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# Catalytic Performance of Pd Deposited on Various Carriers in Hydrogenation of Quinoline

**Abstract**

Pd nanoparticles were deposited on two different grades of activated carbon – NORIT and CAW. In addition, these carbons were pre-treated with $HNO_3$ or covered by polyaniline, and these modified carbons were used as carriers for the Pd deposition. The resulting materials were tested as catalysts for the hydrogenation of quinoline. The best-performing samples were further tested in the hydrogenation of 4-methylquinoline. The structural features of carriers and catalysts were elucidated by the $N_2$ adsorption studies. The grade of activated carbon was found to be a key factor controlling its performance, and the effect of the surface modification was negligible.

***Keywords:*** hydrogenation; palladium; activated carbon; quinoline; specific surface

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**Каталітична ефективність Pd, осадженого на різних носіях, у реакції гідрування хіноліну**

**Анотація**

Наночастинки Pd було нанесено на дві різні марки активованого вугілля – NORIT і CAW. Крім того, ці марки вугілля було попередньо оброблено $HNO_3$ або покрито поліаніліном і далі використано як носії для осадження Pd. Отримані матеріали випробувано як каталізатори гідрування хіноліну. Найкращі зразки було надалі протестовано в реакції гідрування 4-метилхіноліну. Структурні особливості носіїв і каталізаторів з'ясовано за допомогою адсорбційних досліджень $N_2$. Виявлено, що марка активованого вугілля була ключовим фактором, який контролював його ефективність, а ефект модифікації поверхні був незначним.

***Ключові слова:*** гідрування; паладій; активоване вугілля; хінолін; питома поверхня

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## ■ Introduction

Hydrogenation is one of the most important reactions in organic chemistry, and it is widely used for both the fine synthesis and industrial production of chemicals [1, 2]. Among hydrogenation catalysts, Pd-based systems play one of the central roles due to their high efficiency, which includes activity and selectivity, as well as good reproducibility [3, 4]. However, in view of the high price of palladium, searching for ways to reduce the metal consumption is an important task.

In our preliminary studies, it was found that the deposition of Pd nanoparticles on different grades of activated carbon led to the formation of catalysts with a completely different activity.

This difference can be explained by the formation of different particles due to specific surface features (for example, different concentration and activity of "seeding" centers, which act as the growth sites for particles [5]), as well as different influence of the carrier on the electronic structure of Pd particles [6]. Unfortunately, the carbons that give the most active catalysts are the most expensive, and searching for a simple way of modifying the carbon surface to "improve" it is an urgent task.

The aim of this study was to evaluate the role of the activated carbon pre-treatment determining the catalytic performance of Pd/C catalysts. Two samples of activated carbon were chosen for this study: (1) CAW MB240 activated carbon, and (2) NORIT GSX activated carbon. CAW is an activated carbon type, widely used for the purification of wastewater and liquids in different technological processes. Its sorption characteristics depend a lot on the batch; the sample used in this study had $S_{BET}$ = 49 $m^2$ $g^{-1}$, the total pore volume – $V_T$ = 0.164 $cm^3$ $g^{-1}$, and contained almost no micropores, according to the data of the $N_2$ sorption. NORIT is another grade of activated carbon, produced by Norit Ltd., and it can also be manufactured from coconut. The sample used in this study had $S_{BET}$ = 850 $m^2$ $g^{-1}$, the total pore volume $V_T$ = 0.604 $cm^3$ $g^{-1}$, and contained a significant quantity of micropores, with $V_{micro}$ = 0.220 $cm^3$ $g^{-1}$ (by Dubinin-Radushkevich); the *Horvath* and *Kawazoe* median micropore diameter was 0.64 nm. Significantly lower sorption characteristics of CAW compared to NORIT may be caused by a simpler activation process used in the production of CAW; consistently, CAW is much cheaper compared to NORIT. The possible use of CAW instead of NORIT after the modification with PANI seemed to be an attractive outlook.

