

Modifying the Catalyst by Energising through Electron Beam Irradiation for effecting Organic Transformations in Ketones

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Abstract

The effect of electron beam irradiation on the catalyst, 10 % Pd./C in wet and micro powder form in effecting the heterogeneous catalysis reactions like hydrogenation of Alkyl aryl ketone and Diaryl ketone was studied. The irradiation doses of 40 kGy, 60 kGy, 100 kGy, 120 kGy, 200 kGy and 250 kGy were carried out on the catalysts and the time taken for the reaction were noted. The results show that with the increase in dosage the reaction time is found to decrease progressively with a net decrease of 45 -70% relative to that of the original system without irradiation. This reduction in reaction time upon irradiation may be attributed to the increase in surface area as given by the BET surface area studies. The effect of electron beam irradiation on the catalyst was maintained even after 9 months of irradiation.

Key words: Pd/C catalyst, electron beam irradiation, hydrogenation, alkyl aryl ketones

1.Introduction:

Heterogeneous catalytic reaction involves adsorption of reactants from a liquid phase onto solid surface, surface reaction of adsorbed species and desorption of products into the liquid phase. The presence of catalyst provides an alternative sequence of elementary steps to accomplish the desired chemical reaction from that in its absence^{1, 2}. In principle, when a molecule is adsorbed on the surface of a heterogeneous catalyst, it can interact with a large

number of bonding sites. The chemical properties of these bonding sites depend strongly on the chemical environment around them^{3,4}. Effectiveness of heterogeneous catalysis relies on the micro surface nature and structure of the solid phase on to which both the reagent and the starting material get adsorbed prior to the reaction. Uniformity of the surface also 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 solid surface. Microtron-treatment of the solid phase of heterogeneous catalysts could be one such option, but not a well-studied area to effect selective organic transformations.

Non-traditional methods like Electron Beam Treatment of catalyst activation attract significant attention of researchers working in the field of heterogeneous catalysis. This method creates active sites on the catalyst surface possessing higher activity and selectivity. Electron-beam-induced surface chemistry in high vacuum conditions has been studied for various solid surfaces, generating interesting results and enriching the knowledge of the surfaces and surface reactions^{5,6}. Some surface chemical reactions such as decomposition, reduction and oxidation may occur as a result of electron irradiation^{7,8,9}. The electron-beam irradiation of Pd/Al₂O₃ and Pd/C increased dispersion of Pd nanoparticles and activity in toluene hydrogenation by a factor of 3–4¹⁰. The effect of electron irradiation on the properties of the systems 1% Pd/C, 1% Pd/Al₂O₃, and 1% Pd/TiO₂ is studied in gas-phase and liquid-phase toluene hydrogenation has been studied. With the increase in the irradiation dose to 120–900 Mrad the catalytic activity increases by a factor of 2–8 relative to that of the original system¹¹. However, the literature data on studying the impact of the electron irradiation is scarce.

The present study aims at developing the effective heterogeneous catalysts suitable for synthesizing organic compounds through electron beam irradiation. The catalyst selected is palladium adsorbed on carbon (solid and micro powder form). Organic reactions involving palladium catalysed reduction of mono functional organic compounds like acetophenone and benzophenone were carried out. The same reactions were carried out using electron beam irradiated catalysts and the catalytic efficiencies were compared. Further the catalytic efficiency in effecting the hydrogenation of Alkyl aryl, Diaryl ketones with the irradiated Pd/C against the non-irradiated sample of Pd/C was studied. The studies on surface morphological changes of the catalysts were also undertaken.

