catalysts for selective hydrogenation of alkyne to alkene have nonporous supports such as calcium carbonate or barium sulfate. In order to achieve highly selective formation of B2-D, the use of catalyst of low porosity like Pd/$CaCO_3$ is preferred [18].

3.2.2 The Effect of Pd Content

The effect of Pd loading is studied for 0.5%Pd-3, 1%Pd-3 and 2%Pd-3 catalysts with 3% crosslinked resin and the obtained data are collected in Table 2. It is observed that the initial rate of B3-D hydrogenation per 1 g of Pd is very similar at lower Pd content, as in 0.5%Pd-3 and 1%Pd-3 catalysts. In the presence of both catalysts the hydrogenation of C=C in B2-D is strongly suppressed in the stage of C≡C hydrogenation giving the selectivity towards B2-D as high as 86–87%. The activity of catalyst with higher Pd loading, 2%Pd-3 decreases as well as decreases the selectivity to B2-D (80.2%). Because of similar distribution and the size of Pd metal particles in the catalysts, the effect of Pd loading may be related, similarly as in the case of crosslinking degree, to influence of polymer mass swelling that decreases with a rise in Pd content.

3.2.3 The Effect of Initial B3-D Concentration

The effect of initial B3-D concentration is studied in the presence of 1%Pd/OFP-3 catalyst (particles diameter 75–150 μm) within the c°(B3-D) range 0.015–0.1 mol/dm^3. The relationship between the initial rate of B3-D hydrogenation and c°(B3-D) is presented in Fig. 7. From this Figure one can see that the rate of B3-D hydrogenation depends on substrate concentration, but similarly to the observation of other authors this dependence is very complicated [14, 24, 25]. In solutions of low initial c°(B3-D) (0.015–0.052 mol/dm^3) the rate increases with rise in the B3-D concentration reaching the maximum

Table 1 The effect of crosslinking degree of polymer

Catalyst	Catalyst concentration (g/dm^3)	Sieve fraction d_p (μm)	V_S/V_0	R (B3-D) (mol min^{-1} g Pd^{-1})	Selectivity to B2-D (%)	By-products (%)
1%Pd-3	3	150–250	3.41	0.0190	86.0	27.0
1%Pd-10	3	150–250	2.40	0.0154	77.2	22.5
1%Pd-20	3	150–250	1.94	0.0116	77.1	26.6

Reaction carried out in solution of c°(B3-D) = 0.052 mol/dm^3

Table 2 The effect of Pd content in catalysts and the influence of water additives in THF solvent

Sample	Solvent	V_S/V_0	Sieve fraction d_p (μm)	R (B3-D) (mol min^{-1} g Pd^{-1})	Selectivity to B2-D* (%)	By-products (%)
OFP		6	75–150			
0.5%Pd-3	THF	4.1	75–150	0.0177	87.8	24.8
1%Pd-3	THF	4.05	75–150	0.0190	86.1	27.0
2%Pd-3	THF	3.87	75–150	0.0118	80.2	21.2
2%Pd-3	THF + 5 vol% H_2O	6.53	75–150	0.0117	98.8	18.2
1%Pd-3 reduced by N_2H_4	THF	6.2	150–250	0.0136	98.3	36

* Selectivity calculated at 90% conversion of B3-D

Reaction carried out in conditions: catalyst concentration 3 g/dm^3, c°(B3-D) = 0.052 mol/dm^3

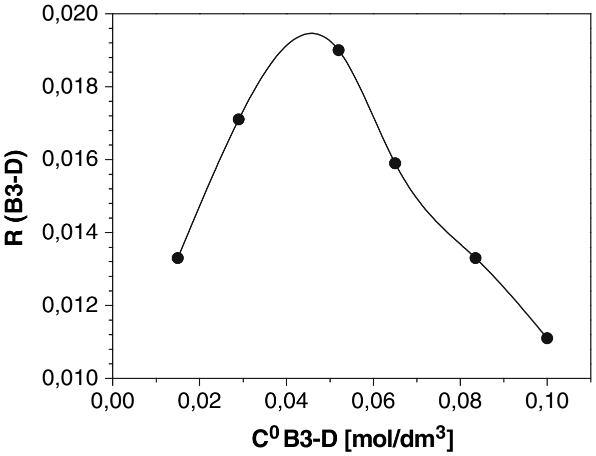


Fig. 7 Initial rate of B3-D hydrogenation [mol min^{-1} g Pd^{-1}] against c°(B3-D). Reactions performed in the presence of 1% Pd-3 catalyst (catalyst concentration 3 g/dm^3)

