

## **VI. Reduction of nitro compound by using nano Pd/CeO<sub>2</sub> catalyst**

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## 6.1 Introduction

Amines and their derivatives are useful in various fields of everyday life. The reduction of nitro aromatic compounds to the corresponding amines is an important step in many industrial processes. Aromatic amines are found in biologically active compounds, pharmaceuticals and agrochemicals [1-4]. They are widely used as dye intermediates for azo dyes, pigments and optical brighteners, as intermediate for photographic chemicals, in polymers via isocyanates for polyurethanes and as oxidants [5,6]. The largest share of aniline is used for the manufacture of isocyanates, primarily for DMI [4,4 - methylenebis(phenylisocyanate)] to make polyurethanes. Many Agrochemicals are made from aniline and its derivatives [7,8].

Moreover, nitro compounds are highly toxic and do not undergo biodegradation easily and thus the elimination of nitro groups can be achieved by reduction of amines, which are much less toxic and can undergo biodegradation easily[9,10].

Synthetic organic transformations performed under unconventional conditions are getting popular primarily to deal with the growing environmental and ecological concern. In recent years, emphasis was placed on viable alternatives for the reductive processes via environmentally benign route.

Various methods are employed for the reduction of nitro compounds [11-13]. These procedures require strong acid medium, hazardous molecular hydrogen and high-pressure reactors. The catalytic hydrogenation reactions are comparatively safer and give greener routes [14-16].

Catalytic transfer hydrogenation reactions can be carried out by hydrogen donors, e.g. isopropanol, ammonium formate, and hydrazine hydrate. These hydrogen donors are safer, highly selective and ecofriendly. Furthermore, unlike conventional hydrogenation methods, these reactions do not require any elaborate experimental set up or high pressure reactor [17]. However, these processes require

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Heterogeneous catalysis for Degradation of Pesticide and Organic Transformations

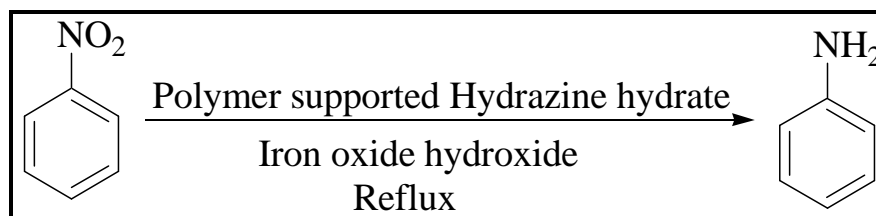
Raney Ni, Pd/C, PtO<sub>2</sub> or moisture sensitive catalysts. Among these Raney Ni catalyst had frequently been used with hydrazine hydrate or isopropanol [18-19]. Although catalytic hydrogen transfer reactions were very facile over these catalysts, they are, however, not selective towards the functional groups such as –CO, –CX and –NO<sub>2</sub>. These all liable functional groups undergo reduction under similar reaction condition.

Many alternative catalysts and catalytic systems were reported for reduction of nitro groups but they have one or the other drawbacks such as typically longer reaction times, nucleophilic attack, by- products, low yields etc. Thus, the highly efficient catalyst that generate low amount of residue/ biproducts with the good activity is one of the main challenges to the scientific community. Hence, attention has been focused on to develop suitable heterogeneous catalyst for catalytic reduction reactions.

Hydrazine hydrate is one of the reagents which is used as the hydrogen donor in catalytic transfer hydrogenation. It is proved that the bi-products of reduction of hydrazine produce harmless nitrogen gas and water. Several solid supported catalysts have been screened for reduction of nitrobenzene to aniline [20-26].

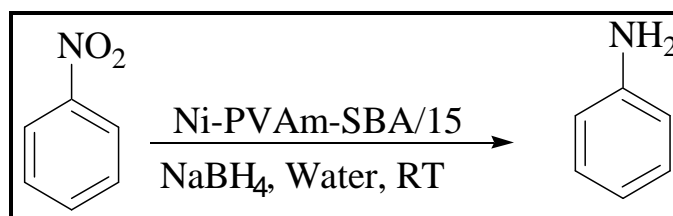
Various compounds of Rh, Pd, Ni and Fe are prominently used as catalysts for the reduction of nitro compounds to their corresponding amines. These catalysts are used in combination with other catalyst or on some support [26-31].

