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Amine groups functionalized gel-type resin supported Pd catalysts: Physicochemical and catalytic properties in hydrogenation of alkynes

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ABSTRACT

Palladium catalysts (0.125–0.5 wt.% Pd) supported by amine groups—functionalized gel-type resin (FCN) were studied in the hydrogenation of alkynes reagents, 2-butyne-1,4-diol and phenylacetylene. The catalysts were prepared by two routes. The first, "OAc" is based on the immobilization of Pd-precursor in the pre-swollen resin from THF solution of $Pd(OAc)_2$, followed by chemical reduction of the Pd-centers. This method produces Pd particles of size in nano-scale. The second procedure, "aq" implies the deposition of Pd-species on dry resin beads using aqueous solution of $PdCl_2$. Reduction of these Pd-species gives relatively large Pd particles, dominating are 30–50 nm in size. The SEM studies performed over the cross-section of catalysts grains showed location of Pd in outer shell of polymer beads in both "OAc" and "aq" catalysts; however, thinner layer of Pd appears in "aq" series catalysts. In the presence of all catalysts, prepared by "OAc" and "aq" methods the selectivity towards alkenes is high, above 90%. The catalysts of "aq' series are much more active and more selective than "OAc" analogues giving selectivity to alkene ca. 94% at almost complete conversion of alkynes. Moreover, catalytic performance of "aq' series catalyst is unchanged under recycling use. The catalyst was recovered and reused 4 times, maintaining its catalytic efficiency.

1. Introduction

Supported palladium catalysts are widely studied in the hydrogenation of alkynes to alkenes. On commonly used inorganic carrier supported palladium catalysts, the selectivity to olefinic molecule (C=C) is frequently reduced due to the formation of fully saturated molecule already in the stage of unsaturated triple C≡C bond hydrogenation.

To explain the activity/selectivity behaviour of Pd catalysts in hydrogenation of alkynes reagents specificity of the interaction of catalytic centres with carbon–carbon multiple bonds of reagents as well as electronic and/or morphological properties of metal particles have been considered [1,2]. High selectivity to alkene is related to the increased Pd electron density that leads to the decreased alkene adsorption. In fact, greater selectivity to alkene has been achieved by employing electron donor compounds, like N-bases (quinoline, pyridine, and ammonia) or by pre-impregnating the additives like metals (Pb, Zn) onto the Pd catalyst. Moreover, carbon monoxide is also widely used as selectivity enhancer. Quite recently its role in activity/selectivity pattern has been described by density functional theory (DFT) studies [3]. They showed that the most notorious effect of CO, besides partial blocking of active sites, is the diminished binding energy of the alkene to the catalyst surface. This leads to a pronounced thermodynamic selectivity mainly due to an electronic contribution that enhances the differential adsorption of the double and triple bonds [3]. Extremely selective hydrogenation of triple bonds in alkyne–alkene mixtures has been observed on gold-supported catalysts [4] and gold can be considered a promising alternative to promote Pd-based catalysts in the deacetylenization of industrial gases. DFT simulations prove that extremely high selectivity for Au catalysts is related to the adsorption of only alkyne C≡C in the periphery of Au nanoparticles, whereas alkene C=C are not bonded [4]. In Pd-catalysed alkyne hydrogenation the role of subsurface carbon and hydrogen has been recently established [5,6]. It has been stated by "in situ XPS" measurements that unselective hydrogenation proceeds on hydrogen-saturated β-hydride, whereas selective hydrogenation of alkyne was only possible after decoupling bulk properties from the surface events.

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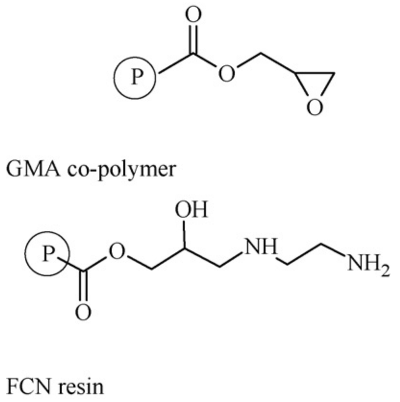


Scheme 1. Schematic formula of GMA co-polymer and final FCN resin.

However, very promising results have been obtained for catalysts supported by polymers that contain N-bases as the constitutional units [7–11]. This type of modification seems to be very durable because unlike commonly used modifiers (NH_3, quinoline) the N-units of polymer cannot be removed or lost during the catalytic reaction. The modification of geometric–electronic properties of Pd centres caused by these polymers resulted in highly selective hydrogenation of numerous alkynes and alkadienes to monoenes over Pd–heterocyclic polyamides [8], Pd–oligoaramides (oligo-p-phenyleneterephtalamide) [9] and Pd and Pt catalysts supported by copolymers containing amino and heterocyclic ligands [10]. Moreover, the advantageous role of polymer has been related to the steric hindrances of polymer network in the vicinity of catalytically active centres [7,11]. Furthermore, the access of metal particles for the migrating reactants may also be affected by the polymer network. This latter effect can be expected especially in the case of gel-type polymers, materials which can swell in contact with reaction medium. Swelling of the polymer effectively separates the polymeric chains resulting in the formation of nanoporosity [12,13]. This can make a substantial fraction of the interior of resin particle available for the reactants molecules. Thus, catalytic centers formed in gel-type resins act in the environment of swollen polymer gel, which may essentially influence not only the reactivity of metallic centers but also the selectivity of catalysed reaction.

In our previous work, gel-type resin functionalized by amine groups (FCN) (Scheme 1) was used as the support for Pd catalysts [14]. The Pd/FCN catalysts were prepared by incorporation of palladium to the microspheres of FCN resin pre-swollen in THF medium. $Pd(OAc)_2$ solution in THF was used as the precursor. Systematic studies performed for these catalysts showed that under these preparation conditions palladium ions were introduced via coordination to functional groups of FCN polymer. Coordinatively bonded Pd complexes resulted in the crosslinking of polymer with consequent difficult reduction of palladium ions. The obtained catalysts exhibited relatively low activity in the hydrogenation of unsaturated C≡C bond in alkyne reagent namely 2-butyne-1,4-diol (B3-D), reaction of industrial relevance (Scheme 2) [15,16]. In the presence of these Pd/FCN catalysts the alkene product (2-butene-1,4-diol) was formed with selectivity ca. 85–90%. Moreover, by-products were also formed at relatively high amounts (ca. 50%).

In this work another procedure (denoted "aq") is used for the preparation of Pd/FCN catalysts. In this procedure dry, powdered beads of FCN polymer are treated by aqueous solution of $PdCl_2$ of very low Cl ions concentration, i.e. of the composition which facilitates the hydrolysis of Pd aquachlorocomplexes present in the precursor solution [17]. It can be expected that alkaline character of amine groups of FCN polymer may also facilitate the hydrolysis of Pd-species. Since the FCN polymer does not swell in aqueous medium it can be expected that penetration of palladium ions inside the polymer beads would be to high extent restricted. This should result in the location of palladium mostly at the periphery of the polymer beads like in "egg-shell" type catalysts.

2. Experimental

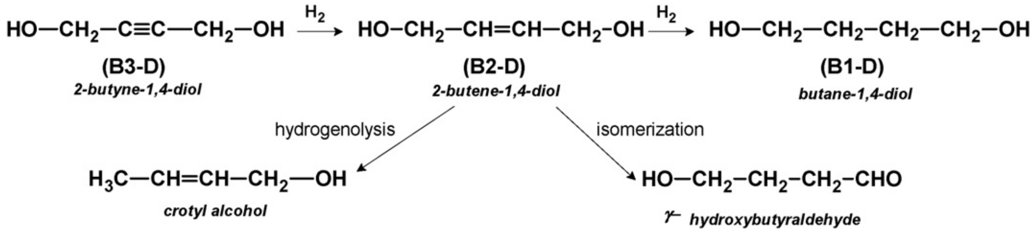
2.1. Synthesis of FCN resin

The preparation route of FCN resin is based on a two-step process involving preparation of GMA-co-polymer and its functionalization by ethylene diamine (Scheme 1). The details concerning the synthesis and characterization of FCN resin have been reported in our previous papers [14,18].

