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Role of polyaniline morphology in Pd particles dispersion. Hydrogenation of alkynes in the presence of Pd-polyaniline catalysts

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Two polyaniline (PANI) samples of various molecular masses were used for the preparation of palladium catalysts (with 2 mass % of Pd). The physicochemical features of starting polyanilines were found to substantially affect the size and extent of palladium nanoparticles aggregation. Strongly aggregated large palladium particles appeared in the PANI sample of more compact morphology (PANI-H), higher crystallinity and lower specific surface area. Pd nanoparticles of a definitively smaller size were formed in the more amorphous PANI sample of looser morphology (PANI-L) and the extent of particles aggregation was markedly lower. The catalytic properties of Pd/PANI samples were studied in a liquid phase hydrogenation of unsaturated triple bond (C=C) in alkynes reactants, phenylacetylene, and cyclohexylacetylene. The 2 mass % Pd/PANI-L catalyst prepared using polymer of less compact texture exhibited much higher activity in both reactions. In the presence of the 2 mass % Pd/PANI-L catalyst, alkene products were formed with a high selectivity (approximately 90 %) attained at the almost complete conversion of alkynes. This highly selective hydrogenation of the C=C to the C=C bond was related to the presence of an electroactive polymer, PANI, in close proximity with Pd active sites. Polyaniline could have a role in a steric effect as well as in a modification of adsorptive properties of Pd centres. © 2013 Institute of Chemistry, Slovak Academy of Sciences

Keywords: polyaniline, palladium, hydrogenation, phenylacetylene, cyclohexylacetylene

Introduction

Polyaniline (PANI) is one of the conductive polymers studied most extensively due to its environmental stability, controllable electrical conductivity and interesting chemical properties (Kang et al., 1998). PANI undergoes protonation with acids to afford the conducting "salt"; the polymer also readily participates in redox reaction. Both these processes have been involved in the synthesis of PANI-transitions metals composites. Nitrogen groups, particularly the imine (—N=) ones, could also be considered as potential centres for the coordination of metal ions, such as Ag, Cu, Pd. In the interaction with metal, the system of π -conjugated bonds could be involved (Kumar et al., 1995). Unpaired electrons and positive charges delocalised over the entire conjugation length of the PANI could provide an environment similar to a π donor ligand (Hirao, 2002; Higuchi et al., 1996; Kumar et al., 1995). Electron interactions between PANI and palladium nanoparticles resulted in a change in the reduction-oxidation properties of PANI examined by the cyclic voltammetry technique (Park et al., 2004). These interactions were also predicted by theoretical calculations performed by quantum chemistry methods (Białek, 2006). In the light of these observations, it might be expected that the PANI matrix could influence the reactivity of Pd-centres in a catalytic reaction. This phenomenon was observed for palladium-polypyrrole catalysts (Drelinkiewicz et al.,

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2004) in the hydrogenation of acetophenone as well as for platinum–polyaniline catalysts (Steffan et al., 2008) in the hydrogenation of unsaturated aldehydes.

In our previous work, laboratory-prepared PANI samples were used for the preparation of Pd-PANI catalysts. These studies concentrated on the interactions between PANI and Pd²⁺ complexes. In particular, the role of the composition of palladium complexes was examined, whereas the role of polymer morphology was not taken into consideration. This appears to be an important effect in the light of growing interest in the PANI-Pd, Pt, Ru, composites which are seen to be potential candidates as electrocatalysts in the fuel cell technology (Antolini & Gonzalez, 2009). Accordingly, the present experiments were undertaken using two samples of PANI with different textural and morphological properties.

The present studies sought to evaluate the role of PANI morphology in the dispersion of palladium particles in the Pd/PANI catalysts. The catalytic behaviour of Pd/PANI samples in the hydrogenation of unsaturated triple bond in alkyne reactants, namely phenylacetylene (Phac) and cyclohexylacetylene (Cyac), was evaluated. These reactions were chosen as both are standard examples of alkyne to alkene and alkane hydrogenations. Moreover, they represent a class of processes of interest to the pharmaceutical and fine chemical industries. In order to achieve selective hydrogenation of alkyne to alkene, metal sites must exhibit appropriate electronic and/or morphological properties (Molnár et al., 2001). The high selectivity to alkene was related to the increased Pd electron density leading to the decreased alkene adsorption. In effect, greater selectivity to alkene was achieved by employing electron donor modifiers such as *N*-bases (quinoline, pyridine, ammonia). Very promising results were also obtained for Pd and Pt catalysts supported by polymers with N-bases as the constitutional units (Michalska et al., 1998; Arena et al., 1996; Telkar et al., 2004; Nadgeri et al., 2008). This type of modification appears to be very durable because, unlike commonly used modifiers, the N-units of the polymer cannot be removed or lost during the catalytic reaction.

