CATALYTIC ACTIVITY OF ELECTRON BEAM IRRADIATED Pd/C ON 2-METHYL NITRO BENZENE

Abstract

In this study nitro compounds viz., 2 – methyl nitro benzene was reduced by 10% Pd/C (50% wet) to 2 – methyl aniline and it is confirmed from MASS and NMR studies. The product yield was 70%. The hydrogenation was complete in 9.30 h. The catalysts were then irradiated by electron beam to various dosages from 0 kGy, 150 kGy, 200 kGy and 250 kGy using Microtron & RF Linac. The reduction reactions were conducted under similar conditions using irradiated 10% Pd/C samples. Now the product yield was 93%. The hydrogenation was fast and completed within 2 h 30 min. With the electron beam irradiated catalyst, the reaction time has decreased by 15 -70% and the completion of reaction is in the order of dosages 250 kGy > 200 kGy >150 kGy > 0 kGy. The fastness of reduction reaction in both the steps upon irradiation could be attributed to the increase in surface area. The studies were also conducted using Micro powder form of Pd/C catalyst both in non-irradiated and in the irradiated form. The decrease in reaction time and the increase in product yield have been attributed to higher dispersion of Pd particles upon irradiation.

Keywords: Electron beam irradiation, Pd/C catalyst, nitro compounds, reduction

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I. INTRODUCTION

Uniformity of the catalyst surface plays a major role in effecting selectivity or specificity. If one were able to treat the solid surface appropriately, it is possible to control the progress and path of the reaction in such a manner to achieve the desired molecular conversion, as the very reaction primarily depends on the micro structural features of the catalyst solid surface.

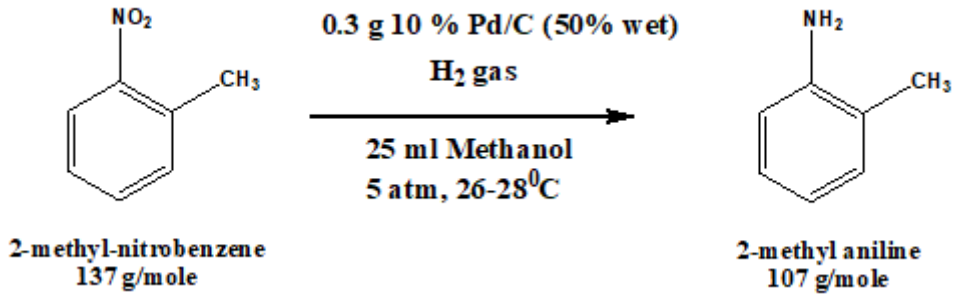
The present study aims at developing the electron beam treated heterogeneous catalysts suitable for synthesizing organic compounds. The catalyst selected is palladium adsorbed on carbon (solid and micro powder form). Organic reaction involving palladium catalysed reduction of 2 – methyl nitro benzene was studied. The same reactions were carried out using electron beam irradiated catalysts and their catalytic efficiencies were compared. The surface morphological studies of the catalysts were also undertaken.

II. EXPERIMENTAL

1. **Chemicals and Instruments:** The chemicals 2 – methyl nitro benzene, methanol were procured form Aldrich Chemical Company (USA), 10% Pd/C from Hindustan Platinum Limited, Mumbai and Micro Pd/C from Sigma Aldrich. All the chemicals were of analytical grade and used as received .Pd/C (10%) samples were irradiated by electron beam of 8 MeV using Microtron at the Microtron Centre of Department of Atomic Energy, Mangalore University. Also, Pd/C (10%) and Micro Pd/C catalysts were irradiated by electron beam of 10 MeV using RF Linac operational at the Electron Beam Centre, BARC, Navi, Mumbai. Hydrogenation reactions were carried out using Catalytic hydrogenation apparatus Low Pressure Shaker Type SUPERFIT Model SS316. Thin layer Chromatography was performed on pre-coated Silica gel plates (Merck F254, 0.2 mm thickness). The NMR spectra for organic compounds were recorded on Bruker 400 MHz FT-NMR spectrometer in $CDCl_3$ Solution. The surface areas of catalysts were measured with a Micromeritises Tristar 3000 model, (USA make). BET and Langmuir Surface area analysis are based on adsorption of N_2. Scanning Electron Microscopy images of catalysts surface were taken with a [SUPRA 55]-CARL ZEISS, (Germany make) and UPRIGHT MICROSCOPE, BX 51, OLYMPUS, (Japan make). The images were registered under magnifications 1 KX and 250 KX . EDS studies were undertaken using Oxford Instruments.