The first step consists in the synthesis of GMA co-polymer by suspension polymerization of the mixture of glycidyl methacrylate (GMA, 20 mol%), styrene (77 mol%) and diethylene glycol dimethacrylate (DEGDMA, 3 mol%) according to previously reported procedure [18]. The GMA co-polymer was obtained in the form of microspheres. The second step is based on the functionalization of GMA co-polymer. Thus, the sieve fraction of beads of diameters within the range 150–250 μm was functionalized by ethylene diamine to produce final FCN resin (Scheme 1). Functionalization was performed by reacting the GMA co-polymer for 24 h with 5-fold excess of ethylene diamine in DMF medium at 80 °C. After completing the reaction, the product was carefully washed with DMF and then several times with methanol and methylene chloride in turn to remove an excess of diamine and amide solvent. After that the obtained FCN resin was dried in vacuum at 40 °C.

2.2. Preparation of Pd catalysts

In this work two series of Pd catalysts termed as Pd-(aq) and Pd-(OAc) were studied. They were prepared by means of two procedures that differed with respect to the state of starting polymer and the nature of palladium precursors. The Pd-(aq) series catalysts were prepared by reacting dry, powdered polymer with aqueous solution of $PdCl_2$ precursor. The composition of $PdCl_2$ solution (molar ratio NaCl:$PdCl_2$ = 2.5, $PdCl_2$ concentration 2.3×10^{-3} mol/dm^3, pH 3–4) was identical to that used in



Scheme 2. Short reaction pattern of 2-butyne-1,4-diol (B3-D) hydrogenation.

our previous studies concerning Pd-polyaniline and Pd-poly(4-vinylpyridine) catalysts [17,19].

For comparison, 0.5%Pd-(OAc) catalyst was prepared by means of an identical procedure to that used in our previous work [14]. In this procedure $Pd(OAc)_2$ solution in THF (4.73×10^{-3} $Pd(OAc)_2$ mol/dm^3) was used as the precursor of palladium. A sample of the resin was first allowed to swell in pure THF solvent for 0.5 h. Then, the excess of THF was removed by decantation and an appropriate volume of $Pd(OAc)_2$ precursor in THF was added into the swollen resin.

In both methods, the suspension of polymer in precursor solution was gently stirred at room temperature when all of Pd ions reacted, as indicated by decolouration of initial yellow solution. This needed ca. 2 h in the case of $Pd(OAc)_2$ solution. Definitively longer time period (ca. 24–48 h) was required in the case of Pd-(aq) series catalysts because palladium was incorporated via the hydrolysis of palladium species present in the $PdCl_2$ precursor solution. The appropriate volumes of the precursor solutions to obtained 0.125 wt% to 0.5 wt% Pd in the final catalyst were used. The obtained Pd/FCN samples were filtered off and dried in air. Prior to the reduction they were allowed to swell in THF solvent. Reduction was performed with 10-times excess of THF–H_2O solution of $N_2H_4 \cdot xH_2O$ (hydrazine hydrate) (0.05 mol/dm^3) under stirring by a shaker. In the course of reduction the colour of the samples changed to grey/black. 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 50 °C).

2.3. Characterization of Pd/FCN catalysts

Swelling ability of starting FCN resin, as-prepared and reduced catalysts was evaluated by the measurement of the bulk expanded volume in THF medium. Swelling ability of samples was determined in the following way. 0.068 g of dry sample (i.e. the same amount as that used in catalytic experiments) was placed into 1 cm^3 graduated (0.02 cm^3) syringe and the volume of polymer was measured (V_0). Then, an excess of THF was introduced. The volume of expanded samples (V_S) was determined after 20–30 min, i.e. when the swelling equilibrium was achieved. As the measure of swelling ability the ratio 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.

The catalysts were characterized by FTIR, XPS, SEM and HRTEM techniques. FTIR studies were carried out using a Bruker-Equinox 55 spectrometer and a standard KBr pellets technique.

Morphology of reduced catalysts was studied by means of field emission scanning electron microscope JEOL JSM-7500 F equipped with the EDS system. Two detectors were used and the images were recorded in two modes. The secondary electron detector provided SEI images and back-scattered electron detector provided BSE (COMPO) micrographs.

In order to examine the Pd concentration profile over the cross-section of catalyst grain the powder samples were embedded in an epoxy resin. After drying for 48 h at room temperature, the embedded samples were trimmed and faced by ultramicrotomy. The faced specimens were coated with a thin conductive carbon layer and examined with a Zeiss DSM 982 field emission gun scanning electron microscope at 20 keV in the backscattered electron mode.

HRTEM analysis was performed using TECNAI G2 high-resolution microscope. Samples for the HRTEM studies were prepared by placing a drop of suspension of catalyst in ethanol (or THF) onto a carbon-coated cooper grid, followed by evaporation of the solvent.

XPS analysis was performed with a VG ESCALAB-210 spectrometer equipped with an aluminum anode as an unmonochromatized X-ray source (Al Kα = 1486.6 eV) run at 15 kV and 20 mA. The analyzer was operating in constant pass energy mode (E_{pass} = 20 eV) with energy step 0.1 eV.

2.4. Catalytic 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 [14,17]. The reactions were carried out in THF solvent. In standard procedure the concentration of hydrogenated reagents, 2-butyne-1,4-diol (B3-D) and phenylacetylene (Phc) was equal to 0.052 mol/dm^3. Prior to 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. Nitrogen (15 min) and subsequently hydrogen (30 min) was passed through the reactor. Since the expansion of catalyst was very quick (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 phenylacetylene, styrene, ethylbenzene, 2-butyne-1,4-diol, 2-butene-1,4-diol (mixture of *cis–trans* isomers 1:1), butane-1,4-diol (Fluka) were used in chromatographic analysis. Side products formed in hydrogenation of 2-butyne-1,4-diol were identified by GC–MS and their cumulative content (termed as P) was calculated from the mass balance.

As a measure of catalyst activity the initial rate of 2-butyne-1,4-diol (B3-D) or phenylacetylene (Phc) hydrogenation expressed as number of B3-D or Phc moles reacted per minute and per gram of Pd in the catalyst (mol min^{-1} g Pd^{-1}) is assumed. The selectivity towards alkene (2-butene-1,4-diol or styrene) is calculated at 90% alkyne (B3-D or Phc) conversion from the formula

$$S(\%) = \frac{\text{number of alkene moles formed}}{\text{number of alkyne moles reacted}}$$

In standard procedure the hydrogenation test was carried out at 22 °C using 40 cm^3 of THF solution of initial reagents (B3-D or PhC) concentration equal to 0.052 mol/dm^3. Catalyst concentration equal to 3 g/dm^3 and 1.7 g/dm^3 was used in B3-D and Phc hydrogenation, respectively. 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 Pd/FCN catalysts

Two different methods of palladium insertion, "OAc" and "aq" produced catalysts of different properties which can clearly be observed already by comparing the colour of as-prepared

Table 1
Surface concentration (at%) determined by the XPS method.

Sample	N	C	O	Pd	Cl	Pd/N
Initial FCN	5.94	81.63	12.43			
0.5% Pd-(OAc) as-prepared	4.33	74.66	20.36	0.65		0.15
0.5% Pd-(OAc) reduced	4.95	88.27	5.92	0.86		0.17
0.5% Pd-(aq) as-prepared	3.69	49.12	34.42	9.92	2.85	2.69
0.5% Pd-(aq) reduced	4.99	74.90	11.02	9.09	–	1.82

0.5%Pd-(OAc) and 0.5%Pd-(aq) catalysts. The former, Pd-(OAc) catalyst is yellow whereas the latter, Pd-(aq) is deep brown.

Using the “aq” procedure the maximum content of Pd which can be introduced to the FCN resin is equal to 0.5 wt% Pd. Therefore, the present study concentrate on the comparison of catalysts of the same Pd loading amounted to 0.5 wt% Pd, prepared by “aq” and “OAc” methods.