Experimental

General

Two commercially available (Sigma–Aldrich, USA) samples of PANI base in the emeraldine oxidation state, differing in average molecular mass of polymer, with a more compact morphology (PANI-H) sample of $M_{\rm w} = 100000$ and a polymer with looser morphology (PANI-L) sample of $M_{\rm w} = 10000$ were used as the matrices for palladium. The catalysts were prepared as previously described (Drelinkiewicz et al., 1998). A PdCl₂ (Sigma–Aldrich) aqueous solution (4.6×10^{-3} mol L^{-1}) of mole ratio NaCl (POCH, Poland)/PdCl₂ equal to 2.5 : 1 and pH of approximately 3–4 was used. Incorporation of the palladium was achieved by exposure of the PANI sample, at ambient temperature, to the appropriate volume of the PdCl₂ solution to obtain 2 mass % Pd in the final catalysts. The suspension was stirred up to the total disappearance of palladium ions in the supernatant liquid (24 h), as confirmed by the colorimetric method. After the incorporation of Pd, the solids were filtered, washed with water until the Cl⁻ anions were absent, and dried at 80 °C for 4 h.

Characterisation of catalysts

Specific surface area was determined in accordance with the standard Brunauer–Emmet–Teller (BET) method from the nitrogen adsorption-desorption isotherm using a Quantasorb Jr. (Ankersmit, USA). Prior to sorption measurements, the samples were pretreated under vacuum at 80 °C for 16 h. The X-ray diffraction (XRD) studies were carried out using an HZG-4 diffractometer (Panalytical X'Pert PRO, The Netherlands) with CuK_{α} radiation. The morphology of the reduced catalysts was studied by means of a Field Emission Scanning Electron Microscope JEOL JSM - 7500 F (Japan) equipped with the energy dispersive EDS system. Two detectors were used and the images were recorded in two modes. The secondary electron detector provided secondary electrons images (SEI) and the backscattered electron detector provided backscattered electrons (BSE COMPO) micrographs.

Hydrogenation experiments

Hydrogenation experiments were carried out in a "batch" type glass reactor (volume of 0.2 L^{-1}) under a constant atmospheric pressure of hydrogen at a temperature of 22°C as previously described (Drelinkiewicz et al., 1999). Stirring of the reaction mixture in the reactor was carried out by using an agitation device with an agitation frequency control. Pentanol (Sigma–Aldrich) was used as the solvent. Prior to the hydrogenation experiment (in a typical procedure), the catalyst was placed inside the reactor by wetting it with an excess of solvent. Nitrogen (Linde Gaz, Poland) (15 min) and subsequently hydrogen (Linde Gaz) (30 min) were passed through the reactor. Next, the catalyst was placed in contact with the hydrogenated solution and the reaction was started by switching on the agitation device. The progress of the hydrogenation was monitored by measuring the volume of hydrogen consumed against the reaction time. The reactor was linked to a system of gas-burettes and an electronic device for registering the volume of hydrogen consumed in the reaction. Samples of solutions were withdrawn from the reactor via a sampling tube at

appropriate time intervals and analysed by the GC method.

Products analysis was performed using a gas chromatograph PE Clarus 500 (USA) equipped with a flame ionisation detector under the following conditions: capillary column Elite-5 MS (30 m × 0.25 mm × 0.25 µm coating) with helium (Linde Gaz) as a carrier gas (flow rate of 1 mL min⁻¹) and injection temperature of 250 °C. Product separation was obtained using temperature ramps of 80 °C (1 min), 15 °C min⁻¹ to 220 °C (3 min). Commercially available (Fluka, Germany; Sigma–Aldrich) analytical standards of reagents, phenylacetylene, styrene, ethylbenzene, cyclohexylacetylene, cyclohexylethylene, and cyclohexylethane were used in the chromatographic analysis.

Typically, the hydrogenation tests were carried out at 22 °C using 40 mL of substrate solution of 0.046 mol L^{-1} concentration and the catalyst concentration of 0.75 g L^{-1} . The hydrogenation was performed up to the point at which the hydrogen uptake was completed. Introductory experiments were performed in which the rate of agitation was changed. Those conditions under which the rate of hydrogen uptake did not depend on an agitation rate were used in further hydrogenation tests.

