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Study of Electron Beam Irradiated Palladium on Carbon Catalysts for Transfer Hydrogenation Reactions of Nitroarenes Compounds

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Palladium-catalyzed hydrogenation is considered a crucial stage in the entire synthesis of difficult natural products as well as a crucial step in the manufacturing of fine compounds used in pharmaceuticals. When it comes to the reaction rate and simplicity of work-up, using Pd/C as heterogeneous catalyst is one of the best choice for process efficiency. In this study, nitroarenes compounds *viz.* 3-bromo nitrobenzene, 4-fluoro nitrobenzene, 3-methyl nitrobenzene, 4-hydroxy nitrobenzene reduced by using macro 10% Pd/C and micro 10% Pd/C to 3-bromo aniline, 4-fluoro aniline, 3-methyl aniline, 4-hydroxy aniline respectively and verified from ^{1}H NMR studies. The reduction reactions were similar conditions using electron beam irradiated 250 kGy macro and micro 10% Pd/C catalyst. The effectiveness of commercial sources of palladium on carbon (Pd/C) varies widely, leading to the appreciable variations in the reaction times. The decrease in reaction time has been attributed to the higher dispersion of Pd particles upon irradiation. The physico-chemical characteristics of effective hydrogenation catalysts were determined to be: (i) small Pd particle size and (ii) homogeneous distribution of Pd on the carbon support. With no significant loss of catalytic activity, the electron beam-irradiated catalyst can be used again for five runs. These days, chemists can determine as well as forecast the effectiveness of catalysts before investing time and money in expensive synthetic materials.

Keywords: Heterogeneous catalysts, Catalytic activity, Hydrogenation, Nitroarenes.

INTRODUCTION

The process of catalysis is one of the key components that support green chemistry. Innovative catalytic systems are paving the way for environmentally friendly production which is also economically viable [1]. Hence, the development of newer synthetic techniques utilizing cost-effective environmentally friendly catalysts results in time and energy savings, thereby enhancing the efficiency of chemical synthesis processes [2].

Heterogeneous catalysts have garnered significant attention in both scientific researchers and the chemical manufacturing sector [3,4]. The development of solid catalysts that promote reduction reactions with high activity and selectivity remains an active area of research. Reduction such as hydrogenation allows the controlled addition of hydrogen to organic substrates. Performing these transformations heterogeneously provides significant advantages over homogeneous catalysis in terms of catalyst separation from products, potential for recovery and reuse and simplified purification.

According to 2020, over 80% of all chemical manufacturing processes utilize heterogeneous catalysts at some stage due to their economic and environmental benefits [5]. Heterogeneous catalysts enable reactions to occur faster, more selectively and at lower temperatures than non-catalyzed processes. This improves energy efficiency and product yield. Unlike homogeneous catalysts, heterogeneous catalysts exist in a different phase from the reactants, which simplifies separation and recycling. The heterogeneous catalysts market is expected to rise from its 2020 valuation of $33.9 billions to $35 billions at rate of 4.4% by 2027, underscoring the increasing significance of this subject [6]. The last stage in difficult complete synthesis to produce the intended target chemical is frequently palladium catalyzed hydrogenation.

Researchers in the field of heterogeneous catalysis exhibit significant interest in novel catalyst activation methods such as microwave irradiation and plasma treatment. These non-traditional methods enable the formation of new active sites on the surface of the catalyst, which display increased activity.

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Irradiating catalysts with an electron beam is an efficient method [7-9]. Electron beam irradiation has emerged as a viable technique in the pharmaceutical sector for improving the structure as well as the properties of heterogeneous catalysts [10]. The properties can be considerably enhanced with catalysts by high-energy beams. The chemical bonds are activated due to several events occurring under the impact of an accelerated electron beam on the surface and within the depth of catalyst. The combined physical and chemical impacts of the enhanced electron flux may lead to the development of new types of active centers [11,12].

Examining the effects of an electron beam on the structure and activity of Pd/C catalysts during hydrogenation is the objective of this work. Herein, we present an easy-to-follow method for employing accelerated electrons to boost the 10% Pd/C catalytic performance. The effort of the irradiation Pd/C on the catalytic properties by the example of the nitroarenes reduction. To ascertain the characteristics of the high performance catalysts, a number of methods like N_2 adsorption and desorption (BET and Langmuir), X-ray photoelectron spectroscopy (XPS), high-resolution transmission electron microscopy (HRTEM) and X-ray diffraction (XRD) analysis were used.