Surface sensitive XPS technique was used to determine surface concentration of palladium in catalysts. The obtained data are collected in Table 1. Within the surface of both catalysts, C, N, O and Pd are detected by the XPS method. As expected, in 0.5%Pd-(OAc) catalyst prepared from $Pd(OAc)_2$ precursor, i.e. under conditions enabling the penetration of palladium inside the swollen polymer mass, the surface concentration of Pd is very low and amounted to 0.65 at% only. On the other hand, under incorporation of palladium from aqueous solution of $PdCl_2$ the polymer beads do not swell, and their interior is practically not accessible for the palladium. As a consequence, surface concentration of palladium in 0.5%Pd-(aq) catalyst is as high as 9.92 at%, being ca. 15.2 times higher than that in 0.5%Pd-(OAc) catalyst. The Pd-(aq) and Pd-(OAc) catalysts differ also remarkably with respect to the value of Pd/N molar ratio. This ratio is very low in the case of Pd-(OAc) catalyst, it amounts to 0.15. On the other hand, in as-prepared Pd-(aq) catalyst the Pd/N ratio is amounted to 2.69, i.e. it is distinctly higher than 1.

The composition of precursor $PdCl_2$ solution used in the present work for the preparation of “aq” series catalysts is identical to the one used in our previous work devoted to palladium–poly(4-vinylpyridine) (Pd/P4VP) catalysts [19]. It has been stated in these previous studies that in aqueous solution of $PdCl_2$ of very low Cl ions concentration aquachlorocomplexes of Pd(II) dominated. Under contacting this $PdCl_2$ solution with poly(4-vinylpyridine) support of alkaline character, the hydrolysis of Pd aquachlorocomplexes proceeded leading to the deposition of Pd(II)-species (like hydrated oxide) mainly onto the surface of polymer particles [19]. Using number of spectroscopic methods the Pd–O, Pd–Cl and Pd–Cl–Pd bridges were identified in these Pd-species. In the Pd/P4VP catalysts prepared by this method the surface concentration of palladium was very high, similarly to the present Pd-(aq) series catalysts. The coordination of Pd(II) to pyridine nitrogen and the formation of “bridged” Pd–Cl–Pd structures has also been observed on reacting the ethanol solutions of $PdCl_2$ with poly(2-vinylpyridine) [20]. The deposition of this type of palladium species also seems to be probable in the presence Pd-(aq) series catalysts. In the as-prepared 0.5%Pd-(aq) catalyst the XPS technique shows the presence of oxygen and chlorine. Moreover, the content of oxygen is evidently higher than that in pure FCN polymer. The content of oxygen decreases to the level comparable to that in pure FCN polymer and the Cl disappears after reduction of catalyst.

This conclusion is supported by the value of binding energy for Pd $3d_{5/2}$ equal to 338.53 eV which is characteristic of Pd(II) coordinated to oxygen atoms [21]. Furthermore, from the XPS peak area ratios the surface stoichiometry $PdN_{0.37}C_{4.95}O_{3.5}Cl_{0.28}$ was calculated for as-prepared 0.5%Pd-(aq) catalyst. Taking into account that the coordination number in the Pd(II) complexes is 4, the formation of more complicated Pd(II) structures in which bridges like Pd–Cl–Pd or Pd–O–Pd appeared may be postulated in the case of 0.5%Pd-(aq) catalyst.

3.1.1. FTIR spectroscopy

In the FTIR spectrum of starting polymer (Fig. 1) a set of bands associated with the presence of carbonyl and nitrogen groups can be observed. Strong and broad bands located at 1725 cm^{-1} and 1601 cm^{-1} are characteristic of the C–O stretching in the carbonyl groups and the bands at 1584 cm^{-1} and 1383 cm^{-1} can be associated with the presence of N-groups (N–H and C–N stretching respectively).

In the Pd-(OAc) series catalysts prepared using $Pd(OAc)_2$ as the precursor interaction between palladium ions and functional groups of FCN polymer was evidenced by changes in the FTIR spectra [14]. Relative to the spectrum of pure polymer, the FTIR spectra of Pd-(OAc) catalysts displayed new distinct bands at 1330 cm^{-1} and 1570 cm^{-1}, i.e. in spectral region characteristic of C–N and N–H bonds. The intensity of bands (1330 cm^{-1}, 1570 cm^{-1}) ascribed to the Pd-ions bonded to the polymer strongly decreases after the reduction of Pd-(OAc) catalysts. From these spectral changes the conclusion was formulated that incorporation of palladium ions into the swollen polymer using $Pd(OAc)_2$ as the precursor was accomplished with the participation of functional groups of polymer [14].

On the other hand, as shown in Fig. 1, no remarkable changes in the spectrum of FCN polymer are observed after incorporation of palladium by means of “aq” procedure, i.e. using aqueous solution of $PdCl_2$. This observation shows quite different “mode” of palladium incorporation using “aq” procedure thus supporting the conclusion about the deposition of Pd-species like palladium hydroxide or oxide.

3.1.2. Swelling measurements

As shown in Scheme 1 the FCN resin consists of non-polar constituents such as styrene as well as polar groups such as carbonyl and amine groups. This composition results in hydrophobic character of FCN resin and as shown in our previous studies THF medium is the solvent leading to the highest expansion of FCN polymer [14]. Therefore THF solvent has been selected for the catalytic studies. The results of swelling measurement performed for starting FCN polymer and “aq” and “OAc” series catalysts are collected in Table 2.

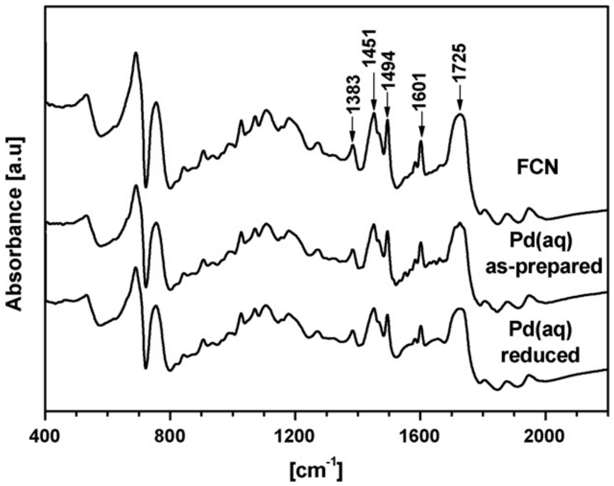


Fig. 1. FTIR spectra of initial FCN resin, as-prepared and reduced 0.5%Pd-(aq).