These carbons were oxidized by the treatment with $HNO_3$, and the oxidized carbons were used as carriers for the Pd deposition. In another series of experiments, a layer of polyaniline (PANI) was deposited on activated carbon to test if the creation of such a "PANI shell" would negate the difference between these materials. The PANI content was chosen at the level of 10% by weight. PANI was chosen as a surface modifier because it was shown that the reduction of $Pd^{2+}$ by PANI led to a very efficient hydrogenation catalyst where PANI served as a carrier for Pd nanoparticles [7]. In addition, the deposition of PANI over activated carbon is a technically accessible task.

The deposition of Pd on the carriers was carried out by the decomposition of the $Pd_2(dba)_3$ complex (dba = dibenzylideneacetone), as previously reported [8, 9]. The decomposition of zero-valent complexes of metals was shown to be an efficient way to obtain hydrogenation catalysts [10–13].

## Materials and methods

Hydrogen (99.99%) was purchased from Galogas Ltd. (Kyiv, Ukraine) and used without further purification. NORIT GSX activated carbon was purchased from Energochimservise (Kyiv, Ukraine). CAW MB240 activated carbon was purchased from Ecofilter Ltd (Kharkiv, Ukraine). Other starting materials and reagents, except hydrogen, were available from Enamine Ltd. (Kyiv, Ukraine) and UkrOrgSyntez Ltd. (Kyiv, Ukraine).

The $N_2$ sorption was measured using Sorptomatic-1990 instrument by the volumetric method at 78 K. Prior to the measurements, the samples were heated at 200°C in a $10^{-4}$ Torr vacuum for 2 hours.

The yield of 1,2,3,4-tetrahydroquinoline was determined by integrating signals of different products in $^1$H NMR spectra and measuring their ratios. No product is volatile; the total quantity of all products is equal to the quantity of the starting compound. In turn, GC-MS was not used for the quantitative analysis of the mixtures because of the need to calibrate columns. GC-MS was used just for verification of the products (by retention times and MS patterns), as well as to ensure that other products did not form. All quantitative analyses were performed using NMR data. $^1$H spectra were measured on a Varian Unity Plus 400 spectrometer at 400 MHz. Mass spectra were measured on an Agilent 1100 LCMSD SL instrument (chemical ionization (CI)) and an Agilent 5890 Series II 5972 GC-MS instrument (electron impact ionization (EI)).

The deposition of Pd on the carriers was carried out, as previously reported [8, 9]. In all cases, the quantity of Pd-containing starting material, $Pd_2(dba)_3$, was chosen to ensure the 1% Pd content in the final product.

The oxidation of activated carbons was performed by treating the carbon sample with boiling diluted (30%) nitric acid for 4 hours [14, 15].

The deposition of PANI on activated carbons was performed as described [8]. Since the deposition was carried out in the acidic medium, the samples that were formed contained protonated PANI (hereinafter denoted as PANI($H^+$)).


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For the conversion of these materials into those containing neutral PANI, samples were treated with an excess of 1% solution of ammonia.

The hydrogenation of quinoline was performed in the high-pressure vessels as previously described [8, 10].

## ■ Results and discussion

Two types of activated carbons, CAW and NORIT, were used as starting materials for further modification and deposition of PANI. The aim of the surface oxidation with $HNO_3$ was to unify the surface, i.e., to eliminate specific functional groups (if any) and convert them into hydroxy- or carboxy-groups. The aim of the PANI deposition was to create a uniform layer of organic polymer, and make the conditions of the Pd nanoparticles deposition closer, regardless of different grades of activated carbon.

The deposition of Pd on all carriers, i.e., NORIT and CAW, treated by $HNO_3$ or covered by PANI (in protonated and neutral forms), was performed by the decomposition of $Pd_2(dba)_3$. The scheme of the catalyst formation, along with their abbreviations, is shown in **Figure 1**.

The hydrogenation of quinoline was chosen as a benchmark reaction for comparing the catalytic properties of the materials. In all cases, 1,2,3,4-tetrahydroquinoline (THQ) was the only hydrogenation product. The yields of THQ achieved in the presence of the catalysts studied are presented in **Table 1**.