Results and discussion

It is widely known that the physico-chemical properties of PANI such as morphology and crystallinity are determined by the molecular mass of the polymer (Stejskal et al., 1998; Li et al., 2004). In general, the degree of crystallinity of PANI, which is associated with the supra-molecular organisation of PANI chains, increases as the molecular mass of the PANI grows. The present work studied two samples of PANI in the form of an emeraldine base differing in their molecular masses. The morphology and textural properties of the starting polyanilines were characterised by sorption (BET), X-ray diffraction, and scanning electron microscopy techniques.

The reflections originating from crystalline and amorphous polymers appear in the diffraction pattern of the PANI-base. However, a broad halo at 2θ at around 20° associated with amorphous polymer dominates, whereas the diffractions at 2θ equal to 16° and 25° originating from the crystalline polymer are definitively weaker (Pouget et al., 1991). The XRD diffraction patterns registered for the PANI-H and PANI-L samples are displayed in Fig. 1.

In the XRD pattern of the PANI-L sample, the broad halo centred at 2θ of approximately 20° strongly predominates, thereby showing the domination of an amorphous polymer. On the other hand, in the XRD pattern of the PANI-H sample, besides the broad diffraction associated with an amorphous polymer, a set of diffractions originating from the crystalline poly-

Fig. 1. XRD diffraction pattern of: 1 – PANI-H and 2 – PANI-L samples.

mer can be seen. The most characteristic diffractions are the peaks at 2θ equal to 16.0° and at 2θ equal to 25.4° . The former, at 2θ equal to 16.0° , has been attributed to the periodicity along the polymer chain and the one at 2θ equal to 25.4° to the periodicity perpendicular to the polymer chain (Murugesan & Subramanian, 2003). This demonstrates that the PANI in the PANI-H sample exhibits a higher degree of crystallinity.

The scanning electron micrographs of the samples studied are shown in Fig. 2. The data in the literature revealed that the morphology of PANI powder could vary because it is the result of the polymerisation conditions. Accordingly, spherical particles, the rice-grain morphology, coral-like cylindrical morphology, nanotubes, nanofibres, and nanowires could be observed as well as fibrous network structures. Fig. 2 shows that both PANI samples consist of granular microparticles almost spherical in shape and 200-500 nm in size. However, the samples differ essentially in the degree of microparticles agglomeration. In the PANI-H sample, consisting of a polymer with the higher molecular mass, spherical microparticles of the polymer are intensively agglomerated forming large aggregates (Fig. 2). This affords the highly compact morphology of the PANI-H sample. The polymer microparticles in the PANI-L sample are markedly less agglomerated; as a consequence the morphology of this PANI is less compact. Apart from these morphological differences, the PANI-H and PANI-L samples also differ in textural features such as specific surface area (Table 1). The more compact morphology of the PANI-H sample results in a specific surface area of $26.8 \text{ m}^2 \text{ g}^{-1}$, while the looser structure of the PANI-L sample gives a higher specific surface area equal to $32.8 \text{ m}^2 \text{ g}^{-1}$.

After the incorporation of palladium, the specific surface area of both samples decreases, albeit to various extents. The decrease is more pronounced in the



 Table 1. Specific surface area of samples and results obtained in hydrogenation of phenylacetylene (Phac) and cyclohexylacetylene (Cyac)

Sample	Surface area	Hydrogenation of Phac		Hydrogenation of Cyac	
		Initial activity $\cdot 10^{-3}$	$Selectivity^a$	Initial activity $\cdot 10^{-3}$	$Selectivity^a$
	$\mathrm{m}^2~\mathrm{g}^{-1}$	mol min ⁻¹ g_{cat}^{-1b}	%	mol min ⁻¹ g_{cat}^{-1b}	%
PANI-H 2 mass % Pd/PANI-H PANI-L 2 mass % Pd/PANI-L	26.8 16.8 32.8 13.8		– no data – 89.7	0.03 1.32	– no data – 90.6

a) Calculated at 94 % alkyne conversion; b) the rate per 1 g of catalyst.



Fig. 2. SEM micrographs of starting polyanilines; PANI-H (a), PANI-L (b).

case of the PANI-L sample exhibiting a less compact structure. This may suggest that a looser morphology of the polymer permits easier penetration of the palladium particles throughout the polymer sample.

As previously described (Drelinkiewicz et al., 1998), treatment of the PANI base with a palladium precursor salt could lead directly to the deposition of Pd-metal particles due to an oxidation-reduction reaction between the Pd^{2+} species and the nitrogen groups of PANI. It is well known that various aquachlorocomplexes of palladium ions coexist in the aqueous solution of $PdCl_2$ consisting of Cl^- ions (excess of HCl or NaCl added). At a given concentration of palladium ions, the type of ligands in the coordination sphere of palladium is determined by the concentration of Cl⁻ ions. In the PdCl₂ precursor solution of low acidity (pH \approx 3–4) used in this work, the [PdCl₂(H₂O)₂] complex was dominant. Under these conditions, palladium ions were reduced to the Pd-metal which was deposited in the PANI matrix.