EXPERIMENTAL

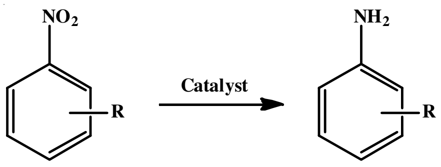
3-Bromo nitrobenzene and 4-fluoro nitrobenzene were obtained from Sisco Research Laboratory, India and 3-methyl nitrobenzene, 4-hydroxy nitrobenzene were procured from Avra Chemical Pvt. Ltd. Methanol was sourced from Aldrich Chemical Company (USA). Every reagent used in this experiment was of analytical grade, requiring no extra purification. Micro Pd/C from SigmaAldrich and macro 10% Pd/C from were procured from Hindustan Platinum Ltd., Mumbai, India. Using an RF Linac operationed at the Electron Beam Centre, BARC, Navi Mumbai, India both the macro and micro 10% Pd/C catalysts were exposed to an electron beam with a 10 MeV energy. The catalytic hydrogenation apparatus, a low-pressure shaker-type SUPERFIT Model SS316, was utilized to conduct hydrogenation reactions. A 0.2 mm and 0.5 mm Kieselgel G F_{254} pre-coated plates (Merck, USA) were utilized for analytical as well as preparative thin-layer chromatography, respectively and the UV light was used to visualize the spots. At 300 MHz, proton NMR spectra were captured using a Bruker 300 5 mm probe.

Catalyst pre-treatment: A 25 mL round bottom flask containing all varieties of 10% Pd/C (0.3 g, Macro, Micro, 250 kGy macro and 250 kGy Micro) was filled with the mixture and suspended in a 6 mL DMF/H_2O mixture (70:30 v/v). The solution was then acidified by adding 800 µL of HCl (37%, pH 2-3), either in the presence of hydrogen gas or not, stirring vigorously (400 rpm) for approximately 30 min. The utilization of ninhydrin staining verified the existence of dimethylamine. By filtration, the treated Pd/C catalyst was separated once again. The hydrogenation reaction was then started immediately with the wet catalyst [13].

Optimized procedure for hydrogenation: The treated catalyst of macro 10% Pd/C (0.3 g) was added to a solution of nitroarenes derivatives (2 g) dissolved in a methanol solution (40 mL). The reaction was placed in a Parr hydrogenator vessel flushed with nitrogen at 5 atm with vigorous stirring (400 rpm) and a temperature of 26-28 ºC. Using normal phase thin layer chromatography (TLC) with a heptane:ethyl acetate combination of 7:3, the reaction's progress was observed. After the reaction was finished, the mixture was filtered using a celite stopper and then concentrated in a vacuum using a Buchi Rotary evaporator. By employing *n*-heptane and ethyl acetate as an eluent in column chromatography on silica gel, the crude product was refined. The reactions were conducted under similar conditions using 250 kGy 10% Pd/C (irradiated). Also, the similar reactions were carried out usingmicro 10% Pd/C and 250 kGy 10% Pd/C (irradiated) catalyst.

Palladium on carbon characterization: The images were taken with a JEOL JEM-2100F transmission electron microscope. Images captured by HRTEM were obtained at 200 kV acceleration voltage. The produced samples were subjected to a Cu-*K*α radiation X-ray diffractometer (XRD, Bruker D8 Advance) with a scanning step of 0.02º to analyze their crystal structure within the 5-90º range. For ascertaining the chemical condition as well as the surface elemental composition of the samples produced, an XPS equipped with a monochromatic Al-*K*α source (hν = 1486.6 eV) was utilized. All the binding energies were calibrated with reference to the C 1s hydrocarbon peak at 284.60 eV. On the [SUPRA 55]-Carl Zeiss, Upright Microscope, BX 51, Olympus, the nitrogen sorption measurement was performed at liquid nitrogen temperature.