It was found that the NORIT-based catalysts possessed high catalytic performance, and the quantitative hydrogenation of quinoline was achieved in the cases of Pd-NORIT and Pd-NORIT-Ox in the presence of 0.1 mol% of Pd at $p(H_2)$ = 30 bar, $T$ = 50 °C for 4 hours in methanol. At 0.025 mol% Pd loading, the yield of THQ was not quantitative,

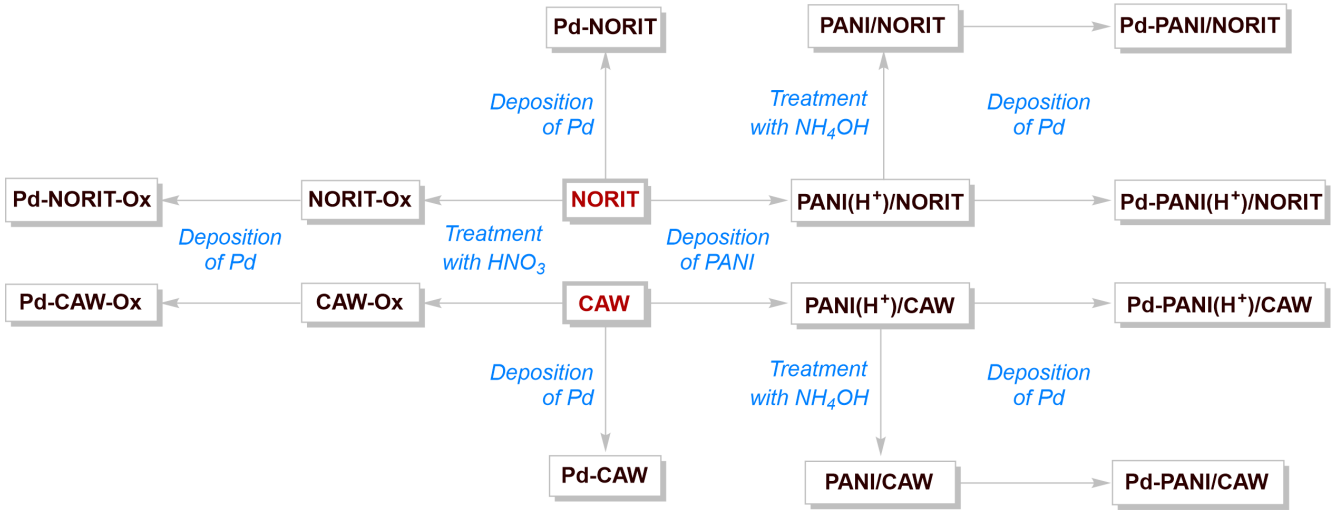


**Figure 1**. The preparation of Pd-containing catalysts

**Table 1**. The yields of 1,2,3,4-tetrahydroquinoline upon the hydrogenation of quinoline in the presence of Pd-containing catalysts under conditions $p(H_2)$ = 30 bar, $T$ = 50 °C, 4 h, methanol

| Catalyst | Pd loading, mol. % per 1 mol of quinoline | Yield of THQ, % | Ref. |
|---|---|---|---|
| NORIT series | | | |
| Pd-NORIT | 0.1 | 100 | this work |
| Pd-NORIT | 0.025 | 92 | this work |
| Pd-NORIT-Ox | 0.1 | 100 | this work |
| Pd-NORIT-Ox | 0.025 | 74 | this work |
| Pd-PANI($H^+$)/NORIT | 1[1] | 100 | 8 |
| Pd-PANI/NORIT | 1[1] | 61 | 8 |
| CAW Series | | | |
| Pd-CAW | 0.2 | 0 | this work |
| Pd-CAW-Ox | 0.2 | 0 | this work |
| Pd-PANI($H^+$)/CAW | 0.2 | 0 | this work |
| Pd-PANI/CAW | 1 | 0 | this work |

**Note:** [1] The Pd content on the catalysts was different from 1%, but the weights of the catalysts were adjusted to ensure 1% of Pd in the reaction mixture