Rongwen Lu et al. had reported polymer supported hydrazine hydrate and iron oxide hydroxide catalyst for reduction of nitrobenzene. Various aromatic amines were prepared with excellent yields through chemoselective reduction of the corresponding aromatic nitro compounds (scheme 6.1) [26].



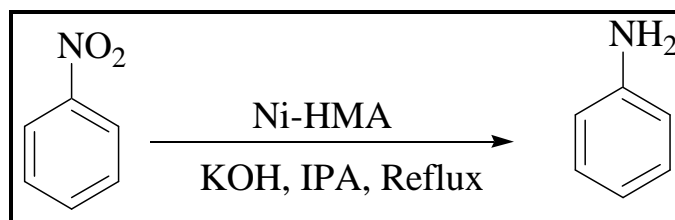
**Scheme 6.1** Iron oxide hydroxide catalysed reduction of nitrobenzene

Kalbasi et al. had prepared novel nickel nanoparticles - PVAm/SBA-15, a polymer inorganic hybrid composite, which was effectively employed as a novel heterogeneous catalyst for reduction of aromatic nitro compounds in the presence of NaBH<sub>4</sub> as a reducing agent. The reaction was carried out at room temperature and in an aqueous medium. The catalyst showed good activity for the reduction of a number of aromatic nitro compounds yielding the respective amine compounds in excellent yields (~98%) (scheme 6.2) [27].



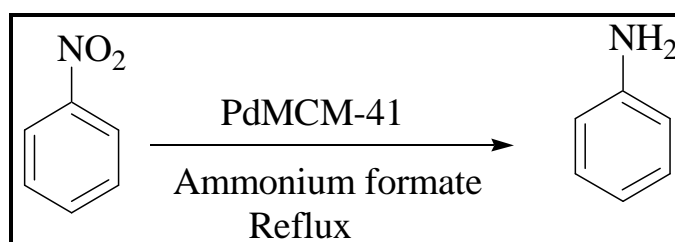
**Scheme 6.2** Ni-PVAm-SBA/15 catalysed reduction of nitrobenzene

P. Selvam et al. had prepared novel nickel-incorporated hexagonal mesoporous aluminophosphate (NiHMA) molecular sieves as a highly efficient heterogeneous catalysts for the chemo- and regioselective reduction of nitroarenes and carbonyl compounds as well as the reductive cleavage of azo functions, including bulkier substrates, by the hydrogen transfer method (scheme 6.3) [28].



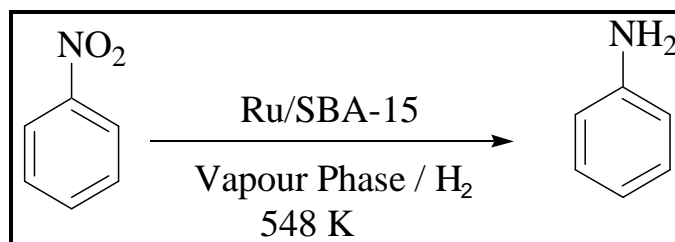
**Scheme 6.3** Ni-HMA catalysed reduction of nitrobenzene

P. Selvam et al. had reported chemoselective reductions of alkenes,  $\alpha,\beta$ -unsaturated carbonyl compounds, nitro and nitroso compounds, N,N-hydrogenolysis of azo and hydrazo functions as well as simultaneous reduction and hydrodehalogenation of substituted aryl halides, including bulkier substrates, were achieved by catalytic transfer hydrogenation (CTH) using mesoporous PdMCM-41 catalyst (scheme 6.4) [29].