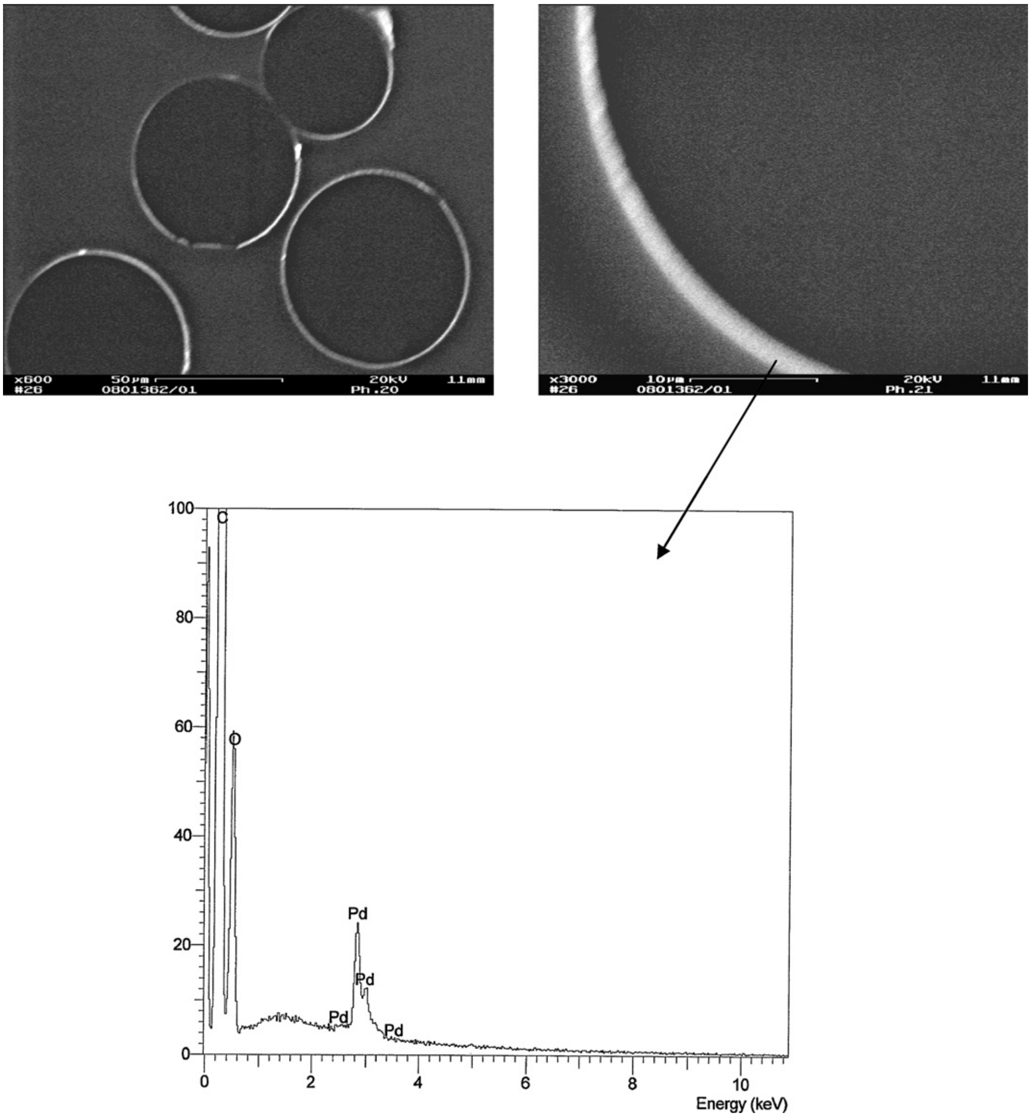


Fig. 2. BSE analysis over cross-section of 0.5%Pd-(aq) catalysts.

Pure polymer swells very well in THF as the volume of polymer particles increases ca. 3.8 times.

Insertion of palladium to the polymer by means of both procedures reduces its expansion. However, the decrease in expansion is much more pronounced for 0.5%Pd-(OAc) catalyst than in the case of 0.5% Pd-(aq) one.

The decrease in swelling ability for Pd-containing composites can be related to the “crosslinking” of polymer by palladium complex formed with the participation of functional groups of polymer. This Pd-crosslinking effect is more pronounced in the case of 0.5%Pd-(OAc) catalyst in which palladium was introduced into the polymer in expanded state. On the other hand, in the Pd-(aq) composite the species of Pd precipitated mostly onto outer surface of polymer beads and it may imply weaker interactions between palladium and functional groups of polymer. As a consequence, swelling ability of polymer mass only slightly decreases in catalyst prepared by means of “aq” procedure.

Table 2
Swelling ability (V_S/V_0) of pure FCN, Pd-(aq) and Pd-(OAc) catalysts determined in THF solvent.

Sample	As-prepared	Reduced by hydrazine
Pure FCN	3.8	3.7
0.5%Pd-(aq)	3.7	3.7
0.5%Pd-(OAc)	3.4	3.5

One can expect that after the reduction of Pd^{2+} ions the expansion of polymer mass would be restored to the initial value. However, treatment of pure polymer with hydrazine leads to slight decrease in its swelling ability. It can be seen that swelling of polymer is almost fully restored after the reduction of 0.5%Pd-(aq) catalyst. On the other hand, in the case of 0.5%Pd-(OAc) catalyst, the swelling of polymer mass increases only slightly and the starting expansion is not attained. This was ascribed in our previous studies to no complete reduction of Pd-ions evidenced by FTIR and XPS techniques [14].

In this work, the influence of hydrogenated reagents on swelling ability of reduced catalysts is also checked (Table 2). To determine this influence, reduced Pd/FCN catalysts are allowed to swell in THF solutions of individual reagents of the same composition (0.052 mol/dm^3) as that used in the hydrogenation experiments. It has been observed that all the reagents, when present in THF, do not influence the expansion of polymer mass.

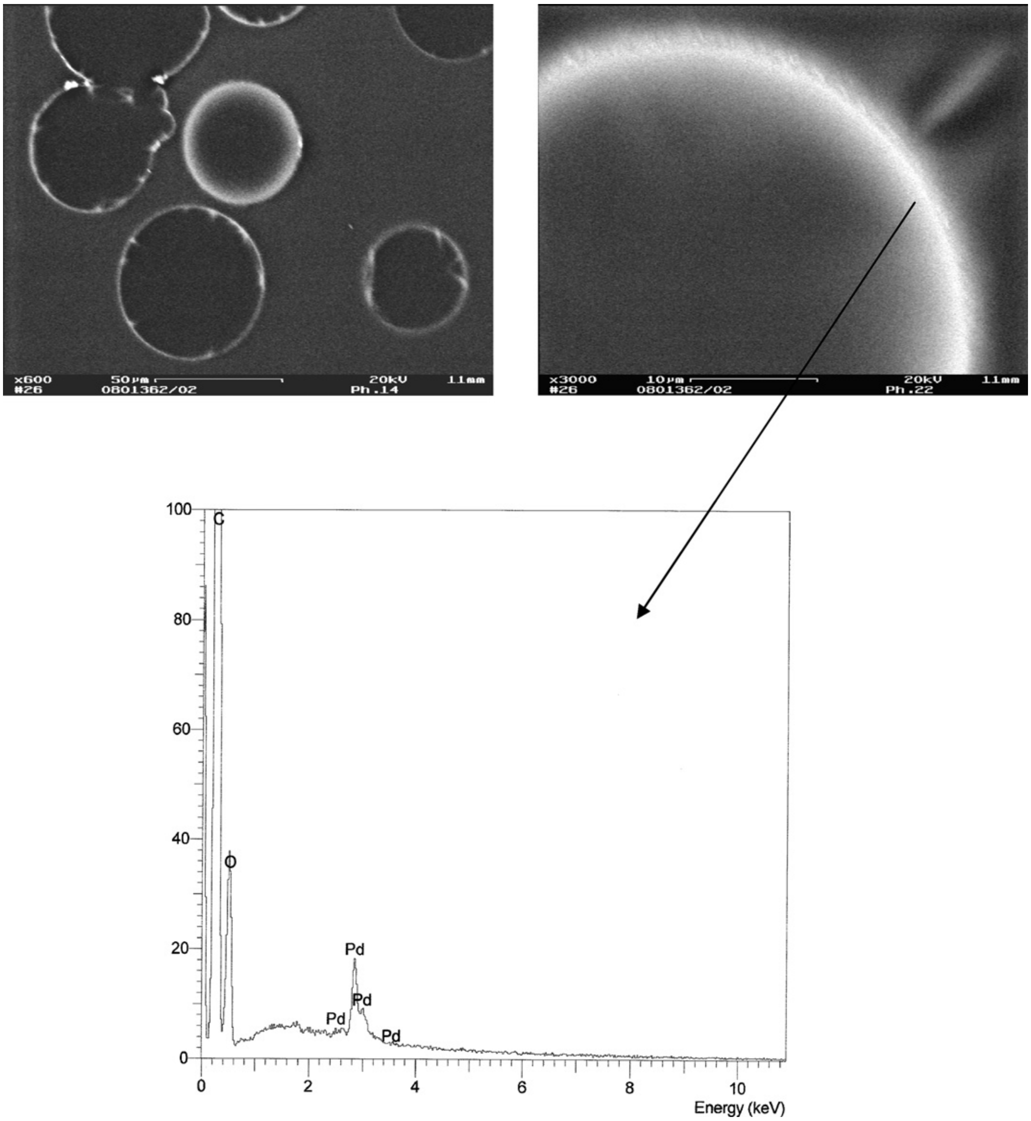


Fig. 3. BSE analysis over cross-section of 0.5%Pd-(OAc) catalysts.