To investigate the catalytic efficacy of 250 kGy irradiated macro 10% Pd/C and 250 kGy irradiated micro 10% Pd/C, the reduction of 3-bromo nitrobenzene, 4-fluoro nitrobenzene, 3-methyl nitrobenzene and 4-hydroxy nitrobenzene were carried out (**Scheme-I**). The efficiency of the optimized catalysts in terms of time taken is shown in Table-1.



R = 3-Bromo, 4-fluoro, 3-methyl, 4-hydroxy

Scheme-I

TABLE-1
TIME TAKEN DATA FOR THE CATALYTIC REDUCTION OF SUBSTITUTED NITROBENZENE TO SUBSTITUTED ANILINE

Catalyst used	Time taken (h)			
	3-Bromo aniline	4-Fluoro aniline	3-Methyl aniline	4-Hydroxy aniline
Macro 10% Pd/C	12	10	11	14
Micro 10% Pd/C	10	8	10	12
250 kGy macro 10% Pd/C	2.5	1.5	3	3.5
250 kGy micro 10% Pd/C	2	1	2	2.5

RESULTS AND DISCUSSION

The structures of the product were characterized by proton NMR spectroscopy. In ^{1}H NMR of 3-bromo aniline, the peaks were observed at δ (ppm): 7.01-6.55 (q, 4H)-aromatic proton, 3.67 (s, 2H)-NH_2; for 4-fluoro bromoaniline: 6.90-6.23 (q, 4H)-aromatic,6.87-6.85 (t, 1H), 6.37 (s, 1H), 6.32-6.29 (m, 2H)], 4.90 (s, 2H)-NH_2, 2.13 (s, 3H)-CH_3; for 3-methyl aniline: 6.90-6.23 (q, 4H)-aromatic, 4.90 (s, 2H)-NH_2, 2.13 (s, 3H)-CH_3; for 4-hydroxy aniline: 8.31 (br, s, 1H)-OH, 6.49-6.40 (q, 4H)-aromatic, 4.35 (br, s, 2H)-NH_2.

Characterization of palladium on carbon catalysts:

XRD spectral studies: Diffraction peaks at 2θ angles of 33.4º, 34.4º, 42.8º and 55.5º were obtained by XRD analysis of the macro 10% Pd/C and micro 10% Pd/C and they are attributed to the (002), (101), (110) and (112) planes of Pd [14,15]. The presence of palladium was verified based on the observed peaks at 2θ angles of 40.2º, 46.6º and 68.3º, which matched the (111), (200) and (220) crystallographic planes of cubic Pd [16,17]. While the XRD pattern for the 250 kGy macro Pd/C and 250 kGy micro Pd/C show clear peaks at 33.4º, 34.5º, 42.8º and 55.5º for irradiated Pd/C (Fig. 1). The intensities of the XRD peaks for the irradiated Pd/C catalyst exhibited a substantial augmentation in comparison to the macro Pd/C and micro Pd/C catalysts (which were not irradiated), thus proving the superior dispersion of Pd/C catalyst. Furthermore, a large peak was observed in all catalysts at 2θ of around 25º. This peak was identified as the (002) diffraction planes of graphite microcrystals in the disordered carbon [18,19].

TEM: The most potent catalysts 250 kGy macro 10% Pd/C and 250 kGy micro 10% Pd/C indicated that Pd particles uniformly dispersed on carbon with a mean size of < 10 nm (Fig. 2). Numerous active sites may be found in the corners as well as edges of nanoparticles with small size, which is in line with the finding of improved catalytic activity during the reduction (hydrogenation) processes.

The HRTEM images of the macro 10% Pd/C and micro 10% Pd/C reveal the presence of two lattice fringes with a separation of 0.224. These fringes can be attributed to the (111) crystalline plane of palladium. The 250 kGy macro 10% Pd/C and 250 kGy micro 10% Pd/C (irradiated) catalysts showed the small particle sizes because of greater size distribution as well as severe particle agglomeration. This correlates with the shorter reaction times and more beneficial for the catalytic process.

XPS spectral studies: In order to examine the catalysts' elemental components and states (Fig. 3), high-resolution XPS was used. The binding energies of 342.5 eV as well as 336.5 have been exhibited by all the catalysts, which was in line with the metallic Pd $3d_{5/2}$ and $3d_{3/2}$ peaks [20-22].

