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Catalytic Properties of Pd Deposited on Polyaniline in the Hydrogenation of Quinoline

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Abstract: A set of Pd-containing composites was prepared by the deposition of Pd on the following carriers: polyaniline (PANI); PANI doped by H2SO4; Norit GSX activated carbon or Aerosil (SiO2) coated by PANI or by H2SO4-doped PANI; PANI after thermal treatment at 300 °C in an atmosphere of H2. One sample was also prepared by the in situ polymerization of aniline in the presence of Pd2+. The decomposition of Pd was carried out via deposition from the solutions of Pd2+ salts or decomposition of Pd0 complex Pd2(dba)3, where dba is dibenzylideneacetone. The composites were studied by powder X-ray diffraction, transmission electron microscopy, IR and Raman spectroscopy. The hydrogenation of quinoline in the presence of composites was carried out; the catalytic performance of the composites was evaluated by the yield of 1,2,3,4-tetrahydroquinoline. It was found that the doping of PANI by H2SO4, inclusion of Norit GSX activated carbon as a component of the carrier or thermal treatment of PANI prior to the deposition of Pd led to significant increase in the catalytic performance of the composites in the hydrogenation of quinoline.

Keywords: polyaniline; palladium; hydrogenation; quinoline; nanocomposites

1. Introduction

The hydrogenation of organic compounds is one of the most demanded and important processes in modern fine organic chemistry or industrial production [1–5]. For example, hydrogenation is the most accessible and simple method of obtaining substituted cyclic compounds from the corresponding aromatic analogs [6]. The importance of hydrogenation cannot be overestimated. At present, the majority of hydrogenation catalysts are Pd-containing systems [7,8]. Despite a long history of research in the field of hydrogenation, improvement of the existing hydrogenation methods and development of new efficient catalysts is an important task, and its urgency has even increased in view of the growing Pd prices.

In some cases, Pd in hydrogenation catalysts can be replaced by cheaper metals, such as nickel [9–14], cobalt [15–21] or other non-noble metals [22–25]. However, such systems usually have significantly lower activity and can lead to the formation of a large quantity of unwanted by-products (due to harsh reaction conditions). Searching ways to increase the catalytic activity of Pd-containing systems is actual task. In recent decades, several papers devoted to the efficient catalysts or organic reactions (including hydrogenation)
based on polyaniline (PANI) have been published [26–31]. The reduction of Pd$^{2+}$ by PANI resulted in the formation of deposited Pd nanoparticles, the system efficiently catalyzed the hydrogenation of alkynes and alkenes at 0.1 mol.% loading at ambient pressure [27]. The capture of Pd$^{2+}$ by PANI in the course of its formation led to the material, which showed itself as an efficient catalyst for Cu-free Sonogashira couplings, and this system provided high product yields at 0.005 mol.% Pd loading [28]. An efficient catalyst for the reduction of nitro compounds by NaBH$_4$ was prepared by PdCl$_2$ capture during the synthesis of PANI, the catalyst provided for high product yields at ca. 0.03 mol.% Pd loading in mild conditions [30]. The productivity of such systems exceeded the productivity of similar catalysts, containing a carbonous carrier (in the criteria of the product yields). The formation of Pd nanoparticles in PANI resulted in the formation of an efficient catalyst for the reductive homocoupling of furfural derivatives [31]. Decoration of the Pt/C catalyst of the oxygen reduction reaction and the formation of the Pt/C@PANI core-shell structure led to enhancement of the catalyst activity and durability [32]. In many cases, the effect of PANI could be explained by the delocalization of electrons between this carrier and metallic nanoparticles; such a charge transfer was experimentally confirmed, in some cases [33].

Being inspired by these reports, we studied a series of Pd-containing composites prepared by the deposition of Pd on PANI with the aim to reveal the influence of the composition of the carrier (pure PANI; PANI doped by the acid; activated carbon or silica coated with PANI) on the catalytic performance of the resulting system.

PANI is an organic polymer, formed upon oxidative polymerization of aniline in the presence of the proper oxidant, such as persulfate [34–37]. Its formula can be represented as shown in Figure 1. The molecule of PANI contains benzene and quinoid rings, as well as secondary amino groups, that can be protonated by the acidic dopant. In addition, amino and imino groups can act as bonding sites for Pd nanoparticles. The level of oxidation of PANI, i.e., $x:y$ ratio, can be varied by treatment with oxidants or reducers [35], and in theory, it can be influenced by treatment with salts of metal cation oxidizers (such as Pd$^{2+}$).

![Figure 1. Structure of PANI. The $x:y$ ratio can vary depending on the polymer formation conditions.](image)

In this study, a series of Pd-containing composites was prepared by the deposition of Pd on the carriers, containing PANI or derived from PANI. In addition, one sample was prepared by in situ polymerization of aniline in the presence of Pd$^{2+}$.

The decomposition of Pd was carried out via deposition from the solutions of Pd$^{2+}$ salts or decomposition of Pd$^0$ complex Pd$_2$(dba)$_3$, where dba is dibenzylideneacetone. It was previously shown that the thermal decomposition of zero-valent complexes could be an efficient way for the production of active hydrogenation catalysts [9,11,12]; for this reason, this approach was employed in this study.

2. Results and Discussion

Several approaches were used for preparation of the composites in this study in order to reveal the influence of the preparation method and composition of the sample on its catalytic performance.

One sample (P1) was prepared by oxidative polymerization of aniline in reaction with (NH$_4$)$_2$S$_2$O$_8$ in the presence of PdCl$_2$ (Figure 2), similar to the method reported in [28,30]. It was expected that aniline would reduce Pd$^{2+}$ to metallic Pd or polyaniline would capture the Pd$^{2+}$ ions during polymerization, the latter forming ultrasmall Pd nanoparticles upon treatment with H$_2$ in the course of hydrogenation. Notably, in our hands, the polymerization of aniline in an aqueous acidic solution in the presence of PdCl$_2$
and aerial oxygen did not occur, and the addition of an oxidant was required for the formation of polyaniline.

\[
\text{NH}_2 \quad + \quad \text{Na}_2\text{PdCl}_4 \quad \xrightarrow{(NH_4)_2S_2O_8} \quad \text{Pd} \quad 0.23 \% \text{Pd}
\]

**Figure 2.** Schematic synthesis of sample P1. The content of Pd determined by AAS is shown for convenience.

For the synthesis of samples P2–P5, PANI was prepared by the oxidative polymerization of aniline under the action of \((NH_4)_2S_2O_8\) using a known method [34]. The molecular weight of PANI, determined by viscometry, was about 4000. This value is a rather low compared to the values of the molecular weights of the PANI samples, formed by oxidative polymerization [38]. The composites, used as the carriers for samples P8–P11, were prepared by a similar polymerization of aniline in the presence of activated carbon Norit GSX or silica Aerosil-300.

The Pd-containing composites were obtained by:

- deposition of Pd on PANI by treatment with a solution of Na\(_2\)PdCl\(_4\) (samples P2 and P3, Figure 3). It was expected that in situ reduction of Pd\(^{2+}\) would occur upon contact of Pd\(^{2+}\) with PANI, the latter playing the role of organic reducer (as shown in [27,39]). Samples P2 and P3 differ by Pd content.