3.1.3. *Electron microscopy studies (SEM, HRTEM)*

After reduction of as-prepared Pd-(OAc) composites with hydrazine solution their colour changes from yellow to grey whereas initially brown Pd-(aq) composites become black. From this very introductory observation one can conclude that Pd-particles are formed in both composites, however they differ essentially with respect to the dispersion and location of palladium in the polymer beads. This conclusion is well evidenced by the microscopic studies performed for reduced catalysts.

The Pd-concentration profile analysis was performed by means of X-ray analysis over the cross-section of grains of reduced 0.5%Pd-(aq) and 0.5%Pd-(OAc) catalysts. The obtained BSE images are displayed in Figs. 2 and 3 respectively. In both catalysts palladium is located in the surface shell of catalyst particles. In 0.5%Pd-(aq) catalyst the Pd-shell is very distinct and thin (Fig. 2). In 0.5%Pd-(OAc) catalyst Pd is also located within the surface layer (Fig. 3), however the Pd-shell is not so much distinct and it is evidently thicker than that in Pd-(aq) catalyst.

Moreover, the catalysts prepared by “aq” and “OAc” procedures substantially differ with respect to the size of Pd particles.

As HRTEM studies showed in the case of 0.5%Pd-(OAc) catalyst very well dispersed Pd-nanoclusters are formed. They are too small to be distinctly observable even by HRTEM technique (Fig. 4). From the HRTEM image only very indistinct “small darker spots” can be recognized.

On the other hand, the particles of Pd of distinctly higher diameters are observed in Pd-(aq) catalysts. The micrographs register by BSE mode (COMPO) for 0.25%Pd-(aq) and 0.5%Pd-(aq) catalysts are displayed in Figs. 5 and 6 respectively. In these micrographs particles of Pd can easily be observable as “individual” spherical white spots more or less occasionally located on the polymer particles. However, besides the individual particles a few small aggregates composed of individual particles can also be seen. From these images the Pd particles-size distribution diagrams are calculated taking into account the individual spots only (Fig. 7). These diagrams show similar distribution of Pd particles sizes in both catalysts of “aq” series, with 0.125% Pd and 0.5 wt% Pd. Palladium particles of size within the range 7–90 nm appear and the particles of size ca. 30–36 nm are predominant ones.

Thus, the methods of Pd incorporation influence the location of palladium as well as the size of Pd particles formed. Incorporation

Fig. 4. HRTEM micrograph of reduced form 0.5%Pd-(OAc) catalyst.

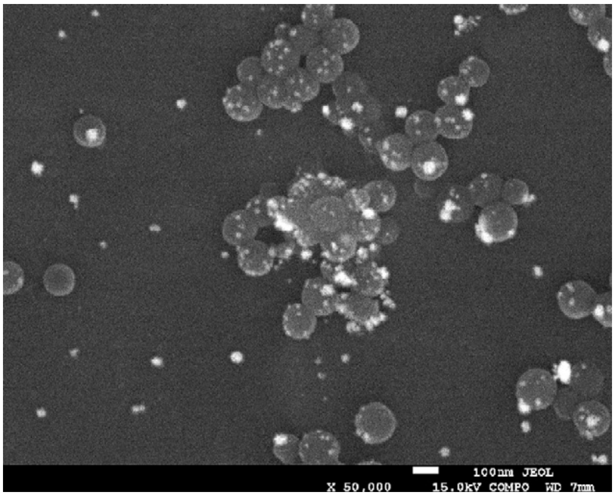


Fig. 5. BSE micrograph of reduced 0.25%Pd-(aq) catalyst.

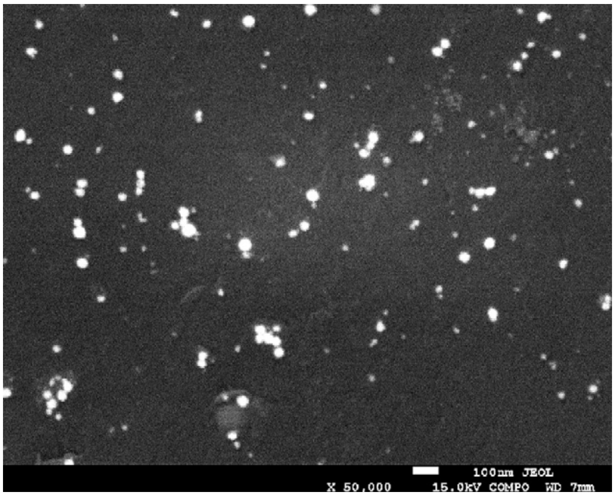


Fig. 6. BSE micrograph of reduced 0.5%Pd-(aq) catalyst.

of palladium to the particles of FCN resin in expanded state using "OAc" procedure (THF solution of $Pd(OAc)_2$) gives 0.5%Pd-(OAc) catalyst in which palladium is highly dispersed. However Pd appears in the form of relatively thick layer. This distribution of palladium results in low surface concentration of Pd. Quite different morphology is observed for "aq" series catalysts prepared by precipitation of Pd-species onto the dry powdered polymer beads. This procedure gives catalysts of evidently larger Pd particles which are located within the surface shell of polymer beads giving very high surface concentration of palladium.

3.2. Catalytic experiments

In this work, the activity/selectivity behavior of Pd/FCN catalysts is studied in the hydrogenation of alkynes reagents, namely phenylacetylene (Phc) and 2-butyne-1,4-diol (B3-D). Hydrogenation experiments are performed in the presence of reduced form of Pd/FCN catalysts using THF solvent, i.e. conditions when the polymer mass is in expanded state. Catalytic experiments concentrate on "aq" series catalysts. In order to examine the role of polymer properties the performance of "aq" series catalysts is compared with that of 0.5%Pd-(OAc) catalyst.

3.2.1. Hydrogenation of 2-butyne-1,4-diol (B3-D)

Typical graph showing the course of B3-D hydrogenation in the presence of Pd-(aq) series catalysts is displayed in Fig. 8. The reaction proceeds through two well separated stages clearly observable on the hydrogen uptake curve. 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

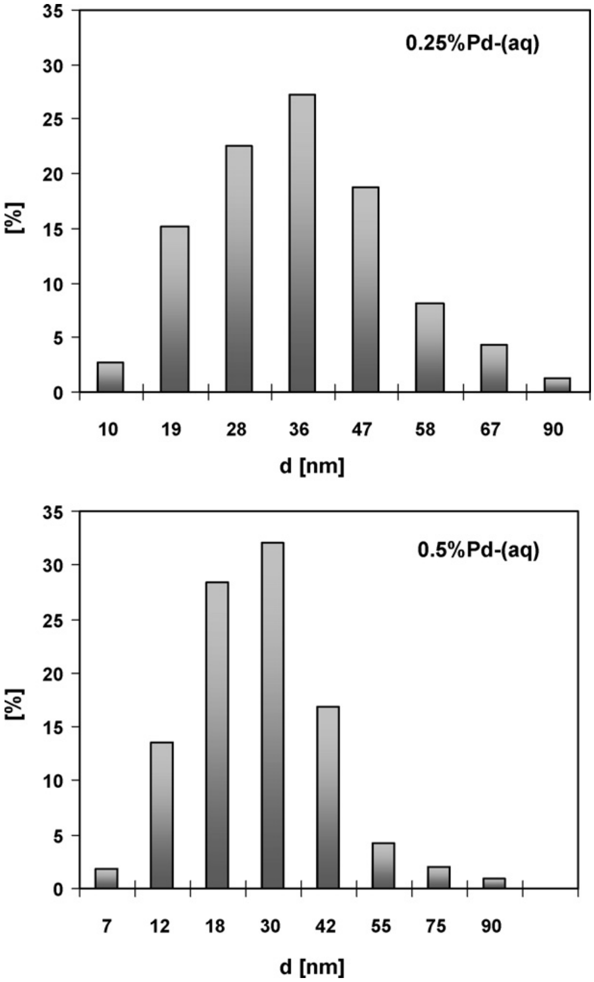


Fig. 7. The Pd particles size distribution diagrams for 0.25%Pd-(aq) and 0.5%Pd-(aq) catalysts.