In the present work, the composition of the palladium precursor solution was identical with the previous one, whereas the polyanilines samples were of various morphologies. Thus, the role of PANI morphology in the deposition of Pd-particles and, in particular,



Fig. 3. XRD diffraction patterns of; 1 - 2 mass % Pd/PANI-Hand 2 - 2 mass % Pd/PANI-L catalysts.

its role in the dispersion of palladium particles can be observed.

The XRD diffraction patterns of catalysts are shown in Fig. 3. In the diffraction of the 2 mass % Pd/PANI-H catalyst, well-resolved small diffractions



Fig. 4. SEM micrographs of 2 mass % Pd/PANI-H (a) and 2 mass % Pd/PANI-L (b) catalysts (magnification × 5000).

at $2\theta = 40.1^{\circ}$ and 46.0° originating from the crystalline Pd metal appear. From the broadening of the diffraction peak at $2\theta = 40.1^{\circ}$, the average diameter of Pd particles is evaluated to be approximately 10–15 nm. On the other hand, no signals of crystalline Pd can be seen in the XRD diffraction of the 2 mass % Pd/PANI-L catalyst. This suggests the presence of Pd-nanoparticles of a size below the detection limit of the XRD technique (below 2 nm).

Fig. 4 shows the SEM micrographs of 2 mass % Pd/PANI-H and 2 mass % Pd/PANI-L catalysts registered at the same magnification (× 5000). A comparison of these micrographs clearly demonstrates the crucial role of polymer morphology in the dispersion of Pd particles. The white spots corresponding to the palladium particles can be observed in the micrograph of the 2 mass % Pd/PANI-H catalyst, i.e. the sample consisting of the polymer of more compact morphology (Fig. 4). On the other hand, in the micrograph of the 2 mass % Pd/PANI-L sample, only a few insufficiently distinct white spots can be seen, showing that the particles are too small to be observed distinctly in the image registered at this relatively low magnification.

Thus, the compact morphology of the polymer in the 2 mass % Pd/PANI-H catalyst results in the formation of relatively large palladium particles which are randomly distributed throughout the polymer grains (Fig. 4). They are of various shapes and their size is within a range of 100–200 nm. The SEM image registered at a higher magnification (\times 20 000) shows these particles to be of irregular shape, which suggests that they represent the aggregates composed of smaller Pd nanoparticles. This observation is consistent with the XRD diffraction (Fig. 3) revealing the particles of 10–15 nm in size. Thus, the compact morphology of the PANI-H sample gives rise to a strong aggregation of palladium nanoparticles leading to large Pd aggregates (Fig. 5).



Fig. 5. SEM micrograph of 2 mass % Pd/PANI-H catalyst (magnification × 20000).

The SEM images registered for the 2 mass % Pd/PANI-L sample (Figs. 4 and 6) demonstrate that the looser morphology of the more amorphous PANI affords a better dispersion of the palladium in this catalyst. The particles of Pd are more homogeneously distributed throughout the polymer grains, as well as being of definitively smaller sizes.

A more detailed examination (images registered at magnification as high as \times 400000) also reveals that in the 2 mass % Pd/PANI-L catalyst the nanoparticles observed are the aggregates composed of primary Pd nanoparticles. However, these primary particles forming the aggregates are of a very small size because no diffractions arising from the Pd-crystalline can be observed in the XRD pattern of 2 mass % Pd/PANI-L catalyst (Fig. 3).

To summarise, the present results indicate that the morphology of the PANI sample exhibits a crucial role



Fig. 6. SEM micrographs of 2 mass % Pd/PANI-L catalyst; magnification (× 100000) (a) and (× 400000) (b).

in dispersion of the palladium particles formed in the palladium–PANI composites. The use of the PANI sample with a high molecular mass (PANI-H) and, thus, compact morphology results in large Pd particles. The particles of a definitively smaller size are formed when the polymer exhibits a less compact and more amorphous structure, i.e. the sample exhibits a lower molecular mass (PANI-L). This result is of interest given that no data on the role of PANI morphology in the dispersion of metal particles have previously been reported.

The results obtained by electron microscopy and XRD techniques show that the primary Pd nanoparticles in both the Pd-polyaniline composites studied are less or more aggregated.