- deposition of the metallic Pd on the carrier by decomposition of Pd\(_2\)(dba)\(_3\), similar to the method proposed in [40–43]. In this case, the following carriers were used:
  - PANI (samples P4 and P5, Figure 3);
  - the composite of PANI and activated carbon, formed by oxidative polymerization of aniline in the presence of activated carbon Norit GSX (hereinafter referred to as PANI/C samples, Figure 4);
  - the composite of PANI and silica, formed by oxidative polymerization of aniline in the presence of Aerosil-300 (hereinafter referred to as PANI/SiO\(_2\), Figure 4);
  - PANI and its composites with activated carbon or silica additionally treated by H\(_2\)SO\(_4\) (doping with acid) prior to the decomposition of Pd\(_2\)(dba)\(_3\) (Figures 3 and 4);
  - PANI after heating at 300 °C in an atmosphere of hydrogen (hereinafter referred to as PANI-300, Figure 3).

The aim of PANI synthesis in the presence of activated carbon or Aerosil was to achieve higher dispersion of the organic component and, finally, to reduce its content in the Pd-containing composite, which can be important for application of the catalyst. The carriers PANI/C and PANI/SiO\(_2\) were prepared by in situ polymerization of aniline in the presence of Norit GSX activated carbon and Aerosil-300, which presumably played the roles of “cores” and were covered by the “shells” of polyaniline, similar to previously reported cases [44,45].

The carbonization of PANI at 300 °C was performed in view of the catalytic activity of carbonized PANI in hydrogenation, shown recently [46]. It was reported that thermal treatment of PANI at 300 °C in an atmosphere of hydrogen led to formation of the sample, possessing the highest catalytic performance in the hydrogenation of unsaturated compounds; thus, this temperature was chosen in the present study for preparation of the carrier for P7. To reveal the influence of the dopant (H\(_2\)SO\(_4\)) in PANI on the structure and catalytic properties of the Pd-containing composites, the carriers PANI, PANI/C and PANI/SiO\(_2\) were treated with sulfuric acid prior to the deposition of palladium (samples P6, P9 and P11).
The aim of PANI synthesis in the presence of activated carbon or Aerosil was to achieve higher dispersion of the organic component and, finally, to reduce its content in the Pd-containing composite, which can be important for application of the catalyst. The carriers PANI/C and PANI/SiO$_2$ were prepared by in situ polymerization of aniline in the presence of Norit GSX activated carbon and Aerosil-300, which presumably played the role of a catalyst.

**Figure 3.** Schematic synthesis of samples P2–P7. Carriers are marked by red, while Pd-containing composites are marked by blue. Contents of Pd determined by AAS are shown for convenience.

**Figure 4.** Schematic synthesis of samples P8–P11, which contain PANI and additional carriers. Carriers are marked by red, while Pd-containing composites are marked by blue. Contents of Pd determined by AAS are shown for convenience.
All samples, prepared in this study, contained polyaniline and Pd, deposited thereon as disperse particles (vide infra). Several comments may be made from the comparison of the expected and actual Pd contents in the samples. The quantity of Pd, deposited on the carriers, was close to theoretical in the case of sample P11 (90% of the theoretical value), while the Pd content in other samples was significantly lower than expected.

In the cases of P1 and P3, the capture of Pd$^{2+}$ from the solutions was not so efficient as to ensure complete deposition of the metal. About 8% of Pd available in the reaction mixture was deposited in the case of P1 and 30% deposited in the case of P3. In both cases, Pd$^{2+}$ ions contacted with PANI and the deposition could be associated with the in situ reduction of Pd$^{2+}$ by the organic compounds. A higher percentage of Pd, as in the case of P3 (compared to P1), could be associated with the neutral medium of the solution in the case of P3, as compared to an acidic one in the case of P1. In the case of P2, the higher Pd content compared to P3 can be explained by a higher concentration of the solution (though the Pd quantity in the reaction mixtures remained the same).

All other samples, P4–P11, were prepared by decomposition of the complex of Pd$^{0}$, Pd$_{2}$(dba)$_{3}$, i.e., in presence of the carrier. The deposition of Pd was at the level of 10–30% in all cases except P6 (60%) and P11 (90%) (the target Pd content in P5 was 4%, and in P4 and P6–P11, it was 1%). A low Pd deposition level, compared to Pd deposition on the charcoal by the decomposition of Pd$_{2}$(dba)$_{3}$ [40], can be caused by the formation of ultrasmall particles that are not captured by the solid and lost upon filtering of the solution; the formation of soluble Pd$^{2+}$ complexes with oligomers of aniline, which also remain in the solution, could be another reason for Pd loss. Notably, the samples formed upon the most complete deposition of Pd from the solution in the process of Pd$_{2}$(dba)$_{3}$ decomposition (P6 and P11) contained PANI, doped by H$_{2}$SO$_{4}$ (PANI-H$_{2}$SO$_{4}$ and PANI-H$_{2}$SO$_{4}$/C, respectively). The acidity of the carrier seems to favor the decomposition of Pd$_{2}$(dba)$_{3}$ and formation of Pd particles, which are captured by the carrier. A similar promoting effect of the acid on the decomposition of Pd$_{2}$(dba)$_{3}$ was reported [41,47]. In this view, it is quite surprising that the Pd content in P9 (PANI-H$_{2}$SO$_{4}$/SiO$_{2}$ as the carrier) was just 20% different from the expected one.

The samples prepared in this study were X-ray amorphous; no reflections of Pd were observed. The absence of distinct reflections of Pd is consistent with its low content in the samples.

The oxidation state of the Pd nanoparticles, formed upon the decomposition of the Pd$_{2}$(dba)$_{3}$ complex, was examined by XPS in a published report [41]. It was found that the nanoparticles, which were in contact with the air, consisted of metallic Pd and PdO; the content of PdO varied between 1/2 and 1/4, depending on the nature of the support (carboneous materials in all cases). It seems to be a typical situation—the catalysts, containing Pd nanoparticles, always contain some quantity of PdO, which is reduced to Pd in situ in hydrogenation experiments [48,49], and the surface composition of such species is very sensitive to the environment [50]. For this reason, the oxidation state of Pd in the nanoparticles, stored in air, does not have a direct relation to the composition of such nanoparticles in the reaction mixture, and the XPS spectra may not correlate with the catalytic activity of such species [51].