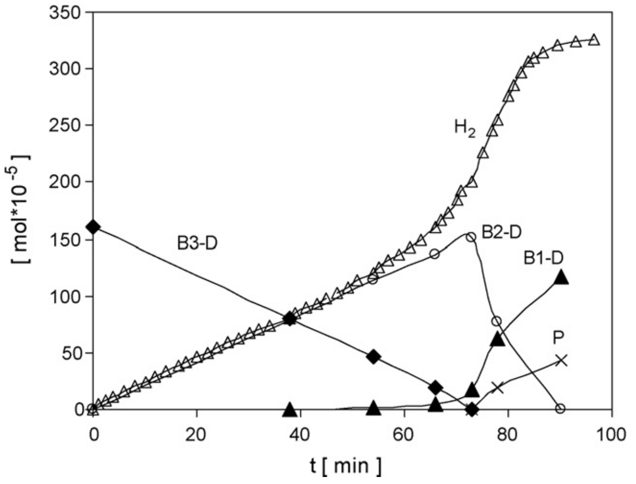


Fig. 8. Typical hydrogen consumption curves in the hydrogenation of 2-butyne-1,4-diol in the presence of Pd/FCN catalysts.

main reaction. The second stage started after 1 equiv. of hydrogen had been consumed. It has been generally observed over Pd-(aq) series catalysts that below 80–85% B3-D conversion range, olefinic diol B2-D is the major product with selectivity 90–95%. The hydrogenation of B2-D to alkane, B1-D and to by-products starts only at almost complete conversion of alkyne, B3-D. It should be stressed that in hydrogenation of B3-D, by-products (crotyl and butyl alcohols, *n*-butyraldehyde, γ-hydroxybutyraldehyde) can also be formed via the transformation of intermediate olefinic diol, *cis*-2-butene-1,4-diol (B2-D) by isomerization and hydrogenolysis reactions (Scheme 2) [22,23]. However, the supposed side products, butyraldehyde, crotyl and butyl alcohols are not observed during the present experiments probably due to their low concentrations. Only one by-product is detected in the presence of Pd/FCN catalysts and this product is identified by GC–MS analysis as γ-hydroxybutyraldehyde. In this work, cumulative content of by-products is calculated from the mass balance and it is termed as P (Fig. 8).

Fig. 9 shows the results obtained at various concentrations of 0.5%Pd-(aq) catalysts. Practically constant value of specific activity (SPC) defined as initial rate of B3-D hydrogenation related to 1 g of Pd [mol B3-D/min g Pd] is observed within the whole range of catalyst concentrations used in the experiments. This indicates that no external mass transfer effect operates under applied conditions. It can also be seen that the selectivity with respect to intermediate olefinic diol B2-D is very high and amounted to ca. 94%. In final solutions corresponding to the completeness of reaction, by-products are detected. Cumulative content of by-products indicates that ca. 23.1–27.9% from the initial content of B3-D is reacted to by-products.

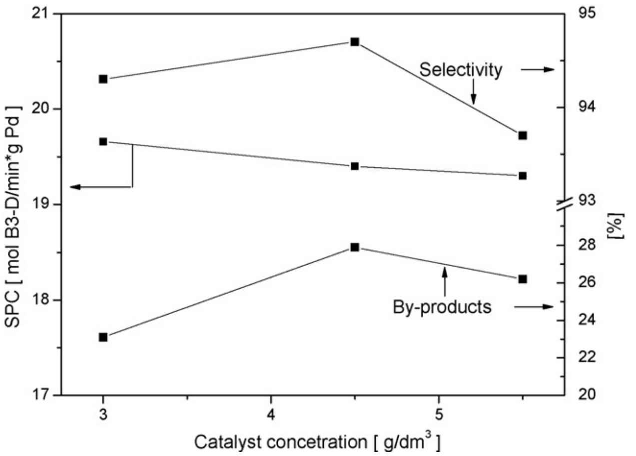


Fig. 9. Hydrogenation of B3-D in the presence of various contents of 0.5%Pd-(aq) catalyst. Specific activity (mol B3-D/min g Pd), selectivity to B2-D (*S* [%] at 90% B3-D conversion) and fraction of B3-D reacted to by-products (*P* [%] determined in final solution).

Table 3
Hydrogenation of 2-butyne-1,4-diol.

Catalyst	Initial rate of B3-D hydrogenation (mol min^{-1} g Pd^{-1})	Selectivity to B2-D at 90% B3-D conversion (%)	B3-D reacted to by-products (%)
0.125%Pd-(aq)	0.0296	94.7	21.5
0.25%Pd-(aq)	0.0255	93.6	20.2
0.5%Pd-(aq)	0.0197	94.3	20.1
0.5%Pd-(OAc)	0.0132	91.3	28.1

3.2.2. *The effect of Pd content*

The effect of Pd loading is studied for 0.125%Pd, 0.25%Pd and 0.5%Pd catalysts and the obtained data are collected in Table 3. It is observed that the initial rate of B3-D hydrogenation related to 1 g of Pd (termed as specific activity, SPC) slowly decreases when the content of Pd grows. Because of similar Pd-particles distribution diagrams, this decrease may be explained taking into account that in the catalysts not only individual Pd particles but also a few small aggregates appear. They are observed by microscopic studies. However, it is difficult to evaluate from these observations how is the effect of Pd loading on the effect of particles aggregation.

However, it seems more interesting that in the presence of all three Pd-(aq) catalysts the selectivity towards B2-D is very high and it is amounted to ca. 94%. This indicates that in the presence of all three catalysts the hydrogenation of C=C in B2-D is strongly suppressed in the stage of C≡C hydrogenation. For the comparison the hydrogenation is performed over 0.5%Pd-(OAc) catalyst of well dispersed Pd particles. In the HRTEM images of this catalyst (Fig. 4) no distinct metal particles are observed, because of their size is below the detection limit of microscope. The activity of this catalyst is distinctly lower compared to that of 0.5%Pd-(aq) one as well as the selectivity to B2-D is lower. In the presence of the latter 0.5%Pd-(OAc) catalyst the content of by-products is also higher than over 0.5%Pd-(aq) one.

3.2.3. *The effect of initial B3-D concentration*

The effect of initial B3-D concentration is studied in the presence of 0.5%Pd-(aq) catalyst within the c^0 (B3-D) range 0.029–0.07 mol/dm^3. The products distribution curves obtained at the lowest and at the highest B3-D concentrations are presented in Fig. 10. One can see that the rate of B3-D hydrogenation depends on substrate concentration being higher at lower initial c^0 B3-D. On the other hand, initial concentration of B3-D does not influence the selectivity to B2-D and the content of by-products formed. Within the whole range of B3-D concentrations the selectivity to B2-D attains ca. 94% and the fraction of B3-D transformed to by-products is amounted to ca. 25%. The observed inhibition in the rate due to increased concentration of B3-D is similar to that reported in the presence of Pd/Al$_2$O$_3$ catalyst modified by NH$_3$ or Pd/CaCO$_3$ modified by Zn additives [16,24]. The authors pointed out that this inhibition in the rate due to increased concentration of B3-D was caused by strong adsorption characteristic of the B3-D molecules, much stronger than that of alkene, B2-D.