value at c°(B3-D) near to 0.052 mol/dm^3. In the range of relatively low c°(B3-D) the selectivity towards B2-D achieves 86–88.5% and very similar content of by-products is formed (27–30%). At B3-D concentration higher than 0.052 mol/dm^3 the rate slowly decreases with rise in c°(B3-D), however the selectivity to B2-D grows reaching 94.4% in the solution of the highest c°(B3-D) (0.1 mol/dm^3). The data in Table 3 show that in the presence of catalyst with larger particles diameter, d_p = 150–250 μm, [at c°(B3-D) = 0.0835 mol/dm^3] the rate and the selectivity to alkene are practically the same as those observed for catalyst with smaller particles diameter (d_p = 75–150 μm). Moreover, at the smallest and at the highest B3-D concentration, the rate for 1%Pd/OFP catalyst calculated per 1 g of Pd does not depend on the content of catalyst (Table 3). Since, the rate does not depend on agitation speed no diffusion limitation is operative under these conditions. The observed inhibition in the rate due to increased concentration of B3-D is similar to that obtained for modified Pd/Al_2O_3–NH_3, Pd–Zn–$CaCO_3$ [15, 18]. The inhibition in the rate due to increased concentration of B3-D is related to strong adsorption characteristic of the B3-D molecules, much stronger than that of alkene, B2-D.

For the Pd/OFP catalysts used in aqueous medium, when the participation of Pd inside the polymer is strongly restricted, the lower rate of B3-D hydrogenation is accompanied by low selectivity to alkene (Fig. 5). It is evident from this result that the Pd centres in Pd/OFP exhibit no specificity for the interaction with unsaturated triple and double bonds when used in aqueous medium.

On the other hand, an "inhibition effect of B3-D" is observed only when the grains of Pd/OFP catalysts are highly expanded in working state and especially when the B3-D/catalyst ratio is relatively high. In these conditions B3-D reacts very rapidly and the fall in rate with increasing concentration may also be a consequence of high rate of removal of hydrogen.

However, a peculiar role of the used polymer related with the steric hindrance in the nano-environment surrounding the Pd centres and influencing the accessibility of reactants to the active sites can also be not excluded. The

Table 3 The effect of initial concentration of B3-D

No.	C°(B3-D) (mol/dm^3)	Catalyst concentration (g/dm^3)	Sieve fraction d_p (μm)	R (B3-D) (mol min^{-1} g Pd^{-1})	Selectivity to B2-D* (%)	By-products (%)
1	0.015	3	75–150	0.0133	86.5	31
2	0.029	3	75–150	0.0171	88.5	30
3	0.052	3	75–150	0.0190	86.0	27
4	0.065	3	75–150	0.0159	96.0	30
5	0.0835	3	75–150	0.0133	93.3	25.1
6	0.0835	3	150–250	0.0137	95.0	26.9
7	0.1	3	75–150	0.0111	94.4	26.0
8	0.1	3.75	75–150	0.0159	–	–

* Selectivity calculated at 90% conversion of B3-D

Reaction performed in the presence of 1%Pd-3 catalyst

enhanced selectivity to butene-1 attained in the hydrogenation of 1,3-butadiene has been attributed by the authors to steric hindrance in the vicinity of Pd centres located in the polymer matrix [14]. Highly selective formation of B2-D observed for colloidal Pd, Pt nano-particles stabilized by various polymers (polyvinylpyrrolidone, polyvinyl alcohol, polymethylvinyl ether) has also been related to the influence of the polymeric stabilizer [20]. The authors pointed out that due to weakly bound ligand, polymeric stabilizer surrounding the metal nano-particles re-adsorption of the olefinic diol (B2-D) is unlikely thus giving the selective formation of B2-D.