2. Experimental:

2.1 Chemicals and instruments:

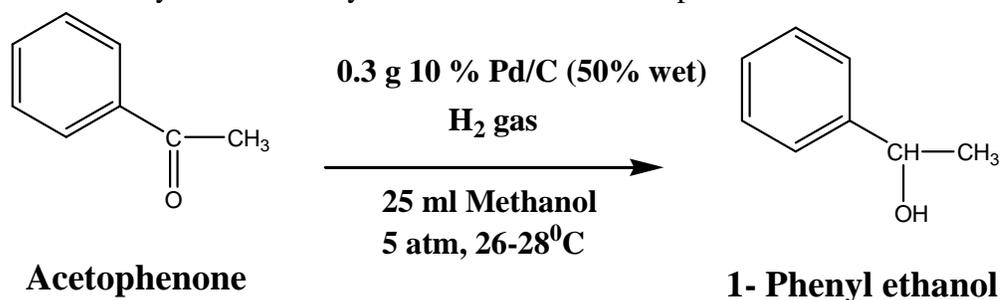
The chemicals - acetophenone, methanol were procured from Aldrich Chemical Company (USA), benzophenone from Merck, 10% Pd/C from Hindustan Platinum Limited, Mumbai and Micro Pd/C from Sigma Aldrich. All the chemicals were of analytical grade and used as received. Pd/C (10%) samples were irradiated by 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 10MeV 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). Electronic absorption spectral analysis was carried out using a Jasco V-650 spectrophotometer (Japan make) in the wavelength region of 200–800 nm. Thermo Scientific Nicolet iS5 spectrophotometer was employed to record the FT-IR spectra at a

resolution of 4.0 cm^{-1} between 4000 and 400 cm^{-1} . 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 Micromeritics 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 K X and 250 K X. EDS studies were undertaken using Oxford Instruments.

2.2 Catalytic Reactions Studied:

i) Reduction of Acetophenone:

A solution of acetophenone (3 g) in methanol (25 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 $26\text{--}28^\circ\text{C}$. The progress of the reaction was monitored by TLC for every half an hour till the completion of the reaction.



Scheme 1 : Conversion of Acetophenone to 1 – phenyl ethanol

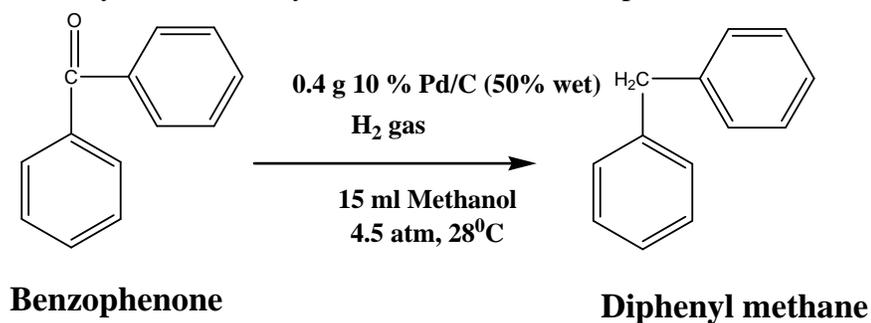
The course of the reaction was monitored by TLC using a mixture of heptane and ethyl acetate (7:3) as mobile phase and silica gel coated alumina plate as Stationary Phase. After completion of the reaction, the reaction mixture was filtered and washed with methanol. The

filtrate was concentrated using a Buchi Rotary evaporator. The Product 1-Phenylethanol (A) was obtained.

The reactions were conducted under similar conditions using 40 kGy, 60 kGy, 100 kGy, 120 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 and illustrated in Fig. 1.

ii) Reduction of Benzophenone:

A solution of benzophenone (2 g) in methanol (15 mL) and 10% Pd/C (0.4 g; 50% wet) were charged into a Parr hydrogenator vessel and flushed with nitrogen. Hydrogen was passed into the vessel at a pressure of 4.5 atm and temperature 26-28 °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 (9:1) 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 diphenylmethane (B) was obtained.

The reactions were conducted under similar conditions using 40 kGy, 60 kGy, 100 kGy, 120 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).