According to the literature, particles of noble metals (Pd, Pt, Rh, etc.) within a very broad size range from 1–2 nm up to 100–200 μm could appear in the PANI composites prepared either by electrochemical or chemical procedures (Amaya et al., 2007; O'Mullane et al., 2004; Hasik et al., 2009; Antolini & Gonzalez, 2009; Kim & Park, 2008). Moreover, some reports in the literature showed aggregation of these metal particles. The aggregation effect was particularly prominent in the case of nanoscale particles. For instance, Amaya et al. (2007) reported that, in the Pd-PANI composite (prepared by chemical procedure), apart from the particles of 5–15 nm in diameter, aggregated particles which formed a number of agglomerates of various shapes and sizes also appeared. The large clusters of platinum (up to 50 nm in diameter) formed in the Pt-PANI composites were identified by O'Mullane et al. (2004) as being composed of primary particles of 1–2 nm in size. The aggregation of bimetallic Pt–Ru particles, ranging from 3 nm up to 8 nm, to form various aggregates was also observed by Kim and Park (2008) in the Pt-Ru-PANI composites prepared electrochemically. Thus, the effect of the Pd nanoparticles' aggregation observed in the composites studied

here is consistent with the observations of other authors.

Hydrogenation experiments

The results in our previous work showed the very promising performance of Pd/PANI catalysts in selective hydrogenation of the unsaturated triple (C \equiv C) bond in the 2-butyne-1,4-diol reactant (Drelinkiewicz et al., 2008). The present work investigates the hydrogenation of other alkyne reactants, namely pheny-lacetylene (Phac) and cyclohexylacetylene (Cyac). Special attention is directed towards the selective hydrogenation of the C \equiv C to the C \equiv C bonds.

Catalytic tests were performed using both 2 mass % Pd/PANI-L and 2 mass % Pd/PANI-H catalysts. The obtained catalysts' activity and selectivity towards alkene are given in Table 1. Polyanilines sample, the support for metal particles, did not exhibit activity in the hydrogenation test. It is why no activity data are given for the initial PANI samples in Table 1.

As a measure of catalyst activity, an initial rate of alkyne hydrogenation (mol min⁻¹) related to the catalyst mass (expressed as mol alkyne min⁻¹ g_{cat}^{-1}) is assumed. In both the reactions studied, the 2 mass % Pd/PANI-L catalyst is much much more active and its activity is distinctly higher (\approx 40-times) than that of the 2 mass % Pd/PANI-H sample, as shown in Table 1. This activity relation is consistent with the electron microscopy data which demonstrate that the palladium particles in the 2 mass % Pd/PANI-L catalyst are better dispersed.

Catalytic hydrogenation of the alkyne reactant is a consecutive process wherein alkene is an intermediate product and alkane is formed via hydrogenation of the C=C bond in the alkene molecule. In order to achieve the highly selective formation of alkene, a catalyst needs to be able to inhibit the hydrogena-



Fig. 7. Hydrogenation of phenylacetylene in the presence of 2 mass % Pd/PANI-L catalyst. Hydrogen uptake (\blacklozenge) and reagents concentration change against reaction time; phenylacetyle (O), styrene (\triangle), and ethylbenzene (\blacktriangle).



Fig. 8. Hydrogenation of cyclohexylethylene in the presence of 2 mass % Pd/PANI-L catalyst. Hydrogen uptake (♦) and reagents concentration change against reaction time; cyclohexylacetylene (O), cyclohexylethylene (△) and cyclohexylethane (▲).

tion of C=C in the alkene intermediate product up to the almost complete hydrogenation of the unsaturated C=C in the alkyne reactant. Consequently, the selectivity towards alkene is commonly considered at conversions of alkyne reactants of approximately 80– 90 %.

The hydrogen consumption curves and products distribution graphs for hydrogenation of Phac and Cyac in the presence of 2 mass % Pd/PANI-L catalyst are plotted in Figs. 7 and 8, respectively. From the very beginning of the reaction, the hydrogenation of C=C in Phac and Cyac yielding alkene products predominates. However, when almost all the alkyne reactants have been consumed, further hydrogenation of the alkenes thus produced, the styrene and cyclohexylethylene to the saturated products proceeds very

slowly. This is demonstrated by the products distribution plots, and also by the shape of the hydrogen uptake curves, especially for the Cyac substrate.

After consumption of 1 eq. of hydrogen (corresponding to the complete hydrogenation of alkyne to alkene hydrogenation) a break appears on the hydrogen uptake curve showing that further hydrogenation of C=C bonds in alkenes to form alkanes is a very slow reaction. The rate is distinctly lower than those of C=C in the alkynes reactants. As a result, in the presence of the 2 mass % Pd/PANI-L catalyst at almost complete conversion of the alkyne reactants (at 94 % alkyne conversion), the selectivity towards alkene is very high, attaining approximately 90 % (Table 1).