3.3 Reaction Conditions for the Best Selectivity

3.3.1 Reduction of Catalyst with Hydrazine

Various modifications of reaction system leading to further increase in the selectivity towards B2-D have been performed. First, 1%Pd-3 catalyst is reduced by hydrazine instead of $NaBH_4$. This reducing agent is used since the reduction of catalysts with $NaBH_4$ resulted in some changes in the polymer backbone with consequent lowering the swelling ability of polymer. Moreover, Na^+ ions are introduced into polymer upon reduction by $NaBH_4$. According to the literature observation, alkaline metals ions, such as Na^+, Cs^+, can also play a role in the modification of adsorption ability of Pd centres towards alkyne/alkene making stronger the adsorption of alkyne. As the data in Table 2 show the use of hydrazine does not induce unprofitable effects as the expansion of hydrazine reduced catalyst ($V_S/V_0 = 6.2$) is even higher than that of the starting polymer ($V_S/V_0 = 5.2$). Moreover, reduction by hydrazine does not essentially affect the dispersion of palladium (Fig. 3d). The catalyst with Pd particles of size in nano-scale is formed, similarly to $NaBH_4$ reduced catalysts. The activity of hydrazine reduced catalyst slightly decreases whereas the selectivity to B2-D increases. B2-D is then formed with 98.3% selectivity at the 90% conversion of B3-D.

3.3.2 The Effect of Water Additives

The most effective system giving almost selective hydrogenation of B3-D to B2-D is obtained using the THF containing 5 vol% H_2O as the hydrogenation medium. The presence of small amounts of H_2O does not essentially change the activity but improves to some extent the selectivity. B2-D is then formed with 98.8% selectivity at the 90% conversion of B3-D (Fig. 8). Smaller amount of by-products is also formed in this reaction medium (Table 2).

The advantageous influence of low content of water may be to some extent related to greater expansion of catalyst observed at 5 vol% of H_2O in THF. As Fig. 9 shows with rise in the content of water in the THF–H_2O mixtures, the expansion of polymer gradually grows and passes over the

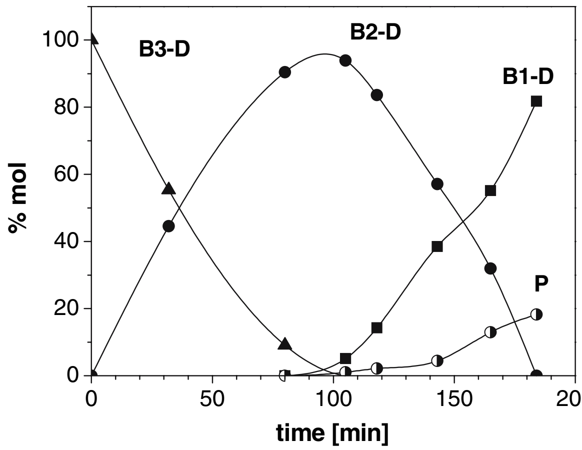


Fig. 8 The change of reagents concentration (mol%) as a function of reaction time. Hydrogenation in the presence of 2%Pd-3 catalyst (d_p = 75–150 μm), c° = 0.052 mol/dm^3, catalyst concentration 3 g/dm^3

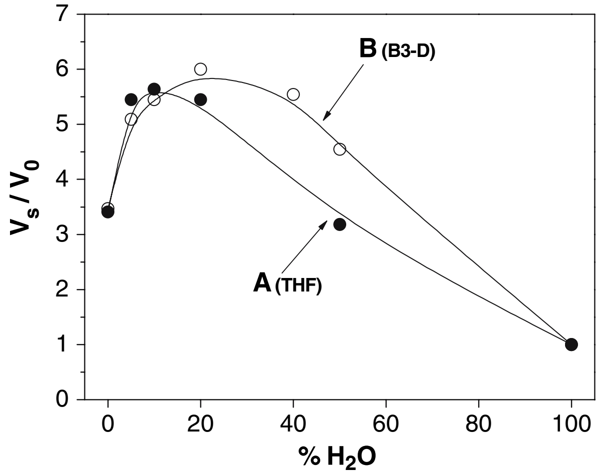


Fig. 9 Swelling ability (V_S/V_0) of reduced 1%Pd-3 catalyst (d_p = 150–250 μm) in THF–H_2O mixtures, without (curve A) and in the presence of B3-D (curve B)