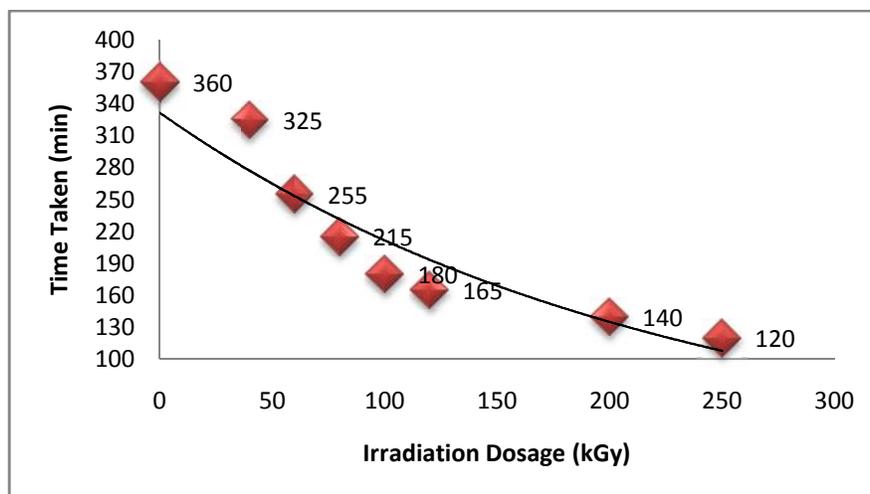
The results are tabulated in Table 3, 4 and illustrated in Fig.2.

Acetophenone taken (g)	Dosage of e ⁻ beam Micro Pd/C in kGy	Reaction Time	Yield of 1-Phenylethanol (g)	% of yield
3	0	4 h 15 min	2.2	73
3	250	1 h 45 min	2.7	90

Acetophenone taken (g)	Dosage of e ⁻ beam 10% Pd/C (50%)wet in kGy	Reaction Time	Yield of 1-Phenylethanol (g)	% of yield
3	0	6 h	2	67
3	40	5 h 25 min	2.1	70
3	60	4 h 15 min	2.2	73
3	100	3 h	2.4	80
3	120	2 h 45 min	2.4	80
3	200	2 h 30 min	2.5	83
3	250	2 h	2.6	87

Fig.1 Reduction of Acetophenone to 1-Phenylethanol

Using 10 % Pd/C (50 % wet)

**Table 3. Reduction of Benzophenone to Diphenylmethane**

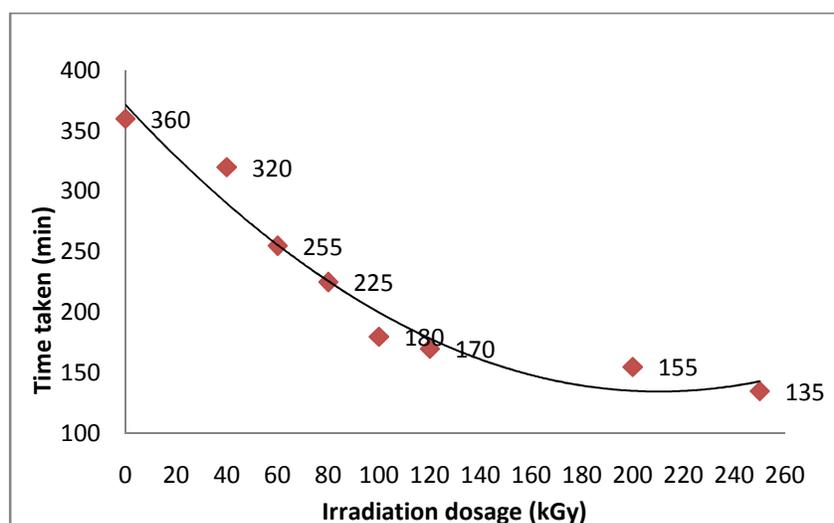
Benzophenone taken (g)	Dosage of e^- beam 10% Pd/C (50%)wet in kGy	Reaction Time	Yield of Diphenylmethane (g)	% of yield
2	0	6 h	1.3	65
2	40	5 h 20 min	1.4	70
2	60	4 h 15 min	1.5	75
2	100	3 h	1.6	80
2	120	2 h 50 min	1.7	85
2	200	2 h 35 min	1.7	85
2	250	2 h 15 min	1.8	90