The activity of 0.5%Pd-(aq) catalyst is also tested in aqueous medium, i.e. in conditions used in the technology of B3-D hydrogenation. In aqueous conditions the polymer does not swell and

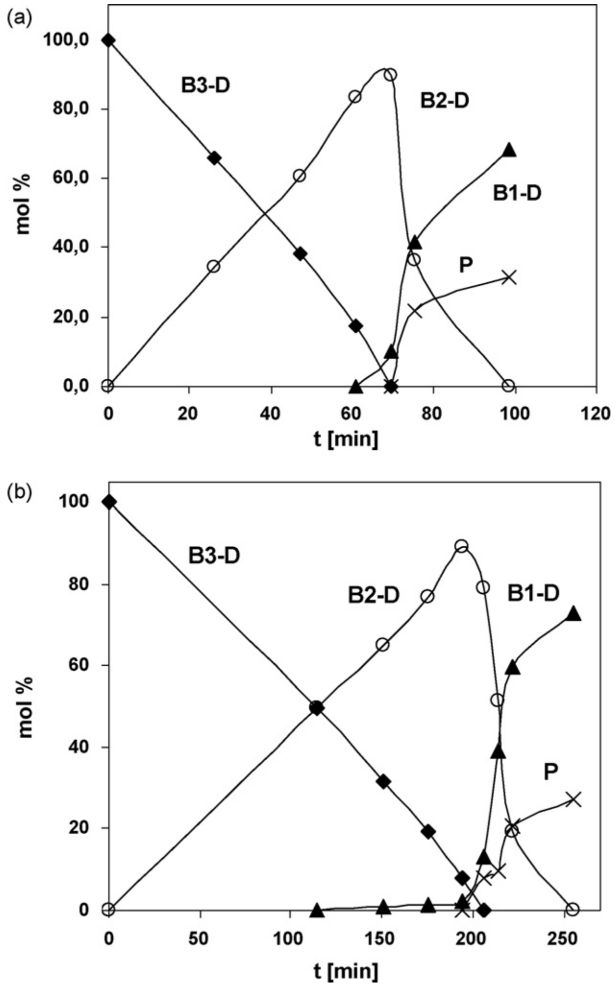


Fig. 10. Products distribution against reaction time in hydrogenation of 2-butyne-1,4-diol, initial concentration of B3-D equal to 0.029 mol/dm^3 (a) and 0.067 mol/dm^3 (b) (catalyst concentration 4.5 g/dm^3).

consequently only Pd-centers located in very external surface participate in the reaction. This leads to lower rate of B3-D hydrogenation, however, very high selectivity to target product (S = 94%), olefinic diol is preserved (Fig. 11). It is evident from this result that the Pd centers in Pd-(aq) catalysts exhibit specificity for the interaction with unsaturated triple and double bonds also when used in aqueous medium.

3.2.4. *The lifetime of 0.5%Pd-(sf) catalyst*

A serious problem in using polymer-supported catalysts is decrease in their activity due to leaching the metal particles under recycling use. To study this effect, in this work, the same sample of 0.5%Pd-(aq) catalyst was recycled 4 times.

After the first hydrogenation test, the catalyst was filtered, washed with THF and dried in air. Then, the recovered catalyst was reused using the same conditions as in the first hydrogenation reaction. This process was repeated 4 times. Fig. 12 shows the hydrogen consumption curves during the hydrogenation of B3-D in 4 catalytic tests and the concentration–time profiles for initial (Fig. 12a) and last (Fig. 12b) catalytic run. As can be seen, in the cycles the activity of 0.5%Pd-(aq) catalyst remains essentially constant or even increases gradually during its recycling use. The products distribution profile after 4 cycles is the same as that for fresh catalyst showing that high selectivity remains unchanged. It has also been checked that the catalyst is stable in air because after 1 year of storage in air the catalyst is still as active and selective as a freshly prepared sample.

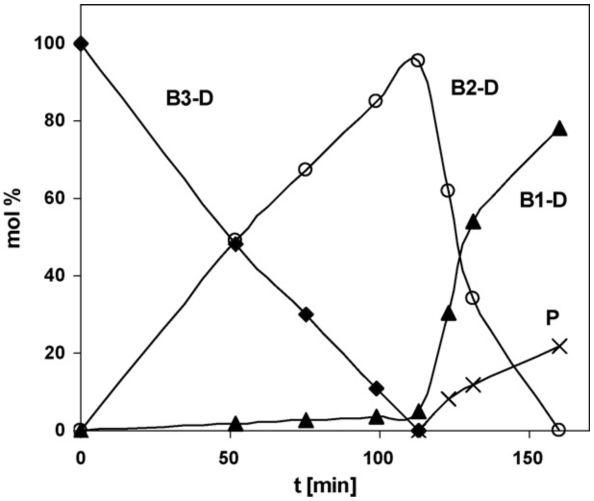


Fig. 11. Hydrogenation of B3-D in aqueous medium in the presence of 0.5%Pd-(aq) catalyst. Products distribution against reaction time (reaction conditions c^0 B3-D = 0.044 mol/dm^3, catalyst concentration 10 g/dm^3).

This result not only demonstrates the reusability of our catalysts but also may confirm the absence of Pd leaching during catalytic run. This was checked (qualitatively) with an analytical test with ethanolic dimethyl glyoxime (DMG, 1 wt%) solution. At high concentration of Pd, the Pd/DMG-complex precipitates and at low concentration of Pd, it results in a yellow orange colour of the solution. Thus, an ethanolic dimethyl glyoxime (DMG) solution (5 cm^3, 1 wt%) was added to a 5 cm^3 of reaction mixture after removing the catalyst and no colour due to the Pd/DMG-complex was observed. Moreover, following the hydrogenation test, the catalyst was removed by careful filtration and the solution was used for a second experiment with new amount of B3-D substrate. In all cases no further hydrogen uptake was observed.

The observed stable activity under recycling use of 0.5%Pd-(aq) catalyst may be related to specific properties of FCN resin. The FCN polymer is multidentate in character as it contains various coordination sites for palladium such as amine and carbonyl groups. This may allow that the metal remains attached to the supporting polymer. In fact, there are reports in the literature showing that leaching of the metal from the polymer can be reduced significantly by using polymer functionalized by chelating ligands [25].

3.2.5. *Hydrogenation of phenylacetylene (Phc)*

Catalytic properties of Pd-(aq) catalysts are evaluated in the hydrogenation of other alkyne reagent, phenylacetylene (Table 4). Typical plot of reagents concentration vs reaction time obtained in the presence of 0.5%Pd-(aq) catalysts is plotted in Fig. 13. Similarly to the B3-D as the substrate, specific activity of Pd-(aq) catalysts slowly decreases when the content of Pd grows. In the presence of all three Pd-(aq) catalysts unsaturated triple bond C≡C in Phc is highly selectively hydrogenated to the double C=C one. In the

Table 4
Hydrogenation of phenylacetylene.

Catalyst	Initial rate of Phc hydrogenation (mol min^{-1} g Pd^{-1})	Selectivity to styrene at 90% Phc conversion (%)
0.125%Pd-(aq)	0.271	91.6
0.25%Pd-(aq)	0.245	93.6
0.5%Pd-(aq)	0.235	93.3
0.5%Pd-(OAc)	0.162	91.4

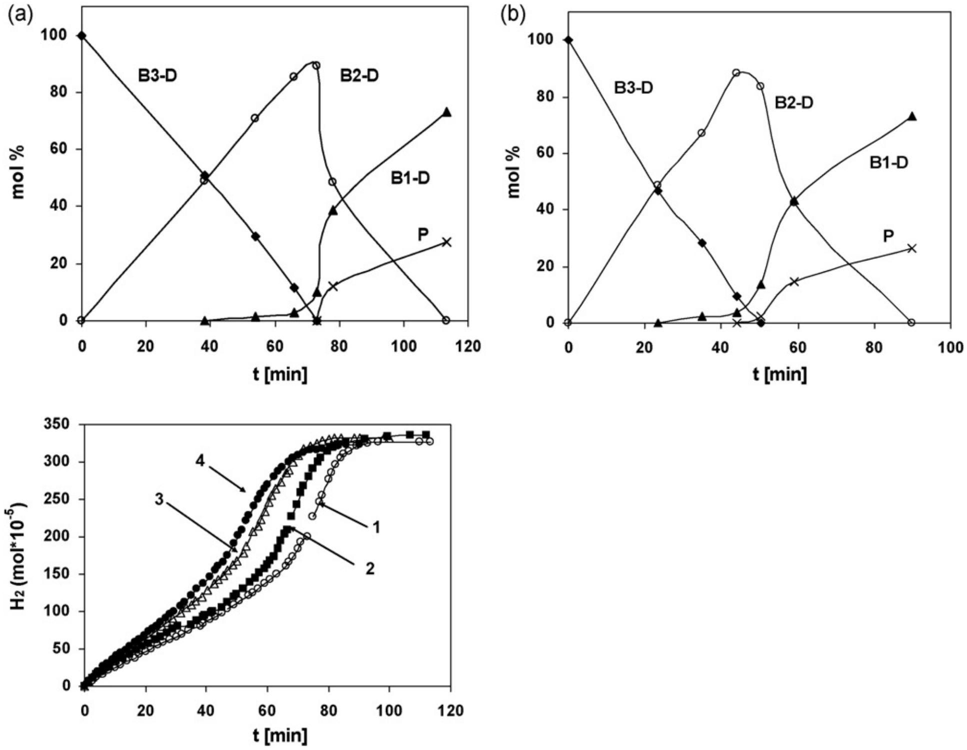


Fig. 12. Hydrogen consumption curves and products distribution vs reaction time during the recycling use of 0.5%Pd-(aq) catalyst (conditions: initial B3-D concentration 0.04 mol/dm^3, catalyst concentration 5.5 g/dm^3).