The substantially lower activity of the 2 mass % Pd/PANI-H catalyst renders observation of the selectivity effect difficult. Because of the very low rate of alkyne hydrogenation on the 2 mass % Pd/PANI-H catalyst, the conversions achieved even after 5 h reaction time were very low (9 % and 15 % for Phac and Cyac hydrogenation, respectively). As a result, the content of the products formed was very low, thus rendering observation of the alkane product particularly difficult.

To summarise, hydrogenation of the unsaturated triple C=C bond in both the alkyne reagents to the C=C bond in the corresponding alkene products is a highly selective reaction on the 2 mass % Pd/PANI-L catalyst. Unfortunately, the very low activity of the 2 mass % Pd/PANI-H catalyst prevents correct observation of the selectivity effect.

The highly selective formation of alkenes attained on the 2 mass % Pd/PANI-L catalyst can be attributed to the presence of PANI in close proximity to the Pd particles. The role of the PANI could be considered in terms of its electronic and steric effects. The selectivity-promoting effect observed for nitrogen-containing polymers was attributed to modification of the adsorption properties of metal centres, leading to inhibited adsorption of the intermediate product, alkene (Christodoulakis et al., 2009; Klasovsky et al., 2009). By this concept, the almost entirely selective hydrogenation of 2-butyne-1,4diol and phenylacetylene to the corresponding alkenes obtained due to the presence of poly(vinylpyridine) and oligoaramides (oligo-p-phenyleneterephtalamide, OPTA) matrices (Arena et al., 1996; Telkar et al., 2004) was explained. The former polymer consists of pyridine units, the latter (OPTA) has both unsaturated aromatic rings as well as -NH₂ groups. In the presence of the latter Pd/OPTA catalyst, the selectivity of styrene formation was as high as 94-96 % when almost all the phenylacetylene underwent the reaction (Arena et al., 1996).

The rate of hydrogenation of alkynes in the present work was independent of the agitation frequency. This confirmed that the results obtained were independent of mass transport resistances. Due to the very small catalyst particles (Fig. 2), liquid-solid mass transfer resistances also do not have any influence. Thus, the effect of PANI on the reactivity of Pd-centres through a moderation of the active sites-reagents' interactions could be taken into consideration. However, these interactions could be partially limited as, in the 2 mass % Pd/PANI-L catalyst, the Pd particles are aggregated to some extent. On the other hand, the activity/selectivity pattern in the hydrogenation of alkyne reactants (2-butyn-1,4-diol) on Pd, Pt, Rh, Ru catalysts was reported to be dependent on the structural units of the polymer, i.e. the nature and number of functional groups (polyvinylpyrrolidone, poly(vinyl alcohol), poly(methylvinyl ether) in close proximity to metal particles (Telkar et al., 2004). The surrounding functional groups of the polymer impeded the reactants from reaching the metal surface and, by changing the polymer, the selectivity pattern was altered. The authors noted that the high selectivity towards alkene may be related to the fact that re-adsorption of the alkene was inhibited due to the polymeric functional groups surrounding the metal nanoparticles. These effects could also be taken into account in the activity/selectivity behaviour of the Pd/PANI catalysts studied. Moreover, the polymer could also sterically affect the access of the reagents to the catalytically active centres, in a similar manner to that observed by other authors (Telkar et al., 2004).

The selectivity changes in the hydrogenation of alkyne reactants were frequently correlated with the presence of the β -hydride phase of palladium $(\beta$ -PdH). The formation of β -PdH promoted overhydrogenation to form alkane. However, it appears from the literature (Molnár et al., 2001) that the role of the β -hydride phase in over-hydrogenation is still unclear as various properties of palladium particles such as surface morphology, crystallinity, and size and shape could influence its formation. Moreover, our previous studies (Drelinkiewicz et al., 2004) revealed that the trend towards the β -hydride phase formation by palladium particles dispersed in the matrix of electroactive polymer, polypyrrole differed from that observed for conventional, alumina-supported palladium catalysts. These literature data clearly demonstrate the complex nature of the role of the polymer in the activity/selectivity pattern of the reaction catalysed by metal particles dispersed in a polymer matrix. Thus, the advantageous performance of the Pd/PANI catalyst could be ascribed to an effect of the electroactive polymer matrix consisting of N-groups and a system of delocalised π -electrons. The steric effect of the polymer in the vicinity of the active Pd centres as well as the modification of Pd-centres reactivity needs to be taken into consideration.