2. **Catalytic Reactions Studied**

Reduction of 2-methyl-nitrobenzene: A solution of 2 – methyl nitrobenzene (2 g) in methanol (40 mL) and 10% Pd/C (0.3 g; 50% wet) were charged into a Parr hydrogenator vessel and flushed with nitrogen. Hydrogen was passed into the vessel at a pressure of 5 atm and temperature of 26-28 ^{0}C.The progress of the reaction was monitored by TLC for every half an hour till the completion of the reaction.



The course of the reaction was monitored by TLC using a mixture of heptane and ethyl acetate (7:3) as mobile phase and silica gel coated alumina plate as Stationary Phase. After completion of the reaction, the reaction mixture was filtered and washed with methanol. The filtrate was concentrated using a Buchi Rotary evaporator. The Product 2-methyl aniline was obtained. The reactions were conducted under similar conditions using 150 kGy, 200 kGy, 250 kGy irradiated 10% Pd/C samples. Also similar reactions were carried out using Micro Pd/C catalyst of both non-irradiated and irradiated forms (250 kGy). The results are tabulated in Table 1 & 2

Table 1: Reduction of 2-methyl-nitrobenzene to 2-methyl aniline

2-methyl-nitrobenzene taken (g)	Dosage of e^- beam Micro 10% Pd/C (50%)wet in kGy	Time Taken
2	0	7 h
2	150	4 h 30 min
2	200	3 h 30 min
2	250	2 h 30 min

Table 2: Reduction of 2-methyl-nitrobenzene to 2-methyl aniline

2-methyl-nitrobenzene taken (g)	Dosage of e^- beam Macro 10% Pd/C (50%)wet in kGy	Time Taken
2	0	9 h
2	150	7 h
2	200	6 h
2	250	4 h

III. RESULTS AND DISCUSSION

1. **NMR Spectroscopy:** The structure of the Product 2-methyl aniline was characterized by ^{1}H NMR spectroscopy. The multiplets between δ 6.48 – 7.24 ppm show the presence of aromatic protons. A signal at δ 3.58 ppm shows the presence of -NH_2 protons. At δ 2.00 – 2.32 ppm reveals –CH_3 protons. (Figure 1).