Table 4. Reduction of Benzophenone to Diphenylmethane

Benzophenone taken (g)	Dosage of e ⁻ beam Micro Pd/C in kGy	Reaction Time	Yield of Diphenylmethane (g)	% of yield
2	0	4 h 15 min	1.5	75
2	250	2 h	1.8	90

Fig.2 Reduction of Benzophenone to Diphenylmethane

Using 10% Pd/C (50 % wet)



3. Results and Discussion:

3.1 UV-Visible Spectroscopy:

The UV-Visible spectra of acetophenone, benzophenone and the products A & B were recorded in 200–800 nm range in an ethanolic solution. The electronic spectrum of acetophenone shows absorption bands in the region 233 nm and benzophenone in the region 265 nm. However, these bands are not observed in the UV-Visible spectra of the products A & B. This disappearance of carbonyl absorption may be due to the reduction of carbonyl group forming 1-phenylethanol and diphenylmethane (Fig. 3-6).

UV-Visible Spectroscopy

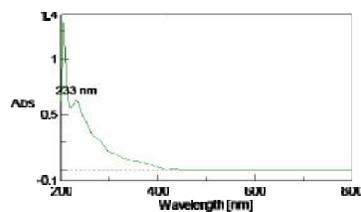


Fig. 3 Acetophenone

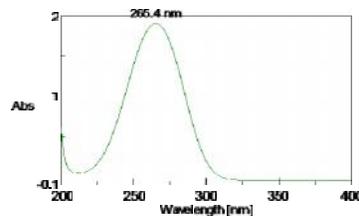


Fig. 4 Benzophenone

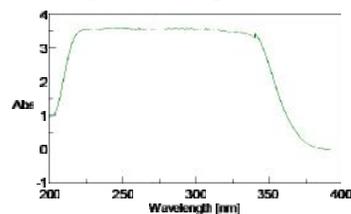


Fig. 5 1-Phenylethanol

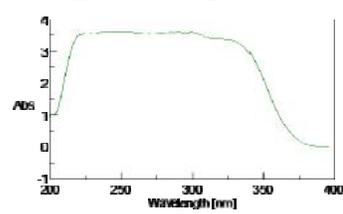


Fig. 6 Diphenylmethane

3.2 Vibrational spectroscopy:

The FT-IR spectrum of Product A exhibiting a band at 3588 cm^{-1} can be attributed to the axial vibration of O-H stretching. The axial C-H stretching band is observed at 3061 cm^{-1} . The symmetrical angular deformations of $-\text{CH}_3$ stretching bands are observed at 1357 cm^{-1} (Fig.7).

The FT-IR spectrum of Product B exhibiting a band at 1448 cm^{-1} can be assigned to C-H bending of methylene. The other band observed at 709 cm^{-1} can be assigned to methylene rocking vibrations (Fig.8).