The identity of polyaniline and its changes, occurring upon the deposition of Pd, were checked by IR spectroscopy. The IR spectrum of PANI (Figure 5) is typical for polyaniline [27,52,53], and the most intense bands can be assigned to C=C stretching vibrations of the quinoid ring (1588 cm$^{-1}$, band A in Figure 5) and benzenoid ring (1496 cm$^{-1}$, band B), C-N stretching in quinoid–benzenoid–quinoid units (1380 cm$^{-1}$, band C), C–N stretching of the secondary aromatic amine (1303 and 1162 cm$^{-1}$, bands D and E), in-plane C–H bending of the aromatic ring (1103 cm$^{-1}$, band F), and out-of-plane C–H deformation of the benzene ring bearing two substituents in para-positions (829 cm$^{-1}$, band G). The polymerization of aniline in the presence of Pd$^{2+}$ (sample P1, Figure 5) led to the formation of polyaniline, very similar to PANI, obtained in the Pd-free polymerization process. Similarly, the deposition of Pd by the treatment of PANI with solutions of Na$_{2}$PdCl$_{4}$ (samples P2 and P3)
did not cause noticeable changes in the IR spectra, indicating that the structure of PANI essentially did not change (Figure 5). Some shifts of the bands and redistribution of the relative intensities can be explained by slight changes in the protonation level, and such changes can be attributed to slight variations of acidity of the reaction mixtures rather than the influence of Pd. It is quite reasonable that the addition of less than 1% of Pd would not change the structure of PANI, even if some fragment of this carrier took part in the reduction of Pd$^{2+}$ to Pd$^0$.

![Figure 5. IR spectra of PANI and P1–P3 (the composites, formed upon the in situ polymerization of aniline or PANI treatment with aqueous solutions).](image)

The deposition of Pd via the decomposition of Pd$_2$(dba)$_3$ (formation of sample P4) caused even smaller changes in the IR spectra of PANI compared to the treatment with aqueous solutions upon the formation of samples P2 and P3 (Figure 6). This observation is consistent with the course of the Pd deposition process: decomposition of the Pd$^0$ precursor, Pd$_2$(dba)$_3$, did not require participation of PANI as a reducer, as well as had a minor influence on the protonation of the carrier, since the process was carried out in chloroform.

The doping of PANI with H$_2$SO$_4$ (formation of the PANI-H$_2$SO$_4$ carrier) led to significant changes in the IR spectrum as compared to the spectrum of PANI. All bands became broader, and the intensity of the band centered at 1350 cm$^{-1}$ (assigned to bands C and D, as above) significantly increased, which is consistent with earlier observations [53]. Such an increase in the band can be associated with the contribution of a new band, resulting from vibrations of the system, containing delocalized $\pi$-electrons; such a system was absent in the PANI base and occurred upon protonation [53]. The band at ca. 830 cm$^{-1}$, which was assigned to out-of-plane C–H deformation of the benzene ring, disappeared, probably because of the low relative intensity. Instead, two new bands at ca. 620 and 590 cm$^{-1}$ (bands H and I, Figure 7) were detected; these bands can be assigned to HSO$_4^-$ and SO$_4^{2-}$ ions [53]. The deposition of Pd onPANI-H$_2$SO$_4$ via the decomposition of Pd$_2$(dba)$_3$ did not result in noticeable changes of the structure of the carrier, as evidenced by the close similarity of the IR spectra (Figure 7).
The doping of PANI with H2SO4 (formation of the PANI-H2SO4 carrier) led to significant changes in the IR spectrum as compared to the spectrum of PANI. All bands became broader, and the intensity of the band centered at 1350 cm$^{-1}$ (assigned to bands C and D, as above) significantly increased, which is consistent with earlier observations [53]. Such an increase in the band can be associated with the contribution of a new band, resulting from vibrations of the system, containing delocalized π-electrons; such a system was absent in the PANI base and occurred upon protonation [53]. The band at ca. 830 cm$^{-1}$, which was assigned to out-of-plane C–H deformation of the benzene ring, disappeared, probably because of the low relative intensity. Instead, two new bands at ca. 620 and 590 cm$^{-1}$ (bands H and I, Figure 7) were detected; these bands can be assigned to HSO4$^-$ and SO4$^{2-}$ ions [53].

The deposition of Pd on PANI-H2SO4 via the decomposition of Pd$_2$(dba)$_3$ did not result in noticeable changes of the structure of the carrier, as evidenced by the close similarity of the IR spectra (Figure 7).

Thermal treatment of PANI in H$_2$ atmosphere at 300 °C did not cause significant changes of the IR spectrum (Figure 8). The positions of the main bands were the same or very similar, implying that the structure of the “building blocks” (oligomeric fragments) of PANI did not change. Thus, heating to 300 °C did not cause carbonization of the polymer, but this observation does not exclude cross-linking of the 1D polymeric chains.
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Figure 8. IR spectra of PANI and PANI-300.

Similar to the formation of P4, the decomposition of Pd₂(dba)₃ in the presence of PANI-300 (formation of sample P7) did not lead to any changes in the IR spectrum, indicating zero sensitivity of PANI-300 to treatment with the chloroform solution of the Pd complex (Figure 9). Quite expectedly, the heating of PANI could induce cross-linking of the polymeric chains and formation of the network, more rigid and inert compared to the initial polymer.

Figure 9. IR spectra of PANI-300 and P7 (the composite, formed upon Pd deposition on PANI-300 via the decomposition of Pd₂(dba)₃).
The IR spectra of the samples, prepared by polymerization of aniline in the presence of activated carbon or Aerosil, were similar to the spectra of PANI; however, significant broadening of the bands was observed. The broadening can be attributed to the interaction of polymeric chains of PANI with activated carbon or silica, which led to the change of some of the bond energies and respective vibrations. It can be concluded that PANI formed in these cases had the structure, essentially similar to the one of pure PANI, but the method of IR spectroscopy is not so informative for the characterization of such composites.

Raman spectra of the composites are also typical for PANI [54]. Upon treatment with sulfuric acid, a significant decrease of the intensity of the band at 1588–1592 cm\(^{-1}\) is observed (attributable to the C=C stretching vibration in the quinonoid ring), while the band at 1350 cm\(^{-1}\) has the highest intensity (probably associated with phenazine rings [54]). A similar situation was observed upon the transition from P4 to P6 (Pd on PANI compared to Pd on PANI-H\(_2\)SO\(_4\) (Figure 10).

The microstructure of the representative set of samples was studied by TEM. This series of samples included the one obtained by in situ polymerization of aniline in the presence of Pd\(^{2+}\) (P1), two samples, which were prepared by the deposition of Pd from the aqueous solutions of Pd\(^{2+}\) compounds on PANI (P2 and P3), and a set of samples, prepared by the decomposition of Pd\(_2\)(dba)\(_3\) in the presence of PANI (P4, P8, P10 and P11) and polyaniline, heated in hydrogen (PANI-300, sample P7) (Figure 11).
Figure 11. TEM images of the selected samples.

In the case of P1, no Pd particles were detected (Figure 11a). The compound contains transparent homogeneous material, and Pd seems to be evenly distributed on the surface of PANI and presumably forms ultrafine nanoparticles, which cannot be detected by the TEM used herein. In contrast, the deposition of Pd from the solutions of Na₂PdCl₄ (samples
P2 and P3, Figure 11b,c) led to the formation of large particles, with sizes up to 50 nm. These particles probably consist of aggregated nanocrystals, because the samples show fine electron diffraction in the TEM experiment (the absence of X-ray diffraction peaks of Pd can be explained by the low content of this crystalline metal). The fine structure of such large aggregates can be seen in the case of P2; single particles of sizes of dozens of nm can be distinguished.