BET studies: The Brunauer-Emmett-Teller (BET) particular surface areas of the catalyst macro 10% Pd/C, micro 10% Pd/C, 250 kGy irradiated macro 10% Pd/C and 250 kGy irradiated micro 10% Pd/C were found to be 572.9564, 702.6882, 807.9050 and 991.8263 m^2/g, respectively.

Langmuir analysis: The Langmuir-specific surface areas of catalyst macro 10% Pd/C, micro 10% Pd/C, 250 kGy irradiated macro 10% Pd/C and 250 kGy irradiated micro 10% Pd/C were 862.8573, 1059.9547, 1200.4033 and 1482.0662 m^2/g, respectively. The reduction of nitroarenes derivatives to aniline derivatives may therefore have better catalytic activity, as evidenced by the specific surface area results of 250 kGy macro and micro 10% Pd/C catalyst. Additionally, the specific surface area of catalysts clearly suggests that the 250 kGy macro and micro 10% Pd/C have many active sites on their surface, which contributes to their catalytic effectiveness.

Catalyst recycling studies: Using 3-bromo nitrobenzene as model substrate, we successfully conducted the recycling study by centrifuging the Pd/C catalyst to separate it again. Following five cycles, yields varied from 94 to 87% with no significant of loss of activity or deactivation of catalyst (Fig. 4).

The XRD as well as TEM analyses of the pretreatment recycled catalyst were subsequently performed XRD verified that Pd was present in catalyst and it was found that its composition had not changed substantially (Fig. 5). Following five cycles, the tiny particles of palladium remained equally distributed, exhibiting no observable ageing or agglomeration growth,