Vibrational Spectroscopy

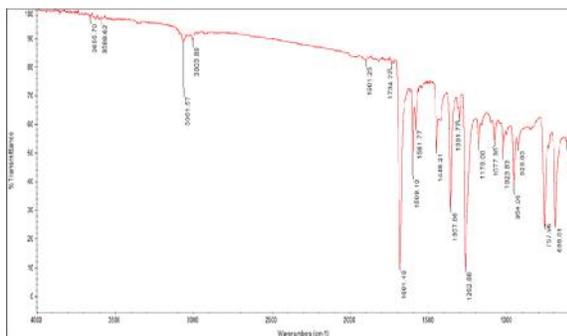


Fig. 7 1-Phenylethanol

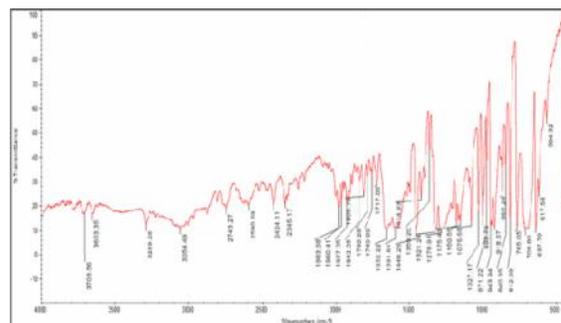


Fig. 8 Diphenylmethane

3.3 NMR spectroscopy:

The structure of the Product A, was characterized by ^1H NMR spectroscopy. The multiplets between 7.23 and 7.33 ppm show the presence of aromatic protons. A signal at 4.86 ppm shows the presence of C-H protons and at 2.5 ppm reveals O-H protons. A signal at 1.42- 1.46 ppm is assigned to methyl protons. For Product B, the multiplets between 7.17 and 7.29 ppm show the presence of aromatic protons. A signal at 3.98 ppm shows the presence of $-\text{CH}_2$ protons.

3.4 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 5.

Table 5. Surface Area

Catalyst	Dosage kGy	BET Surface area m^2/g	Langmuir Surface area m^2/g
Non-irradiated 10% Pd/C	0	621	940
Irradiated 10% Pd/C	150	868	1001
Non irradiated micro Pd/C	0	703	1060
Irradiated micro Pd/C	150	838	1268

It was observed that the surface area of the irradiated catalysts has increased than the non-irradiated ones revealing the dispersion of palladium particles¹¹.

3.5 Scanning electron microscopy:

The SEM pictures (Fig. 9-12) 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.

SEM images of 10% Pd/C

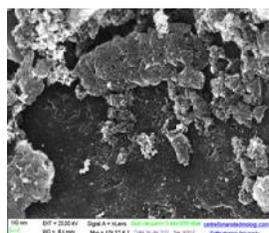


Fig. 9
10%Pd/C (50% wet)

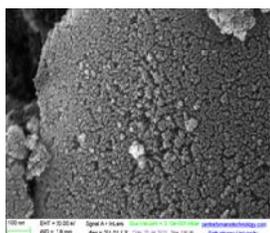


Fig. 10
40 kGy 10% Pd/C (50% wet)

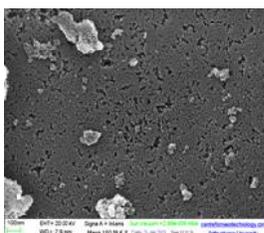


Fig. 11
60 kGy 10% Pd/C (50% wet)

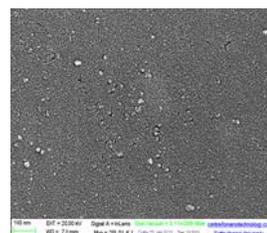


Fig. 12
100 kGy 10% Pd/C (50% wet)

3.6 EDS studies:

EDS studies reveal that Atomic percentage of palladium in 10% Pd/C (50% wet) is 79.91% and the micro powder Pd/C is 94.35%.

3.7 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.

3.8 Summary

The reaction time using Micro Pd/C is in the order of 250 kGy > un-irradiated Micro Pd/C. The rate of the reaction using 10% Pd/C is in the order of 250kGy > 200 kGy > 120 kGy > 100 kGy > 60 kGy > 40 kGy > un-irradiated 10% Pd/C. The results show that with the increase in dosage the reaction time is found to decrease progressively with a net decrease of 45 -70% relative to that of the original system without irradiation. The reaction time using Micro Pd/C is 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 suppressed¹¹. 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.

Compliance with Ethical Standards:

Conflict of interest Authors declare no conflict of interest.

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