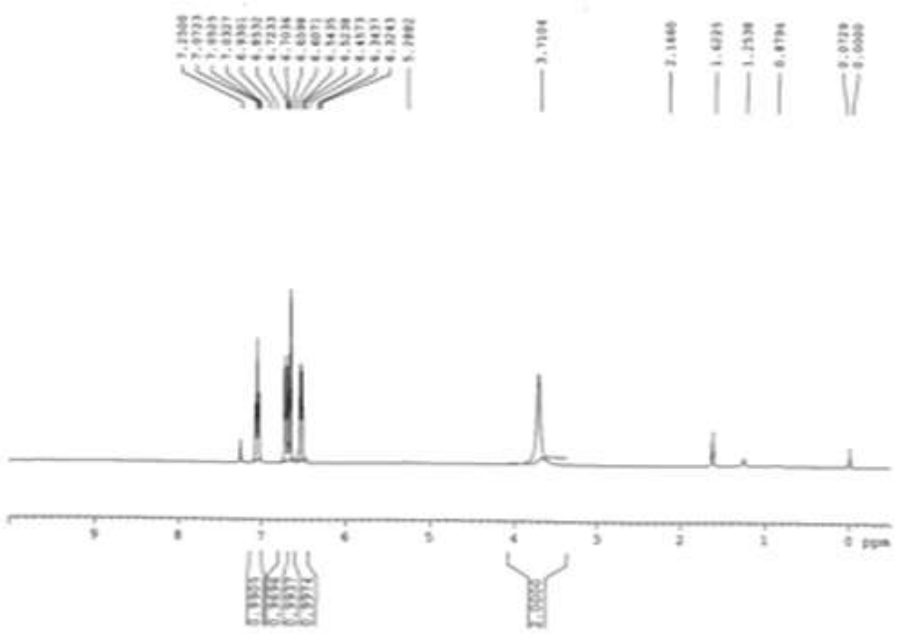


Figure 1

2. **MASS Spectroscopy:** The molecular mass of the product 2-methyl aniline was characterized by MASS spectroscopy. The molecular mass in positive scan is *m/z* **108.2** (Figure 2).

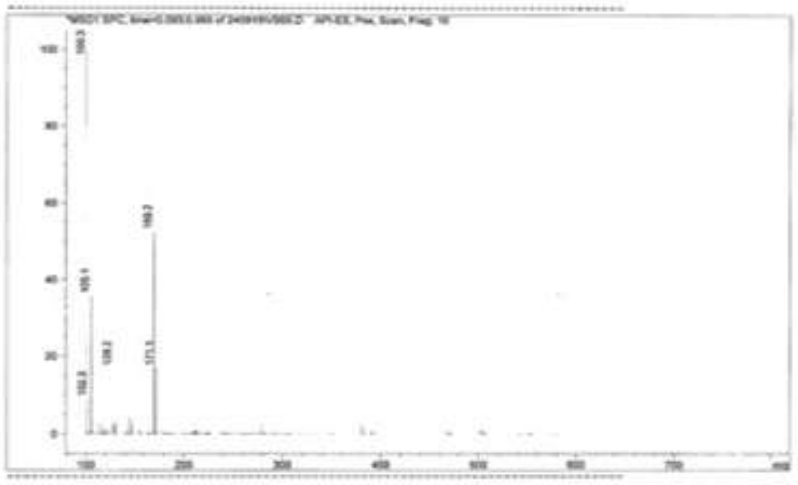


Figure 2

3. **Surface Area Measurements:** The surface area measured by using low pressure N_2 BET surface Analyzer. The surface area of Pd/C catalysts, both irradiated and non-irradiated, are given in Table 3.

Table 3: Surface Area

Sl. No	Catalyst Used	BET surf area m^2/g	Langmuir Surf area m^2/g
1	Macro Pd/C	572.9564	862.8573
2	Macro Pd/C 150 kGy Irradiated	621.1100	939.8726
3	Macro Pd/C 200 kGy Irradiated	743.1941	1104.90
4	Macro Pd/C 250 kGy Irradiated	807.9050	1200.4033
5	Micro powder Pd/C	702.6682	1059.9547
6	Micro powder Pd/C 150 kGy	838.4344	1268.3614
7	Micro powder Pd/C 200 kGy	903.9725	1392.1153
8	Micro powder Pd/C 250 kGy	991.8263	1482.0662

It was observed that the surface area of the irradiated catalysts has increased and it was higher than the non-irradiated ones revealing the dispersion of palladium particles

4. **Scanning Electron Microscopy:** The SEM pictures (Figure 3 - 10) reveal that Pd/C agglomerates are broken into small size particles leading to the increase in surface area. Particle size of Pd/C decreases with the increasing dosages of electron beam irradiation.