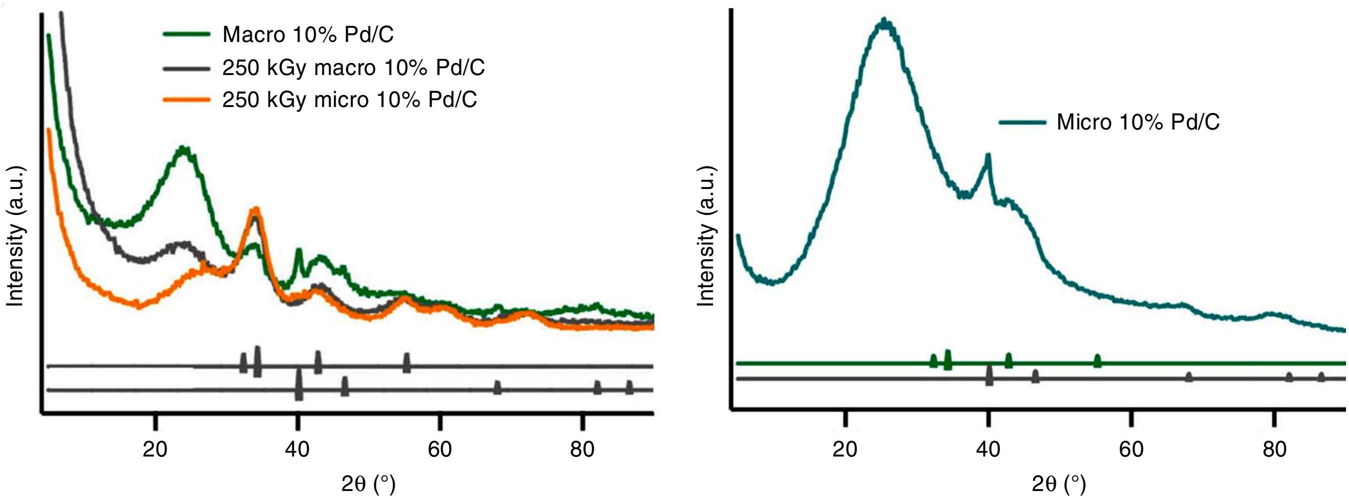


Fig. 1. XRD patterns of the 10% Pd/C

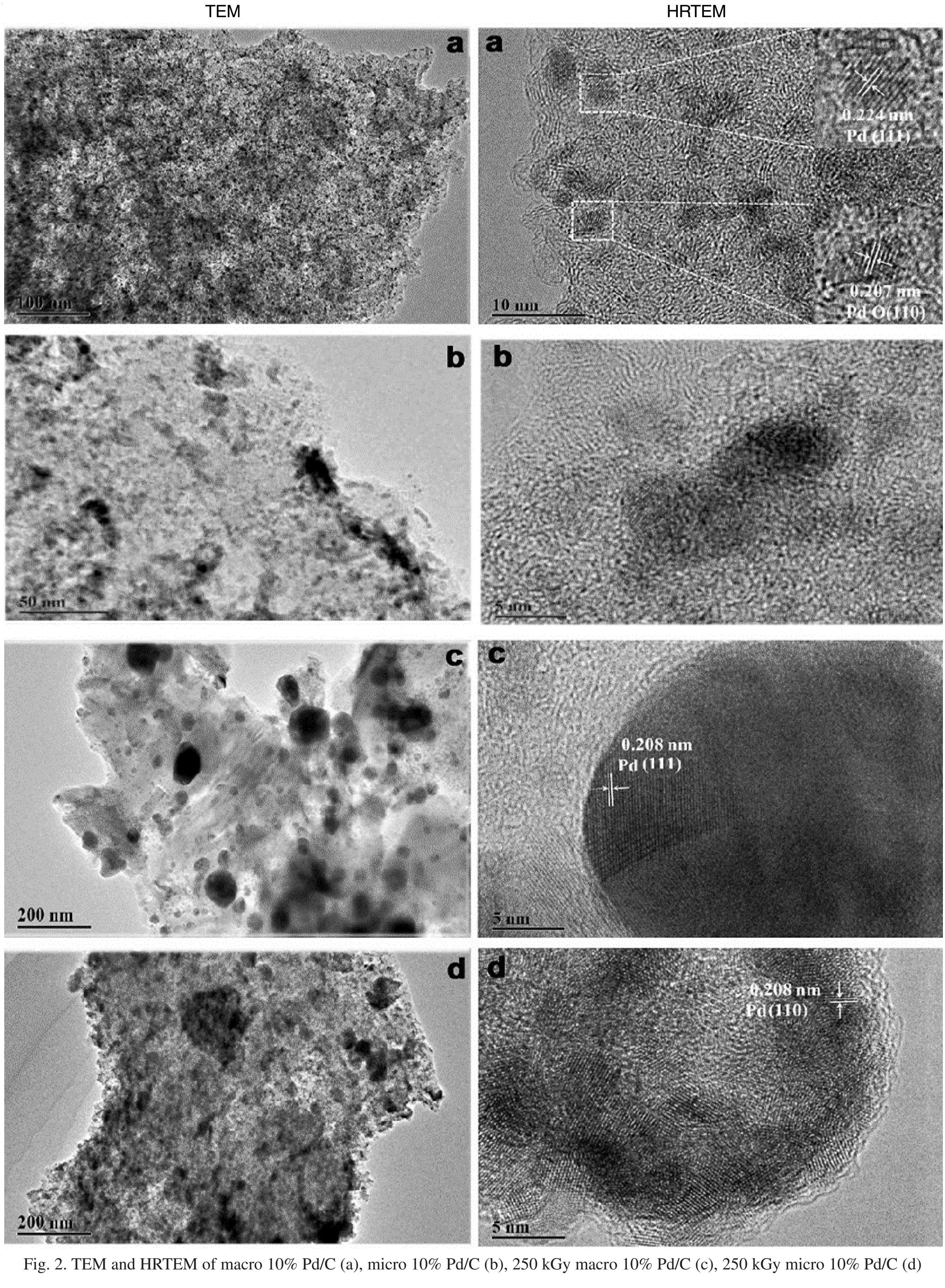


Fig. 2. TEM and HRTEM of macro 10% Pd/C (a), micro 10% Pd/C (b), 250 kGy macro 10% Pd/C (c), 250 kGy micro 10% Pd/C (d)