Sample P4, prepared via the decomposition of Pd2(dba)3, contains large dark particles, which do not have a regular shape, and many of them are transparent or semi-transparent (Figure 11d). Such particles can be considered as PANI with an increased Pd content; it seems that the deposition of Pd on PANI upon the decomposition of Pd2(dba)3 did not occur uniformly but preferentially on certain particles of the polymer, probably most suitable to Pd seeding. Dark spots that could be attributed to Pd nanoparticles were observed in the case of Pd deposition on PANI/C (P10) and PANI-H2SO4/C (P11) carriers (Figure 11g,h). The sizes of such particles did not exceed ca. 10 nm. Finally, the decomposition of Pd2(dba)3 in the presence of PANI-300 (P7) and PANI/SiO2 (P8) did not result in the formation of large Pd particles, which could be detected by TEM in our hands.

The decomposition of Pd2(dba)3 on carboneous carriers led to the formation of Pd nanoparticles with sizes less than 10 nm (typically less than 3 nm) [40]; however, the decomposition of the same complex without a carrier resulted in the formation of significantly larger particles, with sizes between 60 and 200 nm [47] (notably, the assignment of such large particles to metallic Pd is not obvious in all cases, because they can be aggregates of Pd2(dba)3 [42]). The sizes of Pd nanoparticles found in this study fall in the range reported for the products of Pd2(dba)3 decomposition. The size and distribution of Pd nanoparticles by size is probably governed by the balance of the seeding rate and crystals growth rate; the former depends on the nature of the carrier [55].

The catalytic properties of the Pd-containing composites were studied in the process of quinoline hydrogenation, which is a suitable reaction for the evaluation and comparison of the catalytic efficiency of hydrogenation catalysts [5]. 1,2,3,4-tetrahydroquinoline (THQ) was the dominating product of the reaction (Figure 12); the reaction mixture contained negligible quantities of 5,6,7,8-tetrahydroquinonile and N-methyl-1,2,3,4-tetrahydroquinoline, the latter compound formed by the methylation of THQ with methanol (solvent) via a hydrogen-borrowing mechanism [56].

![Figure 12. Reaction used for evaluation of the catalytic properties of the composites.](image)

The results of the testing at p(H2) = 100 bar, T = 100 °C for 24 h in methanol are summarized in Table 1. Since the Pd content in the catalysts was different, for comparison of their efficiency, the catalytic productivity was calculated as the quantity of THQ (n(THQ)) formed per 1 mole of Pd (the last column in Table 1). In contrast to the turnover number (TON), where the quantity of THQ is referred to as the quantity of accessible Pd atoms (potential reaction centers), the quantity of THQ is referred here to the total Pd quantity. This value can be used only for evaluation of the practical feasibility of the catalyst in terms of Pd consumption in a preparative hydrogenation experiment but has no relation to the real activity of Pd. Experimental measurement of the accessible Pd surface, required for the calculation of TON, is not a trivial task in this case because of the very low Pd content.
Table 1. The yields of 1,2,3,4-tetrahydroquinoline (THQ) in the processes of quinoline hydrogenation in the presence of Pd-containing composites based on PANI in conditions \( p(\text{H}_2) = 100 \text{ bar}, T = 100 \, \circ \text{C}, \) methanol, 24 h.

<table>
<thead>
<tr>
<th>Entry No.</th>
<th>Catalyst</th>
<th>Pd Content in the Reaction Mixture, mol% (a)</th>
<th>Yield of THQ, %</th>
<th>( n(\text{THQ}) ) per 1 Mole of Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>P1</td>
<td>0.04</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>P2</td>
<td>0.42</td>
<td>77</td>
<td>180</td>
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<tr>
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<td>53</td>
<td>315</td>
</tr>
<tr>
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<td>24</td>
<td>1272</td>
</tr>
<tr>
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<td>0.17</td>
<td>34</td>
<td>195</td>
</tr>
<tr>
<td>6</td>
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<td>0.11</td>
<td>91</td>
<td>830</td>
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</tr>
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<td>1930</td>
</tr>
<tr>
<td>11</td>
<td>P11</td>
<td>0.17</td>
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(a) mol.% calculated with respect to quinoline; 1 mmol of quinoline, 20 mg of catalyst.

For a set of samples P1–P5 (all of them contain PANI without acidic dopant or additional component), the yield of THQ generally increased with the growth of the Pd content in the reaction mixture (Figure 13). In the case of samples P2, P3 and P4, relatively large Pd particles or their aggregates were found by TEM, and the tendency that the THQ yield increased linearly with the growth of the Pd content was consistent with the observation that these catalysts had similar structures.

![Figure 13. Yield of THQ vs. the Pd content in the reaction mixture (at \( p(\text{H}_2) = 100 \text{ bar}, T = 100 \, \circ \text{C}, \) 24 h, methanol). All samples containing PANI doped by \( \text{H}_2\text{SO}_4 \) are marked by red color; samples containing C or PANI after thermal treatment are marked by blue (sample P11 contains both \( \text{H}_2\text{SO}_4 \) and C, and it can be referred to in both these groups).]
More interesting, a set of samples P6, P7 and P9–P11 showed a significantly higher performance (Figure 13; these samples are shown in a circle). These samples had the highest yields of THQ at relatively low Pd loadings in the reaction mixture, and these samples were characterized by the highest productivity parameter (n(THQ) per 1 mole of Pd, Table 1). For example, the productivity parameter for P7 was 2710, and for P9, it was 2285, while, for the P1–P5 set, the productivity parameter did not exceed 1272. This set of samples contains the composites, which were formed either on the basis of PANI doped by H$_2$SO$_4$ (P6, P9 and P11) or on the basis of Norit activated carbon (P10 and P11) or PANI after thermal treatment at 300 °C (P7). According to the results of the TEM studies, P10 and P11 contained Pd particles with sizes less than ca. 10 nm, and no large Pd particles could be found by TEM in P7, in contrast to P2, P3 and P4 from the previously described series. This observation is consistent with a well-known trend: an increase of Pd dispersion favors a higher catalytic performance [57]. It can be supposed that the higher performance of the samples from series P6, P7 and P9–P11 could be associated with a higher dispersion of Pd. In turn, such dispersion resulted from the specific conditions of Pd$_2$(dba)$_3$ decomposition; probably, these carriers favored the formation of a larger number of Pd nanoparticle growth centers compared to pure PANI and, as a consequence, smaller Pd nanoparticles.

An additional note can be made from the comparison of P3, P5 and P11. All these samples contained 0.9% of Pd, but the catalytic performance of P11 was superior compared to the ones of P3 and P5. On the other hand, the size of the Pd nanoparticles found in P11 by TEM was lower compared to the Pd nanoparticles in P3. These observations support the above supposition—the decomposition of Pd$_2$(dba)$_3$ in the carrier, containing PANI-H$_2$SO$_4$, resulted in the formation of more active Pd nanoparticles with higher dispersion compared to the decomposition of Pd$_2$(dba)$_3$ in pure PANI.