maximum at ca. 10–20 vol% of H_2O (Curve A, Fig. 9). However, at the content of water higher than 20% the swelling ability rapidly decreases and finally, in pure water the catalyst does not swell. Swelling of catalyst is also measured using the B3-D and B2-D solutions in THF–H_2O mixtures (Curve B, Fig. 9). The presence of alkene (B2-D) exhibits not effect on the swelling ability of catalyst within the whole range of the solution composition. On the other hand, the expansion of catalyst changes in the presence of substrate, B3-D, and the influence of B3-D depends on the content of added water to the THF solvent. It is observed that the presence of substrate (B3-D) does not affect the expansion of catalyst in pure THF and at low content of water, up to 10 vol% of H_2O, however, at water content higher than 20 vol% the expansion of catalyst slowly increases and when the content of water reaches 30–40 vol%, a loosening of polymer network proceeds, observed as a partial transformation of spherical grains of Pd/OFP catalyst to the colloid form. Identical effects were observed on studying the esterification of glycerol with fatty acids catalysed by Amberlyst, ion-exchange resin with acid centres [26]. Partial homogenization of Amberlyst resin observed in this system has been ascribed by the authors to strong interactions of glycerol with acid groups of catalysts via the system of hydrogen bonds. This type of interactions seems also be the case in the present catalyst owing to the presence of C=O and carboxylic groups in the OFP polymer. It is very probable, that even at small content of water a loosening of polymer network also proceeds but to definitively lower extent giving the better expansion of polymer only, without remarkable destruction of spherical grains.

Based on the obtained results one may conclude that the functional, crosslinked gel-type resin used in the present work is promising support owing to the specific features of polymer matrix playing an advantageous role under the hydrogenation of B3-D. Swelling of polymer matrix under the catalytic run promotes either, activity and selectivity with respect to B2-D. The formation of alkene diol, B2-D, with selectivity near to 98% up to high conversion of B3-D can be achieved avoiding the use of electron donor alkaline additives. Water molecules play an important role in performance of Pd/OFP catalyst and in particular in the selectivity control. The presence of water molecules facilitates to some extent the interaction via the hydrogen bonds which are formed with the participation of acetylenic diol substrate (B3-D) and functional groups of polymer. At very small content of water, these interactions lead to better expansion of polymer only with consequent improving the selectivity with respect to alkene, B2-D. No more detailed explanation can be given from the obtained results but further experiments are performed using other alkyne type reagents for a better understanding of these systems.

4 Conclusions

Functional, crosslinked gel-type resins are promising supports owing to specific features of polymer matrix playing an advantageous role in the performance of Pd/OFP catalysts under the hydrogenation of B3-D. The OFP resin exhibits high ability for the stabilization of finely dispersed metal nano-particles which are localised throughout the c0atalyst grains. Swelling of polymer matrix under the catalytic run promotes either, the activity and selectivity with respect to target products, alkene diol, B2-D. The suppression of alkene to alkane hydrogenation in the stage of alkyne, B3-D, is ascribed to high ability of Pd centres in the Pd/OFP catalysts to strong adsorption of alkyne substrate. It may also be related to steric hindrances of polymer in the vicinity of active Pd centres. At small content of added water (5% by vol.) to the THF solvent, the catalysts offer very attractive performance. Water facilitates the interactions of B3-D with functional groups of polymer via the system of hydrogen bonds with consequent increase in swelling ability of polymer. Selectivity to B2-D near 98% up to high conversion of B3-D (90%) is then achieved avoiding the use of electron donor alkaline additives.

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