Conclusions

Using PANI samples differing in molecular masses,

crystallinity, morphology, and specific surface areas, catalysts of the same palladium content (2 mass %Pd) were prepared. The dispersion of palladium particles in the Pd/PANI catalysts was found to depend on the morphology of the starting polymer. The compact morphology of the PANI-H sample produced Pd nanoparticles 10–15 nm in size. They were strongly aggregated, forming large irregularly shaped agglomerates. The loose morphology of the PANI-L sample resulted in Pd nanoparticles of markedly smaller size which were noticeably less aggregated. The 2 mass %Pd/PANI-L catalyst exhibited a very promising catalytic performance in the hydrogenation of unsaturated triple C=C bonds to the double C=C bonds in alkynes, phenylacetylene and cyclohexylacetylene. The unsaturated triple C=C bond was almost entirely selectively reduced to the double bond C=C with almost total conversion of alkynes due to the complete suppression of alkane formation. The advantageous performance of the Pd/PANI catalysts could be explained by complex effects constituting a modification of the adsorptive properties of Pd-centres due to the presence of the electroactive matrix consisting of N-groups and a system of delocalised π -electrons. The polymer could also exhibit a steric effect affecting access of the reagents to the active sites.

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References

- Amaya, T., Saio, D., & Hirao, T. (2007). Template synthesis of polyaniline/Pd nanoparticle and its catalytic application. *Tetrahedron Letters*, 48, 2729–2732. DOI: 10.1016/j.tetlet. 2007.02.059.
- Antolini, E., & Gonzalez, E. R. (2009). Polymer supports for low-temeperature fuel cell catalysts. *Applied Catalysis A: General*, 365, 1–19. DOI: 10.1016/j.apcata.2009.05.045.
- Arena, F., Cum, G., Gallo, R., & Parmaliana, A. (1996). Palladium catalysts supported on oligomeric aramides in the liquid-phase hydrogenation of phenylacetylene. *Journal* of Molecular Catalysis A: Chemical, 110, 235–242. DOI: 10.1016/1381-1169(96)00188-4.
- Białek, B. (2006). Computational studies of the interactions between emeraldine and palladium atom. Surface Science, 600, 1679–1683. DOI: 10.1016/j.susc.2005.12.059.
- Christodoulakis, K. E., Palioura, D., Anastasiadis, S. H., & Vamvakaki, M. (2009). Metal nanocrystals embedded within polymeric nanostructures: Effect of polymer-metal compound interactions. *Topics in Catalysis*, 52, 394–411. DOI: 10.1007/s11244-008-9172-2.
- Drelinkiewicz, A., Hasik, M., & Choczyński, M. (1998). Preparation and properties of polyaniline containing palladium. *Materials Research Bulletin*, 33, 739–762. DOI: 10.1016/s0025-5408(98)00042-7.
- Drelinkiewicz, A., Hasik, M., & Kloc, M. (1999). Liquid-phase hydrogenation of 2-ethylanthraquinone over Pd/polyaniline catalysts. *Journal of Catalysis*, 186, 123–133. DOI: 10.1006/ jcat.1999.2493.
- Drelinkiewicz, A., Waksmundzka, A., Makowski, W., Sobczak, J. W., Król, A., & Zięba, A. (2004). Acetophenone hy-

drogenation on polymer–palladium catalysts. The effect of polymer matrix. *Catalysis Letters*, 94, 143–156. DOI: 10.1023/b:catl.000020539.31128.d4.