**Table 2.** The yields of 4-methyl-1,2,3,4-tetrahydroquinoline upon the hydrogenation of 4-methylquinoline in the presence of Pd-containing catalysts in conditions $p(H_2)$ = 30 bar, $T$ = 50 °C, 4 hours, methanol

| Catalyst | Pd loading, mol % per 1 mol of quinoline | Yield of THQ, % | Ref. |
|---|---|---|---|
| NORIT series | | | |
| Pd-NORIT | 0.2 | 98 | this work |
| Pd-NORIT | 0.1 | 27 | this work |
| Pd-NORIT-Ox | 0.2 | 55 | this work |
| Pd-NORIT-Ox | 0.1 | 26 | this work |

and it could be found that the performance of Pd-NORIT was better compared to Pd-NORIT-Ox (the yields of THQ were 92% and 74%, respectively). Anyhow, the catalytic performance of these materials was superior compared to those containing PANI since in these conditions, the quantitative conversion of quinoline to THQ was not achieved in the case of Pd-PANI/NORIT at 1 mol% Pd loading.

It was previously shown that the catalysts containing Pd nanoparticles on the carriers made of PANI and NORIT had better performance compared to "classical" Pd-charcoal systems where Pd was deposited on the BAU activated carbon [8]. From the results of the present study, we must conclude that the high performance of such systems was due to NORIT, and not because of the PANI "shell".

In contrast to NORIT-based systems, catalysts made using CAW activated carbon did not possess any catalytic activity in the conditions used herein, i.e., $p(H_2)$ = 30 bar, $T$ = 50 °C, 4 hours in methanol. Their performance could not be improved by the surface oxidation with $HNO_3$ or the deposition of a PANI layer. We have to admit that the idea of cheap activated carbon transformation into analogues of expensive, but active ones, is not so simple and cannot be implemented by covering with a PANI layer.

The catalytic performance of the best catalysts considered herein, i.e., Pd-NORIT and Pd-NORIT-Ox, was checked in the hydrogenation of 4-methylquinoline. It was found that the yields of 4-methyl-1,2,3,4-tetrahydroquinoline were higher in the case of Pd-NORIT both at 0.2 and 0.1 mol% Pd loading. These yields were expectedly lower compared to the hydrogenation of non-substituted quinoline, but the tendency was the same (**Table 2**).

It was previously shown that the treatment of activated carbon with $HNO_3$ led to the enhancement of its sorption capacity in the processes of the sorption of heavy metal ions [16], the catalytic thermal decomposition of pentachlorobenzene [17], and in the case of the use as a carrier for hydrogenation catalysts [18]. In contrast, in our case, the treatment of NORIT with $HNO_3$ prior to the deposition of Pd nanoparticles led to the formation of a less active catalyst, and a similar procedure had no effect on the catalyst properties in the case of CAW.

To determine changes in the structural properties of carriers and catalysts during various treatments, and to assess their possible effect on the catalytic performance of Pd-containing samples, $N_2$ adsorption experiments were carried out for the NORIT series. The results are presented in **Table 3**.

The oxidation of NORIT with $HNO_3$ led to a *ca.* 2% decrease in $S_{BET}$. However, the deposition of PANI resulted in abrupt, about 50%, growth of $S_{BET}$. In addition, the pore volume also significantly increased. This effect can be explained by the formation of new roughness and folding

**Table 3.** Structural properties of the NORIT-based carriers and catalysts determined from $N_2$ adsorption isotherms

| Catalyst | $S_{BET}$, $m^2\ g^{-1}$ | Pore volume (Gurvich) at $p/p^0$ = 0.95, $cm^3\ g^{-1}$ | Median micropore diameter by *Horvath* and *Kawazoe*, nm | $V_{micro}$ (by Dubinin-Radushkevich), $cm^3\ g^{-1}$ |
|---|---|---|---|---|
| NORIT | 850 | 0.604 | 0.64 | 0.220 |
| Pd-NORIT | 605 | 0.572 | 0.83 | 0.202 |
| NORIT-Ox | 830 | 0.588 | 0.74 | 0.284 |
| Pd-NORIT-Ox | 750 | 0.553 | 0.68 | 0.265 |
| PANI($H^+$)/NORIT | 1310 | 0.948 | 0.75 | 0.452 |
| Pd-PANI($H^+$)/NORIT | 1080 | 0.759 | 0.74 | 0.384 |
| PANI/NORIT | 1280 | 0.857 | 0.71 | 0.450 |
| Pd-PANI/NORIT | 1115 | 0.802 | 0.76 | 0.390 |


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of the surface, including new pores, due to the PANI layer.