For comparison of the catalytic efficiency of the composites, based on PANI, the most efficient samples were used as catalysts for the hydrogenation of quinoline at p(H$_2$) = 30 bar, T = 50 °C in methanol, and the reaction time was 4 h. The hydrogenation of quinoline in such conditions allowed for direct comparison of the composites from this study with some previously reported analogs tested in the same conditions (Table 2). It was found that the performance of P7 and P11 significantly exceeded the values found for Pd-containing composites prepared using other carriers. From this study, it can be concluded that the use of PANI for the modification of activated carbon or as a starting material for the PANI-300 carrier can be a way for the preparation of hydrogenation catalysts possessing high performance in the hydrogenation of heterocyclic compounds. It should be noted that the catalysts from entries 6–12 were prepared using BAU activated carbon [58], and their lower performance compared to P10 and P11 (samples containing activated carbon) can be caused both by the effect of PANI and the effect of Norite GSX activated carbon. From the other hand, sample P7 ensured the complete hydrogenation of quinoline, similar to P11, so PANI-300 can be considered as a promising alternative to expensive Norite GSX. This advantage diminished upon catalyst preparation at the 10 g scale, vide infra.

<table>
<thead>
<tr>
<th>Entry No.</th>
<th>Catalyst (a)</th>
<th>Pd Content, mol.% Per 1 mole of Quinoline</th>
<th>Yield of THQ, %</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>P7</td>
<td>1</td>
<td>100</td>
<td>this work</td>
</tr>
<tr>
<td>2</td>
<td>P8</td>
<td>1</td>
<td>60</td>
<td>this work</td>
</tr>
<tr>
<td>3</td>
<td>P9</td>
<td>1</td>
<td>29</td>
<td>this work</td>
</tr>
<tr>
<td>4</td>
<td>P10</td>
<td>1</td>
<td>61</td>
<td>this work</td>
</tr>
<tr>
<td>5</td>
<td>P11</td>
<td>1</td>
<td>100</td>
<td>this work</td>
</tr>
</tbody>
</table>
Table 2. Cont.

<table>
<thead>
<tr>
<th>Entry No.</th>
<th>Catalyst (^{(a)})</th>
<th>Pd Content, mol.% Per 1 mole of Quinoline</th>
<th>Yield of THQ, %</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>Pd/C-1</td>
<td>1</td>
<td>42</td>
<td>[58]</td>
</tr>
<tr>
<td>7</td>
<td>Pd/C-2</td>
<td>1</td>
<td>28</td>
<td>[58]</td>
</tr>
<tr>
<td>8</td>
<td>Pd/C-3</td>
<td>1</td>
<td>10</td>
<td>[58]</td>
</tr>
<tr>
<td>9</td>
<td>Pd/C-4</td>
<td>1</td>
<td>9</td>
<td>[58]</td>
</tr>
<tr>
<td>10</td>
<td>Pd(OH)(_2)/C-1</td>
<td>1</td>
<td>61</td>
<td>[58]</td>
</tr>
<tr>
<td>11</td>
<td>Pd(OH)(_2)/C-2</td>
<td>1</td>
<td>67</td>
<td>[58]</td>
</tr>
<tr>
<td>12</td>
<td>Pd(OH)(_2)/C-3</td>
<td>1</td>
<td>55</td>
<td>[58]</td>
</tr>
<tr>
<td>13</td>
<td>PdCl(_2)/MIL-101(Cr)</td>
<td>2</td>
<td>30</td>
<td>[13]</td>
</tr>
</tbody>
</table>

(a) Samples P7–P11 were prepared at the 1 g scale, as described in the Materials and Methods section. Pd/C-1–Pd/C-4 catalysts were prepared by the deposition of Pd on the BAU activated carbon from the solutions of \(\text{H}_2\text{PdCl}_4\), followed by a reduction with formaldehyde by generally recognized methods used since the middle of the 20th century \([59]\); the samples differ by the conditions of preparation. Pd(OH)\(_2\)/C are Pearmann catalysts, prepared by generally recognized methods, using BAU activated carbon \([60]\); the samples differ by the conditions of preparation. PdCl\(_2\)/MIL-101 is a porous coordination polymer \(\text{Cr}_3(\text{OH})(\text{H}_2\text{O})_2\text{O(bdc)}_3\text{I}_n\) containing PdCl\(_2\) in pores; bdc\(^{-}\) is 1,4-benzenedicarboxylate \([61]\).

In order to test if the catalysts could be prepared at a larger scale and used for the hydrogenation of a wide range of compounds, three samples, namely P7, P9 and P11, were resynthesized at the 10 g scale. In such cases, the masses of all reagents and solvents were proportionally increased by factors of 20 (P7), 55 (P9) and 20 (P11); however, the rates of solutions heating in the hot oil bath were apparently lower because of the heat exchange limitations. The resulting composites were tested as the catalysts of quinoline hydrogenation in the same conditions as shown in Table 2 (\(p(\text{H}_2) = 30\) bar, \(T = 50^\circ\)C, methanol, 4 h, at 1 mol.% of Pd). It was found that the yields of 1,2,3,4-tetrahydroquinoline in the presence of P7 and P9 were 52 and 43%, respectively, while, in the case of P11, full conversion of quinoline to 1,2,3,4-tetrahydroquinoline was achieved with 100% selectivity. Increase of the catalyst loading in the cases of P7 and P9 to 2 mol.% of Pd in the same conditions led to an increase of the yields of 1,2,3,4-tetrahydroquinoline to 70 and 63%, but complete conversion of quinoline was not achieved. Thus, among the samples checked, in the case of P11, a scale up from 0.5 to 10 g led to the formation of the catalysts, which ensured the expected high performance; at the same time, the performance of P7 (10 g scale) was two times lower compared to the small-scale prototype. The performance of P9 (10 g scale) was almost two times higher than the prototype, but it still did not ensure complete conversion of the quinoline. It should be noted that the results of catalyst scale-ups are not usually straightforward \([62]\).

The sample P11, prepared at the 10 g scale, was tested as the catalyst in the hydrogenation of a number of organic compounds (Table 3). The use of P11 ensured the complete or almost complete hydrogenation of alkenes (entries no. 6, 8 and 10) and alkyne (entry 9), as well as non-substituted quinoline (entry 1). Isomeric 2- and 4-methylquinolines (entries 2 and 3) were hydrogenated, giving respective methyl-1,2,3,4-tetrahydroquinolines with 69 and 14% yields. Lower yields in the hydrogenation of methylquinolines compared to quinoline are in line with previously reported results \([9,17,63]\). The nitro group was expectedly converted to an amino group (entry 8) with a very high yield. The hydrogenation of 1-acetylnaphtalene (entry 4) resulted in the formation of the respective alcohol, along with the product of deeper hydrogenation, 1-ethylnaphtalene. In turn, the hydrogenation of 4-phenylbut-3-en-2-one (entry 6) containing conjugated C=C and C=O bonds led to the complete transformation of the CH=CH bond to a CH\(_2\)-CH\(_2\) fragment, while the respective alcohol formed with a 28% yield. Preferential hydrogenation of the C=C bond in the presence of the C=O bond is a typical situation in Pd-catalyzed processes \([5,64]\). The
hydrogenation of quilonile-2(1H)-one (entry 7) led to 3,4-dihydroquilonile-2(1H)-one with a 16% yield. Finally, the attempt of the hydrogenation of 1-cyanonaphtalene (entry 5) failed.