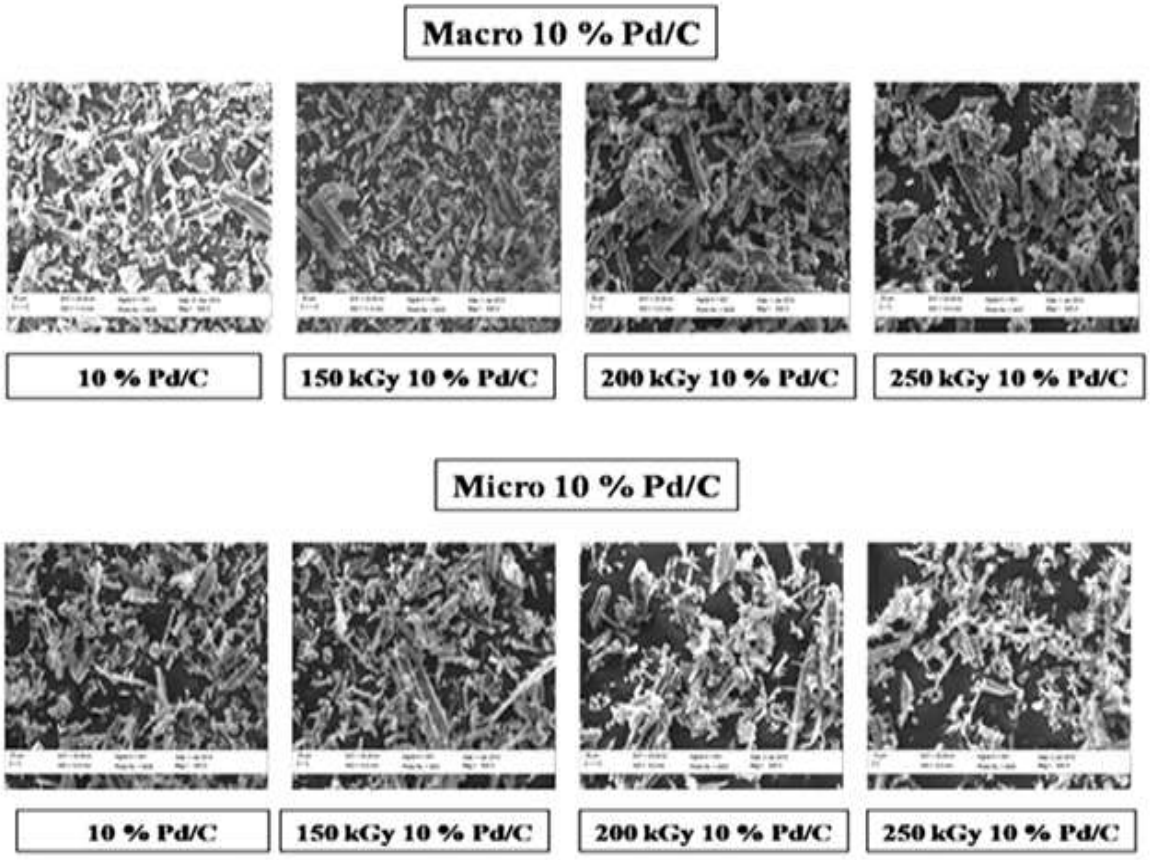


Figure 3 – 10: SEM Images of 10% Pd/C

5. **EDS Studies:** EDS studies (Figure 11 – 18) reveal that Atomic percentage of palladium in 10% Pd/C (50% wet) is 79.91% and the micro powder Pd/C is 94.35%.