The deposition of Pd in all cases led to some decrease in the specific surface probably due to the fact that Pd particles filled the asperities of the surface. Similarly, the total pore volume and the volume of micropores decreased upon the deposition of Pd, indicating the localization of Pd nanoparticles in pores. However, 1% of Pd could not ensure such a significant decrease in the pore volume, and probably Pd nanoparticles blocked some part of the pores, making them inaccessible for $N_2$ probe molecules. It should be noted that a 1% decrease of the specific surface should have been due to the "addition" of a heavy metallic phase to the porous carrier.

The efficient pores diameter determined using the *Horvath* and *Kawazoe* model, did not change regularly upon the deposition of Pd nanoparticles (for example, it increased in the case of NORIT or decreased in the case of NORIT-Ox), and such irregular variation could be an argument in favor of the pore blocking by Pd nanoparticles, instead of filling the pores volume by Pd in full.

## ■ Conclusions

The main conclusion from this study is that the grade of activated carbon governs the properties of the deposited Pd-containing hydrogenation catalysts, and the performance of the catalyst cannot be significantly changed by the simple treatment of the carbon. In other words, the use of suitable activated carbon as a carrier is a key point, and the transformation of cheap activated carbon (which acts as a carrier for the catalysts of low activity) into a "good carrier" cannot be achieved by the oxidative treatment with nitric acid or the polyaniline layer formation. In addition, PANI is a good carrier for Pd nanoparticles for creating hydrogenation catalysts only if one compares PANI and a "non-active" carbon, such as CAW. PANI can be an alternative to cheap carbons, but the performance of activated carbon like NORIT is superior (though it is much more expensive). The deposition of a PANI layer on the surface of activated carbon does not improve its performance as a catalyst carrier, despite some reports about the formation of highly active catalysts based on PANI.

The nature of activated carbon itself is a key factor, which controls the performance of the catalysts, containing Pd nanoparticles, at least in the series where Pd was deposited in the same way. Thus, the activated carbon grade should be carefully selected for the preparation of Pd catalysts for the hydrogenation.

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## ■ References

1. Jackson, S. D. (Ed.). *Hydrogenation: Catalysts and Processes*; De Gruyter: Berlin, Boston, 2018.
2. Stoffels, M. A.; Klauck, F. J. R.; Hamadi, T.; Glorius, F.; Leker, J. Technology Trends of Catalysts in Hydrogenation Reactions: A Patent Landscape Analysis. *Adv. Synth. Catal.* **2020**, *362*, 1258–1274. https://doi.org/10.1002/adsc.201901292.
3. Zhao, X.; Chang, Y.; Chen, W.-J.; Wu, Q.; Pan, X.; Chen, K.; Weng, B. Recent Progress in Pd-Based Nanocatalysts for Selective Hydrogenation. *ACS Omega* **2022**, *7*, 17–31. https://doi.org/10.1021/acsomega.1c06244.
4. Andrade, M. A.; Martins, L. M. D. R. S. Supported Palladium Nanocatalysts: Recent Findings in Hydrogenation Reactions. *Processes* **2020**, *8*, 1172. https://doi.org/10.3390/pr8091172.
5. He, M.-Q.; Ai, Y.; Hu, W.; Guan, L.; Ding, M.; Liang, Q. Recent Advances of Seed-Mediated Growth of Metal Nanoparticles: From Growth to Applications. *Adv. Mater.* **2023**, *35*, 2211915. https://doi.org/10.1002/adma.202211915.
6. Li, Y.; Xu, X.; Zhang, P.; Gong, Y.; Li, H.; Wang, Y. Highly Selective Pd@mpg-$C_3N_4$ Catalyst for Phenol Hydrogenation in Aqueous Phase. *RSC Adv.* **2013**, *3*, 10973–10982. https://doi.org/10.1039/C3RA41397G.
7. Gao, Y.; Chen, C.-A.; Gau, H.-M.; Bailey, J. A.; Akhadov, E.; Williams, D.; Wang, H. L. Facile Synthesis of Polyaniline-Supported Pd Nanoparticles and Their Catalytic Properties toward Selective Hydrogenation of Alkynes and Cinnamaldehyde. *Chem. Mater.* **2008**, *20*, 2839–2844. https://doi.org/10.1021/cm7030416.
8. Kompaniiets, O. O.; Subotin, V. V.; Poturai, A. S.; Yurchenko, A. A.; Gorlova, A. A.; Bychko, I. B.; Kotenko, I. Y.; Pariiska, O. O.; Ryabukhin, S. V.; Volochnyuk, D. M.; et al. Catalytic Properties of Pd Deposited on Polyaniline in the Hydrogenation of Quinoline. *Chemistry* **2024**, *6*, 738–759. https://doi.org/10.3390/chemistry6040044.
9. Yakukhnov, S. A.; Pentsak, E. O.; Galkin, K. I.; Mironenko, R. M.; Drozdov, V. A.; Likholobov, V. A.; Ananikov, V. P. Rapid "Mix-and-Stir" Preparation of Well-Defined Palladium on Carbon Catalysts for Efficient Practical Use. *ChemCatChem* **2018**, *10*, 1869–1873. https://doi.org/10.1002/cctc.201700738.
10. Subotin, V. V.; Ivanytsya, M. O.; Terebilenko, A. V.; Yaremov, P. S.; Pariiska, O. O.; Akimov, Y. M.; Kotenko, I. E.; Sabov, T. M.; Kurmach, M. M.; Ryabukhin, S. V.; et al. Air-Stable Efficient Nickel Catalyst for Hydrogenation of Organic Compounds. *Catalysts* **2023**, *13*, 706. https://doi.org/10.3390/catal13040706.
11. Sergeev, A. G.; Webb, J. D.; Hartwig, J. F. A Heterogeneous Nickel Catalyst for the Hydrogenolysis of Aryl Ethers without Arene Hydrogenation. *J. Am. Chem. Soc.* **2012**, *134*, 20226–20229. https://doi.org/10.1021/ja3085912.