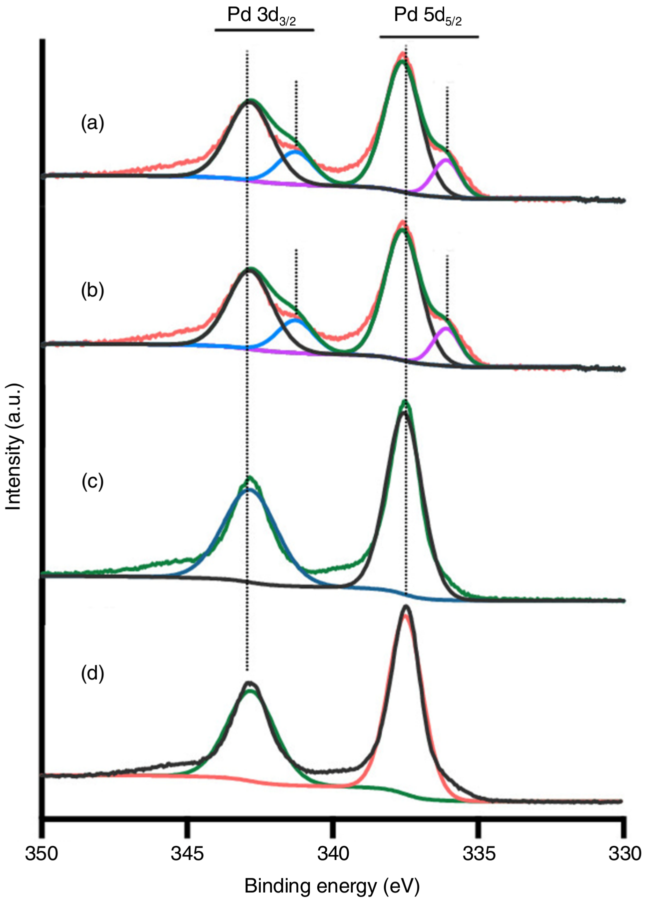


Fig. 3. XPS for Pd 3d electrons of macro 10% Pd/C (a), micro 10% Pd/C (b), 250 kGy macro 10% Pd/C (c), 250 kGy micro 10% Pd/C (d)

as indicated by TEM image (Fig. 6a) indicating that the Pd/C catalyst surface chemistry is not considerably changed by the pre-treatment procedure.