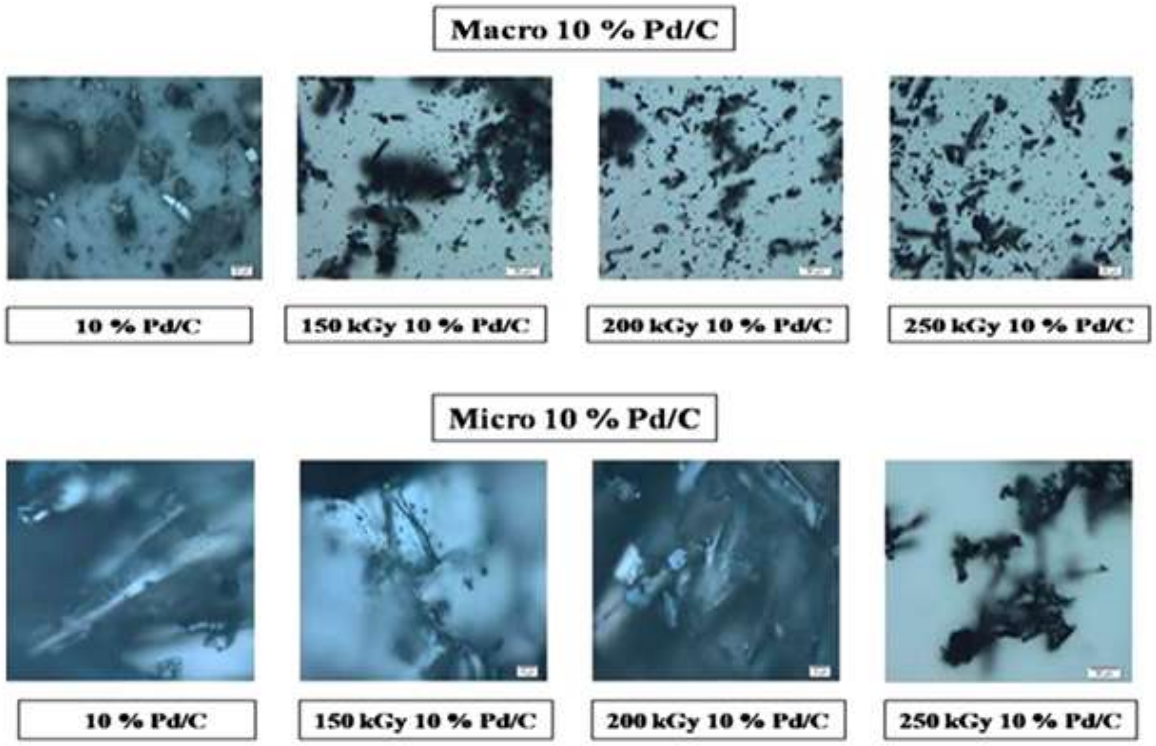


Figure 11 - 18

6. **Catalytic Studies:** All these reduction reactions using various electron beam treated Pd/C catalysts showed, enhanced catalytic activity. Upon repeating the same reactions after 3, 6 and 9 months using the irradiated Pd/C catalyst, the reaction efficiency with respect to product yield and reaction time for hydrogenation were found to be maintained while comparing with the freshly irradiated catalysts. The irradiated catalyst efficiency has been found to be unaltered for nearly one year. So this study enhances the greener approaches of Pd/C catalyst.

IV. CONCLUSION

The reaction time using Micro Pd/C is in the order of 250 kGy > 200 kGy > 150 kGy> un-irradiated Micro Pd/C (0 kGy). The rate of the reaction using 10% Pd/C is in the order of 250kGy > 200 kGy > 150 kGy > un-irradiated 10% Pd/C (0 kGy). The results show that with the increase in dosage the reaction time is found to decrease progressively with a net decrease of 55 -75% relative to that of the original system without irradiation. The reaction time using Micro Pd/C is found to be lesser than that of 10% Pd/C. This may be attributed to the high BET surface area and atomic percentage of Micro Pd/C. XPS data for the Pd/C catalyst suggests that, after irradiation with high-energy electrons, the metal particles are stabilized on the surface of the carbon support, their degree of dispersion is increased, and their sintering is suppressed. The increase in BET and Langmuir surface area of the irradiated catalysts confirms the increase in the degree of dispersion of Pd particles which

contributes to the enhanced catalytic activity. This study enhances the efficient usage of Pd/C catalyst in a green manner.

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