12. Gao, F.; Webb, J. D.; Hartwig, J. F. Chemo- and Regioselective Hydrogenolysis of Diaryl Ether C–O Bonds by a Robust Heterogeneous Ni/C Catalyst: Applications to the Cleavage of Complex Lignin-Related Fragments. *Angew. Chem. Int. Ed.* **2016**, *55*, 1474–1478. https://doi.org/10.1002/anie.201509133.
13. Leonard, D. N.; Franzen, S. Is $Pd_2(DBA)_3$ a Feasible Precursor for the Synthesis of Pd Nanoparticles? *J. Phys. Chem. C* **2009**, *113*, 12706–12714. https://pubs.acs.org/doi/10.1021/jp903417r.
14. Noh, J. S.; Schwarz, J. A. Effect of $HNO_3$ Treatment on the Surface Acidity of Activated Carbons. *Carbon* **1990**, *28* (5), 675–682. https://doi.org/10.1016/0008-6223(90)90069-B.
15. El-Hendawy, A. A. A. Influence of $HNO_3$ Oxidation on the Structure and Adsorptive Properties of Corncob-Based Activated Carbon. *Carbon* **2003**, *41* (4), 713–722. https://doi.org/10.1016/S0008-6223(03)00029-0.
16. ShamsiJazeyi, H.; Kaghazchi, T. Investigation of nitric acid treatment of activated carbon for enhanced aqueous mercury removal. *J. Ind. Eng. Chem.,* **2010**, *16*, 852–858. https://doi.org/10.1016/j.jiec.2010.03.012.
17. Takaoka, M.; Yokokawa, H.; Takeda, N. The effect of treatment of activated carbon by $H_2O_2$ or $HNO_3$ on the decomposition of pentachlorobenzene. *App. Catal. B: Env.* **2007**, *74*, 179–186. https://doi.org/10.1016/j.apcatb.2007.02.009.
18. Liang, Z.; Guo, S.; Dong, H.; Li, Z.; Liu, X.; Li, X.; Kang, H.; Zhang, L.; Yuan, L.; Zhao, L. Modification of Activated Carbon and Its Application in Selective Hydrogenation of Naphthalene. *ACS Omega* **2022**, *7*, 38550–38560. https://doi.org/10.1021/acsomega.2c03914.

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