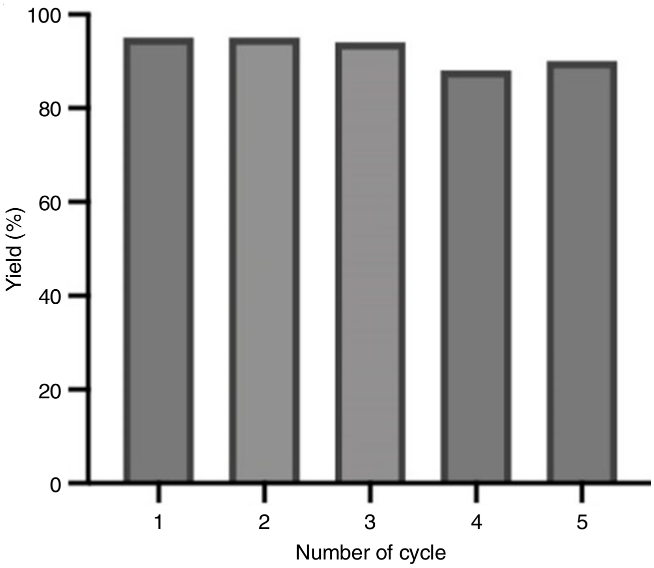


Fig. 4. Catalyst recycling of the pretreated catalyst

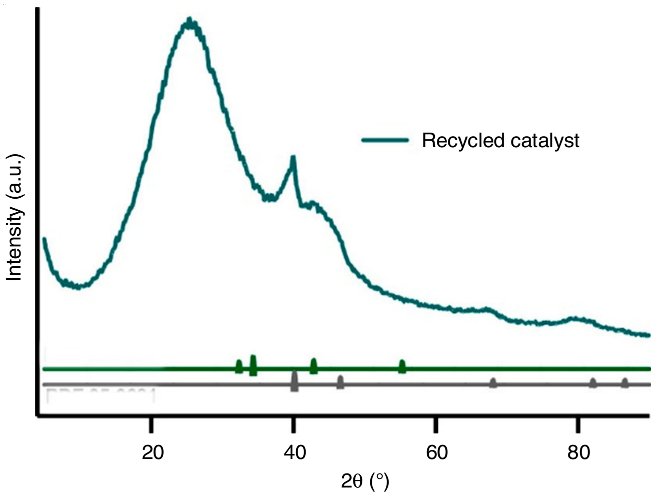


Fig. 5. XRD patterns of the recycled catalyst 10% Pd/C

Conclusion

An efficient and considerable variability of four types of catalyst *viz.* macro 10% Pd/C, micro 10% Pd/C, 250 kGy irradiated macro 10% Pd/C and 250 kGy irradiated micro 10% Pd/C were investigated for the transfer hydrogenation reactions of nitroarenes compounds. The most efficient 250 kGy macro