Table 3. The results of the hydrogenation of different substrates in the presence of P11 in conditions p(H₂) = 30 bar, T = 50 °C, methanol, 4 h. Pd loading was 1 mol.% in all cases. Sample P11 was prepared at the 10 g scale.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Starting Compound</th>
<th>Products and Their Yields</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1" alt="image" /></td>
<td><img src="image2" alt="image" /> 100%</td>
</tr>
<tr>
<td>2</td>
<td><img src="image3" alt="image" /></td>
<td><img src="image4" alt="image" /> 69%</td>
</tr>
<tr>
<td>3</td>
<td><img src="image5" alt="image" /></td>
<td><img src="image6" alt="image" /> 14%</td>
</tr>
<tr>
<td>4</td>
<td><img src="image7" alt="image" /></td>
<td><img src="image8" alt="image" /> 75% OH</td>
</tr>
<tr>
<td></td>
<td></td>
<td><img src="image9" alt="image" /> 17%</td>
</tr>
<tr>
<td>5</td>
<td><img src="image10" alt="image" /></td>
<td>no reaction</td>
</tr>
<tr>
<td>6</td>
<td><img src="image11" alt="image" /></td>
<td><img src="image12" alt="image" /> 72%</td>
</tr>
<tr>
<td>7</td>
<td><img src="image13" alt="image" /></td>
<td><img src="image14" alt="image" /> 16%</td>
</tr>
<tr>
<td>8</td>
<td><img src="image15" alt="image" /></td>
<td><img src="image16" alt="image" /> 95%</td>
</tr>
<tr>
<td>9</td>
<td><img src="image17" alt="image" /></td>
<td><img src="image18" alt="image" /> 100%</td>
</tr>
<tr>
<td>10</td>
<td><img src="image19" alt="image" /></td>
<td><img src="image20" alt="image" /> 100%</td>
</tr>
</tbody>
</table>
Sample P11 (10 g scale) was stable upon storage in ambient conditions in air for at least 6 months. The reusability of sample P11 (10 g scale) was checked in several repeated experiments on the hydrogenation of quinoline and 1-ethynylnaphthalene. The hydrogenation of these substrates was performed in the conditions as shown in Table 3; then, the catalyst was collected by filtration and used again for repeated hydrogenation. All procedures with the catalyst were carried out in air. The catalyst loss (by weight) was less than 10% in the first step and less than 5% in the consequent steps; the same filter from porous glass was used to minimize the catalyst losses. The quantity of substrate was respectively reduced in order to adjust it to the actual weight of the catalyst after each run. It was found that the yields of 1-ethynaphthalene were 100% in five runs of hydrogenation (Figure 14). At the same time, the yield of 1,2,3,4-tetrahydroquinoline on the second run decreased to 26%, and then, it gradually decreased to 17% on the fifth run (Figure 14). Such a decrease could be associated with deactivation of the Pd active sites or Pd loss; in any case, this catalyst can find very limited applications for repeated use. On the other hand, it can be noted that the catalytic performance of P11 in the process of alkyn hydrogenation seemed to be “excessively high”, and after five runs, the performance of the catalyst (even if it decreased) was still sufficient to ensure complete hydrogenation of this substrate.

![Graph](image_url)

**Figure 14.** The yields of the products (1,2,3,4-tetrahydroquinolone and 1-ethynaphthalene) in the subsequent hydrogenation of quinoline and 1-ethynaphthalene, respectively, in the presence of the P11 (same sample was isolated and reused for the next runs). Conditions: p(H₂) = 30 bar, T = 50 °C, methanol, 4 h. Pd loading was 1 mol.% for the first run.

3. Materials and Methods

Aniline (95%) was purchased from Vesthym LLC (Kyiv, Ukraine), HCl and H₂SO₄ were purchased from Khimreaktiv (Kyiv, Ukraine), ammonium persulfate (98%) was purchased from Sigma-Aldrich, activated carbon Norit GSX was purchased from Energohimservice LLC (Kyiv, Ukraine), Aerosil-300 (SiO₂) was purchased from Chemical Reagents Plant (Kharkiv, Ukraine), PdCl₂ (98%) was purchased from Nanjing Chemlin Chemical Industry Co. Ltd. (Nanjing, China) and Pd₂dba₃ (98%) was supplied by BLD Pharmatech Ltd. (Shanghai, China). All other reagents and materials were obtained from UkrOrgSintez Ltd. (Kyiv, Ukraine) and used as received. Anhydrous methanol (water content less than 0.05% by weight) was used for the hydrogenation experiments. Methanol and other solvents were purified according to the standard procedures [65].

Powder X-ray diffraction patterns were measured using a Bruker D8 Advance diffractometer (Bruker Corp., Billerica, MA, USA) with CuKα radiation (λ = 1.54056 Å). TEM
measurements were performed using a PEM-125K instrument (SELMI, Sumy, Ukraine) operating at 100 kV acceleration voltage. Samples were prepared as described previously [18]. IR spectra were measured using the Spectrum One instrument (Perkin Elmer, Waltham, MA, USA). Spectra were recorded for pressed KBr pellets in the wavenumber range from 400 cm\(^{-1}\) to 4500 cm\(^{-1}\). Raman spectra of the composites were measured using a NovaTions spectrometer (Kyiv, Ukraine) in the range of 0–2000 cm\(^{-1}\) at excitation wavelength \(\lambda = 514\) nm, laser power 6 mW and spectrum accumulation time 10 s. The molecular weight of PANI was determined using a rotary Brookfield DVE viscometer (AMETEK Brookfield, Middleboro, MA, USA at 100 rpm\(^{-1}\). Molecular weight of the obtained PANI was determined by viscometry. The characteristic viscosity for the PANI-DMF system was determined experimentally. The relationship between the characteristic viscosity and the molecular weight was described by the Mark–Kuhn–Hauwink equation [66]. For the PANI-DMF system at 25 \(^\circ\)C, the coefficients were equal to \(K = 1.4 \cdot 10^{-4}\); \(\alpha = 0.93\) [67]. The Pd content in the composites was determined by atomic adsorption using a SOLAARS4 DoubleBeam analyzer (ThermoElectron, Waltham, MA, USA) with acetylene-air flame atomization. For the analysis, samples that did not contain SiO\(_2\) or activated carbon were dissolved in a boiling aqua regia. Samples containing SiO\(_2\) were first dissolved in HF, and then, the solutions were evaporated to dryness, and the resulting precipitates were dissolved in boiling aqua regia. Samples containing carbon were burned, and then, the residues were dissolved in a boiling aqua regia. The obtained solutions were diluted to the desired concentration with 1% aqueous HNO\(_3\). Palladium dimethylglyoximate was used for preparation of the analytical standards.