- Drelinkiewicz, A., Zięba, A., Król, A., Sobczak, J. W., & Grzywa, M. (2008). Polyaniline supported Pd and Pt catalysts. Role of metal in hydrogenation of 2-butyne-1,4-diol. *Polish Journal of Chemistry*, 82, 1717–1732.
- Hasik, M., Turek, W., Nyczyk, A., Stochmal, E., Bernaisk, A., Sniechota, A., & Sołtysek, A. (2009). Application of conjugated polymer–platinum group metal composites as heterogeneous catalysts. *Catalysis Letters*, 127, 304–311. DOI: 10.1007/s10562-008-9679-y.
- Higuchi, M., Imoda, D., & Hirao, T. (1996). Redox behavior of polyaniline-transition metal complexes in solution. *Macromolecules*, 29, 8277–8279. DOI: 10.1021/ma960761f.
- Hirao, T. (2002). Conjugated systems composed of transition metals and redox-active π -conjugated ligands. Coordination Chemistry Reviews, 226, 81–91. DOI: 10.1016/s0010-8545(01)00436-2.
- Kang, E. T., Neoh, K. G., & Tan, K. L. (1998). Polyaniline: A polymer with many interesting intrinsic redox states. *Progress in Polymer Science*, 23, 277–324. DOI: 10.1016/s0079-6700(97)00030-0.
- Kim, S., & Park, S. J. (2008). Electroactivity of Pt–Ru/polyaniline composite catalyst-electrodes prepared by electrochemical deposition methods. *Solid State Ionics*, 178, 1915–1921. DOI: 10.1016/j.ssi.2007.12.074.
- Klasovsky, F., Claus, P., & Wolf, D. (2009). Influence of preparation parameters on the performance of colloid-derived oxidic palladium catalysts for selective hydrogenation of colloid-derived oxidic palladium catalysts for selective hydrogenation of C–C triple bonds. *Topics in Catalysis*, 52, 412–423. DOI: 10.1007/s11244-008-9173-1.
- Kumar, S., Verma, R., Venkataramani, B., Raju, V. S., & Gangadharan, S. (1995). Sorption of platinum, palladium, iridium, and gold complexes on polyaniline. Solvent Extraction and Ion Exchange, 13, 1097–1121. DOI: 10.1080/07366299508918320.
- Li, J., Fang, K., Qiu, H., Li, S. P., & Mao, W. M. (2004). Micromorphology and electrical property of the HCl-doped and DBSA-doped polyanilines. *Synthetic Metals*, 142, 107–111. DOI: 10.1016/j.synthmet.2003.08.014.
- Michalska, Z. M., Ostaszewski, B., Zientarska, J., & Sobczak, J. W. (1998). Catalytic hydrogenation of alkadienes and alkynes by palladium catalysts supported on heterocyclic polyamides. *Journal of Molecular Catalysis A: Chemical*, 129, 207–218. DOI: 10.1016/s1381-1169(97)00212-4.

- Molnár, A., Sárkány, A., & Varga, M. (2001). Hydrogenation of carbon-carbon multiple bonds: chemo-, regio- and stereoselectivity. *Journal of Molecular Catalysis A: Chemical*, 173, 185–221. DOI: 10.1016/s1381-1169(01)00150-9.
- Murugesan, R., & Subramanian, E. (2003). Effect of organic dopants on electrodeposition and characteristics of polyaniline under the varying influence of H₂SO₄ and HClO₄ electrolyte media. *Materials Chemistry and Physics*, 80, 731– 739. DOI: 10.1016/s0254-0584(03)00127-5.
- Nadgeri, J. M., Telkar, M. M., & Rode, C. V. (2008). Hydrogenation activity and selectivity behaviour of supported palladium nanoparticles. *Catalysis Communications*, 9, 441– 446. DOI: 10.1016/j.catcom.2007.07.023.
- O'Mullane, A. P., Dale, S. E., Macpherson, J. V., & Unwin, P. R. (2004) Fabrication and electrocatalytic properties of polyaniline/Pt nanocomposites. *Chemical Communications*, 2004, 1606–1607. DOI: 10.1039/b404636f.
- Park, J. E., Park, S. G., Koukitu, A., Hatozaki, O., & Oyama, N. (2004). Electrochemical and chemical interactions between polyaniline and palladium nanoparticles. *Synthetic Metals*, 141, 265–269. DOI: 10.1016/s0379-6779(03)00410-7.
- Pouget, J. P., Jozefowicz, M. E., Epstein, A. J., Tang, X., & MacDiarmid, A. G. (1991). X-ray structure of polyaniline. *Macromolecules*, 24, 779–789. DOI: 10.1021/ma00003a022.
- Steffan, M., Klasovsky, F., Arras, J., Roth, C., Radnik, J., Hofmeister, H., & Claus, P. (2008). Carbon-carbon double bonds versus carbonyl group hydrogenation: Controlling the intramolecular selectivity with polyaniline-supported platinum catalysts. Advanced Synthesis & Catalysis, 350, 1337– 1348. DOI: 10.1002/adsc.200800035.
- Stejskal, J., Riede, A., Hlavatá, D., Prokeš, J., Helmstedt, M., & Holler, P. (1998). The effect of polymerization temperature on molecular weight, crystallinity, and electrical conductivity of polyaniline. *Synthetic Metals*, 96, 55–61. DOI: 10.1016/s0379-6779(98)00064-2.
- Telkar, M. M., Rode, C. V., Chaudhari, R. V., Joshi, S. S., & Nalawade, A. M. (2004). Shape-controlled preparation and catalytic activity of metal nanoparticles for hydrogenation of 2-butyne-1,4-diol and styrene oxide. *Applied Catalysis A: General*, 273, 11–19. DOI: 10.1016/j.apcata.2004.05.056.