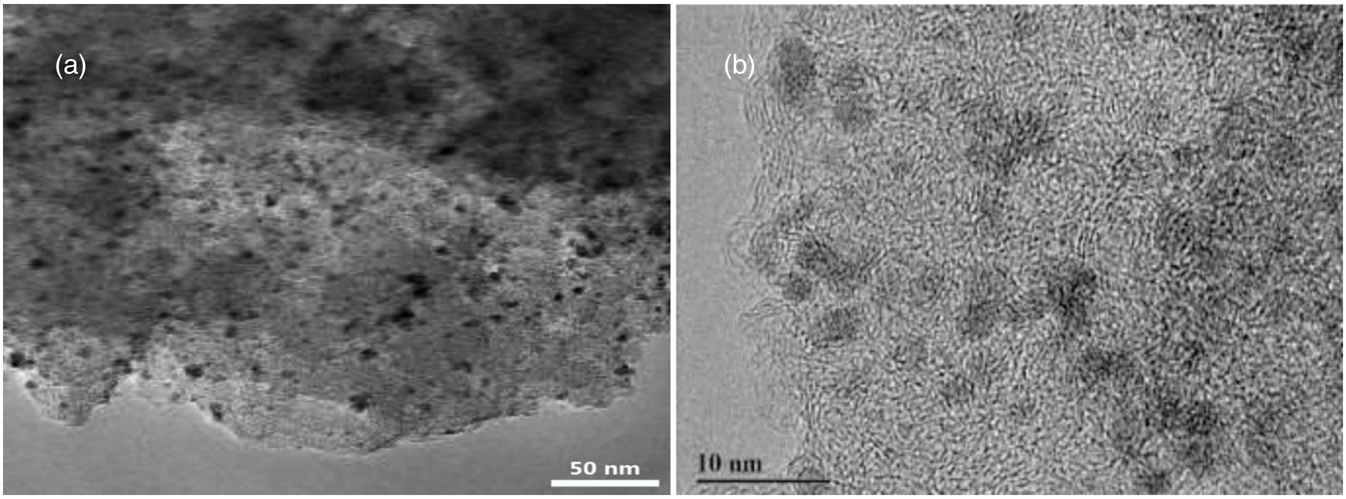


Fig. 6. TEM and HRTEM of the recycled catalyst 10% Pd/C

10% Pd/C and 250 kGy micro 10% Pd/C for hydrogenating nitroarenes were found to have the shortest reaction duration and the lowest amount of saturated impurities in the model systems. Three important conclusions emerged from the study: (i) tiny Pd particle size inefficient Pd/C catalysts; (ii) homogenous distribution of Pd on the carbon support; and (iii) no loss of activity after multiple cycles. It is suggested that the Pd/C catalyst that has been exposed to electron beam radiation is a good indicator of catalytic performance.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. P.T. Anastas, M.M. Kirchhoff and T.C. Williamson, *Appl. Catal. A Gen.*, **221**, 3 (2001); https://doi.org/10.1016/S0926-860X(01)00793-1
2. C. Rizzo, A. Pace, I. Pibiri, S. Buscemi and A.P. Piccionello, *ChemSusChem*, **17**, e202301604 (2024); https://doi.org/10.1002/cssc.202301604
3. X. Liu and H.-J. Peng, *Engineering*, **39**, 25 (2024); https://doi.org/10.1016/j.eng.2023.07.021
4. K.F. Kalz, R. Kraehnert, M. Dvoyashkin, R. Dittmeyer, R. Gläser, U. Krewer, K. Reuter and J.-D. Grunwaldt, *ChemCatChem*, **9**, 17 (2017); https://doi.org/10.1002/cctc.201600996
5. R. Schlogl, *Angew. Chem. Int. Ed.*, **54**, 3465 (2015); https://doi.org/10.1002/anie.201410738
6. X. Hu and A.C.K. Yip, *Front. Catal.*, **1**, 667675 (2021); https://doi.org/10.3389/fctls.2021.667675
7. Z.-Y. Yuan, W. Zhou, V. Parvulescu and B.-L. Su, *J. Electron Spectrosc. Relat. Phenom.*, **129**, 189 (2003); https://doi.org/10.1016/S0368-2048(03)00068-9
8. J. Jun, J.-C. Kim, J.-H. Shin, K.-W. Lee and Y.S. Baek, *Radiat. Phys. Chem.*, **71**, 1095 (2004); https://doi.org/10.1016/j.radphyschem.2003.07.006
9. V. Múèka, B. Otáhal and R. Silber, *Radiat. Phys. Chem.*, **65**, 177 (2002); https://doi.org/10.1016/S0969-806X(02)00191-3
10. W. Wesch and E. Wendler, Ion Beam Modification of Solids; In Ion-Solid Interaction and Radiation Damage, Springer Series in Surface Sciences, Springer International Publishing: Cham, Switzerland, vol. 61 (2016).
11. P.V. Markov, A.S. Pribytkov, N.N. Tolkachev, A.Y. Stakheev, L.M. Kustov, V.N. Golubeva and A.V. Tel'nov, *Kinet. Catal.*, **49**, 765 (2008); https://doi.org/10.1134/S0023158408050236
12. A.S. Pribytkov, O.P. Tkachenko, A.Y. Stakheev, K.V. Klementiev, W. Grunert, M.W.E. van den Berg, L.M. Kustov, V.N. Golubeva and A.V. Tel'nov, *Mendeleev Commun.*, **16**, 254 (2006); https://doi.org/10.1070/MC2006v016n05ABEH002371
13. C. Crawford and S. Oscarson, *Eur. J. Org. Chem.*, **2020**, 3332 (2020); https://doi.org/10.1002/ejoc.202000401
14. W. Hu, G.X. Li, J.J. Chen, F.J. Huang, Y. Wu, S.D. Yuan, L. Zhong and Y.Q. Chen, *Chem. Commun.*, **53**, 6160 (2017); https://doi.org/10.1039/C7CC01997A
15. H.J. Cho, V.T. Chen, S. Qiao, W.-T. Koo, R.M. Penner and I.-D. Kim, *ACS Sens.*, **3**, 2152 (2018); https://doi.org/10.1021/acssensors.8b00714
16. J. Zhao, W. Jing, T. Tan, X. Liu, Y. Kang and W. Wang, *New J. Chem.*, **44**, 4604 (2020); https://doi.org/10.1039/C9NJ06259A
17. P. Xi, F. Chen, G. Xie, C. Ma, H. Liu, C. Shao, J. Wang, Z. Xu, X. Xu and Z. Zeng, *Nanoscale*, **4**, 5597 (2012); https://doi.org/10.1039/c2nr31010d
18. L. Lan, F. Du and C. Xia, *RSC Adv.*, **6**, 109023 (2016); https://doi.org/10.1039/C6RA21213A
19. W. Xu, C. Lv, Y. Zou, J. Ren, X. She, Y. Zhu, Y. Zhang, S. Chen, X. Yang, T. Zhan, J. Sun and D. Yang, *J. Power Sources*, **442**, 227184 (2019); https://doi.org/10.1016/j.jpowsour.2019.227184
20. S. Meher and R.K. Rana, *Green Chem.*, **21**, 2494 (2019); https://doi.org/10.1039/C9GC00116F
21. J. Lv, S. Wu, Z. Tian, Y. Ye, J. Liu and C. Liang, *J. Mater. Chem. A Mater. Energy Sustain.*, **7**, 12627 (2019); https://doi.org/10.1039/C9TA02045D
22. L. Han, Q. Li, S. Chen, W. Xie, W. Bao, L. Chang and J. Wang, *Sci. Rep.*, **7**, 7448 (2017); https://doi.org/10.1038/s41598-017-07802-8