Hydrogenation experiments were carried out in a steel high-pressure reactor RVD-250 from stainless steel (Riva-Stal LLC, Kyiv, Ukraine), equipped with a manometer, Teflon liner, magnetic stirrer (10 × 6 mm in size) and temperature controller, similar to the previously reported techniques [14,17,18]. The high-pressure reactor was charged with reagents and solutions in air and purged with hydrogen three times (filling to the 3 bar and released) before filling with hydrogen at a high pressure. Continuous stirring of the reaction mixture was carried out during the whole time of the experiment, and the stirring speed was 750 min\(^{-1}\). \(^1\)H spectra of the reaction mixtures were measured using a Varian Unity Plus 400 spectrometer; chromatomass analysis of the reaction mixtures was carried out using an Agilent 1100 LCMSD SL instrument (chemical ionization (CI)) and an Agilent 5890 Series II 5972 GCMS instrument (electron impact ionization (EI)) installed at Enamine Ltd. (Kyiv, Ukraine).

3.1. Synthesis of Polyaniline (PANI)

PANI was synthesized according to the method described previously [34]. In particular, 10 g of aniline were dissolved in 500 mL of 1 M aqueous HCl and cooled to 10 \(^\circ\)C. Then, 36 g of \((\text{NH}_4)_2\text{S}_2\text{O}_8\) were dissolved in 240 mL of 1 M aqueous HCl, and the solution was added dropwise to the aniline solution, maintaining the temperature regime. After the addition, the reaction mixture was stirred for an additional 4 h. The solid precipitate was filtered, washed with water and acetonitrile and dried at 80 \(^\circ\)C for ca. 2 h. After that, the polymer was poured with 1 l of a 5% aqueous solution of NH\(_4\)OH, stirred for one hour, filtered and washed with water to a neutral pH and dried at 80 \(^\circ\)C in air during ca. 16 h.

3.2. Synthesis of P1

First, 466 mg of aniline were dissolved in 50 mL of 1 M aqueous HCl. Then, 22 mg of PdCl\(_2\) \((1.2 \cdot 10^{-4}\) mol) and 14 mg of NaCl \((2.4 \cdot 10^{-4}\) mol) were added. The reaction mixture was heated to boiling with stirring until the dissolving of PdCl\(_2\). Then, the mixture was cooled down to 10 \(^\circ\)C, and a solution of 0.797 g of \((\text{NH}_4)_2\text{S}_2\text{O}_8\) in 11 mL of aqueous 1 M HCl was added dropwise. After the addition, the reaction mixture was stirred for another 4 h at 10 \(^\circ\)C. Then, the solid was filtered, washed with water and acetonitrile and dried at 80 \(^\circ\)C in air for ca. 2 h. After that, the solid was placed in a beaker and poured with 100 mL of a 5%
aqueous solution of NH\textsubscript{4}OH and stirred for one hour, filtered and washed with water to a neutral pH and dried at 80 °C in air during ca. 16 h. Analysis: Pd content 0.2% by weight.

3.3. Synthesis of P2 and P3

First, 25 mg of PdCl\textsubscript{2} (1.41 \times 10^{-4} mol) were dissolved in a boiling solution of 1 g of NaCl (1.7 \times 10^{-2} mol) in 47 mL of water for P2 or 240 mL of water for P3. The concentration of the Na\textsubscript{2}PdCl\textsubscript{4} solution was 3.1 mM for P2 or 0.6 mM for P3. Then, 0.5 g of PANI were added to the resulting solution at room temperature, mixed and left for a day. The composite was then filtered, washed with 20 mL of water and dried at 80 °C during ca. 16 h. Analysis: Pd content 2.2% (P2) or 0.9% (P3) by weight.

3.4. Synthesis of P4 and P5

First, 0.5 g of PANI were placed in a glass vial, and a solution of 22 mg of Pd\textsubscript{2}(dba)\textsubscript{3} (2.4 \times 10^{-5} mol) for P4 or 110 mg of Pd\textsubscript{2}(dba)\textsubscript{3} (1.2 \times 10^{-4} mol) for P5 in 25 mL of CHCl\textsubscript{3} was added. The concentration of the solution was 1.9 mM for P4 or 9.6 mM for P5 (per 1 mol of Pd). The vial was closed and put in an oil bath heated to 80 °C. After standing for three minutes, the content of the vial was filtered, washed with 3 mL of chloroform and dried at 80 °C in air for ca. 30 min. Analysis: Pd content 0.1% (P4) or 0.9% (P5) by weight.

3.5. Synthesis of P6

Polidiane, doped by H\textsubscript{2}SO\textsubscript{4} (PANI-H\textsubscript{2}SO\textsubscript{4}), was prepared as PANI (Section 3.1), but 1 M HCl was replaced by 0.5 M H\textsubscript{2}SO\textsubscript{4}, and the polymer was not treated by a solution of NH\textsubscript{4}OH. Then, 0.136 g of PANI-H\textsubscript{2}SO\textsubscript{4} were placed in a glass vial, and a solution of 9 mg of Pd\textsubscript{2}(dba)\textsubscript{3} (1 \times 10^{-5} mol) in 10 mL of CHCl\textsubscript{3} was added. The vial was tightly closed and put into an oil bath heated to 80 °C. After standing for three minutes, the product was filtered, washed with 3 mL of chloroform and dried at 80 °C in air for ca. 30 min. Analysis: Pd content 0.6% by weight.

3.6. Synthesis of P7

First, 1 g of PANI was treated at 300 °C in a H\textsubscript{2} atmosphere for 2 h (the resulting sample is hereinafter referred to as PANI-300). The yield of PANI-300 was 0.595 g (weight loss 40.5%). Pd was deposited on PANI-300 (0.5 g) using 22 mg of Pd\textsubscript{2}(dba)\textsubscript{3} (2.4 \times 10^{-5} mol) in 25 mL of CHCl\textsubscript{3}, as described in Section 3.4. Analysis: Pd content 0.2% by weight. In the scale-up experiment, all masses of compounds and volumes of solvents were multiplied by a factor of 20 (starting from 10 g of PANI-300).

3.7. Synthesis of P8

First, 2.7 g of Aerosil-300 (SiO\textsubscript{2}) were mixed with 0.27 g of aniline in 35 mL of 1 M aqueous HCl and kept in an ultrasonic bath for 10 min. After that, a solution of 0.463 g of (NH\textsubscript{4})\textsubscript{2}S\textsubscript{2}O\textsubscript{8} in 6.5 mL of 1 M aqueous HCl was added dropwise at 10 °C. After the addition, the reaction mixture was stirred for another 4 h at 10 °C. The solid was filtered, washed with water (20 mL) and acetonitrile (20 mL) and dried at 80 °C for ca. 2 h. After that, the solid was placed in a glass and poured with 100 mL of a 5% aqueous solution of NH\textsubscript{4}OH. After stirring for an hour, the solid was filtered and washed with water until reaching a neutral pH. The product, hereinafter referred to as PANI/SiO\textsubscript{2}, was dried at 80 °C for 16 h. Then, 0.136 g of PANI/SiO\textsubscript{2} was placed in a glass vial, and a solution of 6 mg of Pd\textsubscript{2}(dba)\textsubscript{3} (0.65 \times 10^{-5} mol) in 8 mL of CHCl\textsubscript{3} was added. The vial was tightly closed and put into an oil bath heated to 80 °C. After standing for three minutes, the product was filtered, washed with 3 mL of chloroform and dried at 80 °C on air for ca. 30 min. Analysis: Pd content 0.3% by weight.