presence of 0.25%Pd-(aq) and 0.5%Pd-(aq) catalysts the selectivity to styrene reaches ca. 93% at almost complete conversion of Phc (conversion 90%) and is higher than that obtained on 0.5%Pd-(OAc) one. As the data in Table 4 show 0.5%Pd-(aq) catalyst exhibits also higher activity compared to that of 0.5%Pd-(OAc) one. It should be stressed that contrary to the B3-D, the hydrogenation of styrene to ethylbenzene is a slow reaction.

To summarize, in the presence of all catalysts studied, prepared by “OAc” and “aq” methods highly selective hydrogenation of triple C≡C to double C=C bonds in alkyne reagents is reached. However, performance of “aq” series catalysts is advantageous over “OAc” series ones, because the former are more active and more selective than the “OAc” series catalysts.

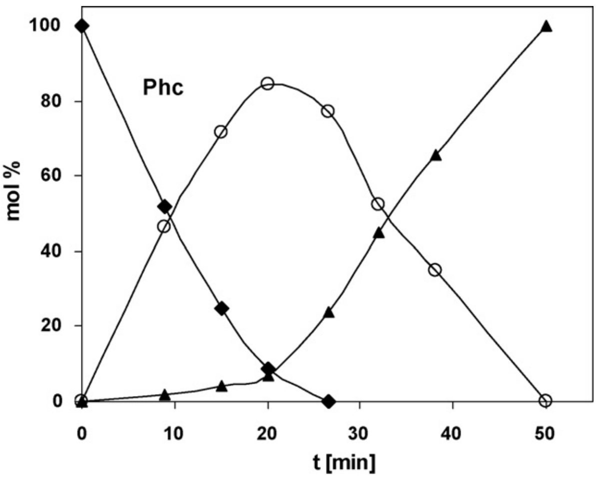


Fig. 13. Hydrogenation of phenylacetylene in the presence of 0.5%Pd-(aq) catalyst (conditions: THF solution of Phc 0.052 mol/dm^3, catalyst concentration 1.7 g/dm^3).

As mentioned before, in considering the role of polymer matrix the steric hindrances (nano-environment) in the vicinity of active centres as well as the influence of functional groups of the polymer on properties of catalytic centres are discussed. Furthermore, the polymer matrix may also exert an influence on the accessibility of reactants migrating through the polymer network to the Pd-particles located in the interior of resin particle. This influence is to high extent dependent on the degree of swelling of catalysts beads in their working state. Swelling of the polymer results in the formation of nano-porosity and this can make easier migration of reagents.

An improved performance of Pd/FCN catalysts, in particular with respect to highly selective formation of intermediate alkenes may be explained by a peculiar role of FCN polymer mostly related to steric hindrance in the nano-environment surrounding the Pd centers. This type of polymer influence has been observed in the hydrogenation of 1,3-butadiene [26]. The improved selectivity to butene-1 has been attributed by the authors to steric hindrance in the vicinity of Pd centers surrounded by the polymer. Similarly, highly selective formation of B2-D observed for Pd, Pt nano-particles stabilized by various polymers (polyvinylpyrrolidone, polyvinyl alcohol, polymethylvinyl ether) has been related to the influence of the polymeric stabilizer [27]. The authors pointed out that due to weakly bound ligand from the polymeric stabilizer surrounding the metal nano-particles re-adsorption of the olefinic diol (B2-D) was unlikely thus giving the selective formation of B2-D.

In the case of 0.5%Pd-(OAc) catalysts, the Pd nano-particles locate in outer shell of polymer beads and this shell is relatively wide. Moreover, the beads of 0.5%Pd-(OAc) catalyst swell less than pure polymer (Table 2). This implies that the accessibility of reactants (B3-D or Phc) to the Pd-centers located inside the polymer is to some extent difficult thus giving lower rate of hydrogenation. In these conditions the selectivity towards B2-D is also lower, whereas the content of by-products formed is high. This may indicate unprofitable role of microporous structure existing in the expanded state of 0.5%Pd-(OAc) catalyst. This observation is consistent with generally presented opinion, that in the course of alkynes hydrogenation, the selectivity towards olefin, an intermediate product, is reduced due to pore 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 catalysts of low porosity like Pd/$CaCO_3$ are preferred [24].

In Pd-(aq) series catalysts the palladium particles of relatively larger sizes are formed. However in these catalysts palladium is mainly located in outer shell of catalysts beads. This leads to more effective utilization of Pd-centres and thus higher activity of Pd-(aq) catalysts. As a consequence of this palladium location the influence of polymer matrix on the migration of reagents is to high extent restricted and the selectivity to B2-D is higher and lower content of by-products is formed.

However, the type of polymer (polyvinylpyrrolidone, polyvinyl alcohol, polymethylvinyl ether) used for the preparation of nanosize Pd, Pt, Rh, Ru and Ni catalysts was found to play an important role in activity and selectivity behaviour of catalysts in the hydrogenation of B3-D and styrene oxide [27]. It has been observed that the activity/selectivity pattern depended on nature and number of functional groups of the polymers. However, the role of polymers was ascribed not only to the stabilization of well dispersed metal nano-particles. The surrounding weakly bound ligands (functional groups of polymer) affected the access of reactants to reach the metal surface, and by changing the polymer-stabilizer, the selectivity pattern was altered [27]. Thus, functional groups of FCN polymer may also exert profitable role in selectivity behaviour of present catalysts.

High selectivity to the target product, B2-D, is also observed in aqueous medium, i.e. in conditions when the polymer does not swell. This indicates the specificity of Pd-centers in Pd-(aq) catalyst for the interaction with unsaturated triple and double bonds also in an aqueous medium, maybe owing to the influence of functional groups of FCN polymer.

4. Conclusions

Hydrogenation of alkynes reagents, 2-butyne-1,4-diol (B3-D) and phenylacetylene (Phc) was studied in the presence of palladium catalysts supported by amine groups—functionalized gel-type resin (FCN). Two different procedures of palladium incorporation to FCN polymer produced catalysts differing in the location and the dispersion of Pd-particles. The first, "OAc" basing on the immobilization of Pd-precursor in the pre-swollen resin from THF solution of $Pd(OAc)_2$ produced Pd particles of size in nano-scale located in relatively wide shell. The second procedure, "aq" implying the deposition of Pd-species on dry resin beads using aqueous solution of $PdCl_2$ yielded relatively large Pd particles (dominating are 30–50 nm in size. However Pd was located mostly in outer shell of polymer beads in the form of thinner layer. In the presence of all catalysts, prepared by "OAc" and "aq" methods the selectivity towards alkenes was high, above 90%. The Pd-(aq) catalyst proved to be more efficient than "OAc" analogues, since the desired alkene was obtained in ca. 94% selectivity after the complete hydrogenation of alkynes. This catalyst also presented the advantage being easily recovered and recycled. The advantage of Pd-(aq) catalyst over Pd-(OAc) one is ascribed to more effective utilization of Pd-centers in the case of "aq" series catalysts. Owing to the location of palladium in outer shell of polymer beads in "aq" series catalysts, the influence of polymer matrix on the migration of reagents is to high extent restricted thus giving very high selectivity to desired alkenes (B2-D, styrene) as well as low content of by-products is formed.

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