3.8. Synthesis of P9

First, 0.18 g of PANI/SiO\textsubscript{2}, prepared as described in Section 3.7, was placed in a flask, 150 mL of 0.5 M aqueous H\textsubscript{2}SO\textsubscript{4} were added and the mixture was stirred for about 1 h. The
solid, hereinafter referred to PANI-H2SO4/SiO2, was filtered, washed with 20 mL of water and dried at 80 °C for ca. 2 h.

P9 was prepared as described in Section 3.4, starting from 0.18 g of PANI-H2SO4/SiO2 and 8 mg of Pd2(dba)3 dissolved in 8 mL of chloroform. Analysis: Pd content 0.2% by weight. In the scale-up experiment, all masses of the compounds and volumes of solvents were multiplied by a factor of 55 (starting from 10 g of PANI-H2SO4/SiO2).

3.9. Synthesis of P10

Composite PANI/C, where C is Norit GSX activated carbon, was prepared as described in Section 3.7, with the difference that Aerosil-300 was replaced by the same mass of Norit GSX activated carbon. P10 was prepared as described in Section 3.7, starting from 0.136 g of PANI/C and 6 mg of Pd2(dba)3. Analysis: Pd content 0.25% by weight.

3.10. Synthesis of P11

P11 was prepared as described in Section 3.8, starting from 0.5 g of PANI-H2SO4/C and 22 mg of Pd2(dba)3. Analysis: Pd content 0.9% by weight. In the scale-up experiment, all masses of the compounds and volumes of the solvents were multiplied by a factor of 20 (starting from 10 g of PANI-H2SO4/C).

4. Conclusions

It can be concluded from this study, that modified polyaniline (PANI) can be a promising carrier for preparation of Pd-containing catalysts for quinoline hydrogenation. Within the examined series of samples the best results were achieved upon deposition of Pd on the following carriers: (i) PANI, doped by H2SO4, or (ii) the composite PANI/Norit GSX activated carbon, or (iii) PANI after thermal treatment in hydrogen at 300 °C. Among the methods of Pd deposition, tested in this work, thermal decomposition of Pd0 complex, Pd2(dba)3, led to formation of the most efficient catalysts in contrast to Pd deposition from the solutions of Pd2+ or in situ polymerization of polyaniline in presence of Pd2+ ions. The catalytic performance of the catalysts prepared using the above mentioned modified PANI (on criteria of the yield of 1,2,3,4-tetrahydroquinoline) was higher compared to similar Pd-containing catalysts based on pure PANI or activated carbon BAU. Use of four studied composites as catalysts ensured more than 90% yield of 1,2,3,4-tetrahydroquinoline in hydrogenation of quinoline at less than 0.2 mol.% Pd loading (at 100 bar, 100 °C, 24 h).

Superior performance of the catalysts, prepared by decomposition of Pd2(dba)3 on the modified PANI (doped by H2SO4, composite with Norit GSX or PANI after thermal treatment) compared to pure PANI can be explained by higher dispersion of Pd. In turn, such higher dispersion probably resulted from the specific features of Pd seeding on the surface of these solids, i.e., formation of large quantity of nanoparticle growth centers. Formation of smaller Pd nanoparticles on acidic carriers was consistent with the cases reported in the literature.

Deposition of Pd on PANI via decomposition of Pd2(dba)3 at the level of 0.1% led to formation of the catalysts, which possessed relatively high catalytic performance, however increase of Pd loading on PANI to 0.9% resulted in drastic deterioration of the catalytic properties. Such effect was not observed when PANI-H2SO4/C was used as a carrier, and in such case deposition of 0.9% of Pd led to formation of the catalyst which ensured high yield of 1,2,3,4-tetrahydroquinoline in hydrogenation of quinoline.

The sample Pd/PANI-H2SO4/C (P11) could be prepared in 10 g scale without loss of productivity compared to 0.5 g scale. Such catalyst was successfully used for hydrogenation of a series of compounds, including alkenes, alkynes, ketones, compound with nitro group and substituted quinolines, and ensured high yields of the products at 1 mol.% Pd loading at 30 bar, 50 °C, 4 h. The performance of this catalyst did not decrease in hydrogenation of alkynie in five runs, but significantly fell down in the case of hydrogenation of quinoline after the first run.
The results of this study can be important for development of highly efficient catalysts for hydrogenation of organic compounds with low Pd content. Use of such catalysts can result in reduction of Pd consumption and facilitate purification of the organic compounds (products of hydrogenation) from traces of Pd.

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**References**

5. Ivanystsya, M.O.; Subotin, V.V.; Gavrilenko, K.S.; Ryabukhin, S.V.; Volochnyuk, D.M.; Kolotilov, S.V. Advances and challenges in development of transition metal catalysts for heterogeneous hydrogenation of organic compounds. *Chem. Rec.* 2024, 24, e202300300. [CrossRef]


Polym. Int. 2023, 59, 193–199. [CrossRef]

Zaleskiy, S.S.; Ananikov, V.P. Pd2(dba)3 as a Precursor of Soluble Metal Complexes and Nanoparticles: Determination of Palladium Active Species for Catalysis and Synthesis. Organometallics 2012, 31, 2302–2309. [CrossRef]


Cirić-Marijanović, G.; Trchová, M.; Stejskal, J. The chemical oxidative polymerization of aniline in water: Raman spectroscopy. J. Raman Spectrosc. 2008, 39, 1375–1387. [CrossRef]


Reed-Berendt, B.G.; Polidano, K.; Morrill, L.C. Recent advances in homogeneous borrowing hydrogen catalysis using earth-abundant first row transition metals. Adv. Mater. 2023, 35, 2219195. [CrossRef]


Subotin, V.V.; Vashchenko, B.V.; Asaula, V.M.; Verner, E.V.; Ivanystsya, M.O.; Shvets, O.; Ostapchuk, E.N.; Grygorenko, O.O.; Ryabukhin, S.V.; Volochenyuk, D.M.; et al. Screening of Palladium/Charcoal Catalysts for Hydrogenation of Diene Carboxylates with Isolated-Rings (Hetero)aliphatic Scaffold. Molecules 2023, 28, 1201. [CrossRef] [PubMed]


Rossetti, I.; Compagnoni, M. Chemical reaction engineering, process design and scale-up issues at the frontier of synthesis: Flow chemistry. Chem. Eng. J. 2016, 296, 56–70. [CrossRef]

Pariiska, O.O.; Mazur, D.O.; Asaula, V.M.; Buryanov, V.V.; Socha, R.; Kurys, Y.I.; Kolotilov, S.V.; Koshechko, V.G.; Pokhodenko, V.D. Carbonized Polyaniline as a Catalyst for Hydrogenation with Molecular Hydrogen of Organic Substrates with C=C Double Bond and Nitro Group. Theor. Exp. Chem. 2023, 12, 773–779. [CrossRef]

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