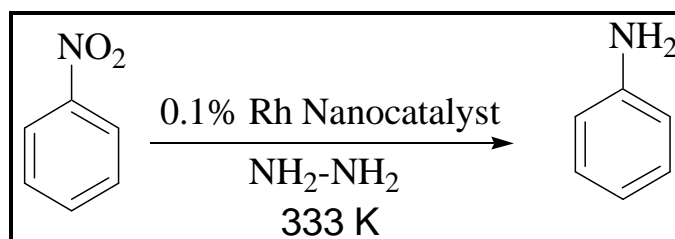
**Scheme 6.4** PdMCM-41 catalysed reduction of nitrobenzene

K. V. R. Chary et al. had prepared series of Ru/SBA-15 catalysts (0.5–6.0 wt%) are prepared by impregnation method. The catalytic activities were evaluated for the vapor phase hydrogenation of nitrobenzene. The catalysts exhibit high conversion/selectivity at 4.5 wt% Ru loading during hydrogenation reaction. Ru/SBA-15 catalysts are found to show higher conversion/selectivities during hydrogenation of nitrobenzene than Ru/SiO<sub>2</sub> and Ru/Al<sub>2</sub>O<sub>3</sub> catalysts (scheme 6.5) [31].



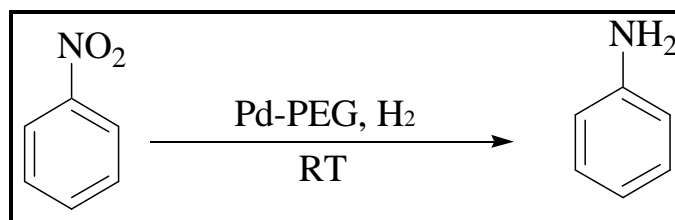
**Scheme 6.5** Ru/SBA-15 catalysed reduction of nitrobenzene

Jun Huang et al. had reported highly efficient and selective Rh nanocatalyst for the reduction of nitroarenes with hydrazine monohydrate under mild conditions. The reaction was carried out at 60 °C. Functional groups such as halides (F, Cl, Br and I), CN, NH<sub>2</sub>, OH, alkene, ester and amide groups were untouched during the hydrogenation of the nitroarenes, and the corresponding anilines were obtained quantitatively (scheme 6.6) [32].



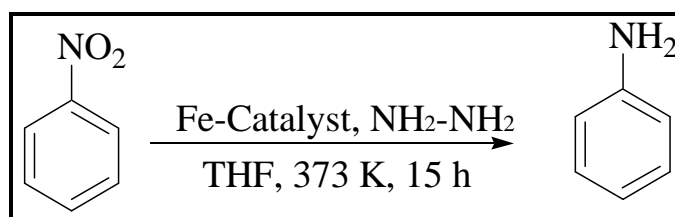
**Scheme 6.6** Nano Rh catalysed reduction of nitrobenzene

F.A. Harraz et al. developed an efficient, simple chemical reduction method to produce highly active palladium (Pd) nanoparticles in polyethylene glycol (PEG) with no other stabilizer. The as-prepared Pd/PEG catalyst demonstrated a remarkable catalytic activity toward hydrogenation of both styrene and nitrobenzene under mild conditions (scheme 6.7) [33].



**Scheme 6.7** Pd-PEG catalysed reduction of nitrobenzene

Matthias Beller et al. had reported a highly selective novel iron–phenanthroline complex supported on carbon for the reduction of structurally diverse nitroarenes to anilines in 90–99% yields. This catalyst system was introduced for the efficient reduction of nitro compounds using hydrazine hydrate at 100 °C. This catalyst chemoselectively reduced the nitro group in the presence of other sensitive groups such as C=C, C-C triple bond, -CN triple bond, OH, ether, thioether and ester groups (scheme 6.8) [34].



**Scheme 6.8** Fe(OAc)<sub>2</sub> catalysed reduction of nitrobenzene

In all above reported work, the reduction of nitro groups to amine can be carried out by using various catalysts under various temperature ranges and with or without solvent. In this paper, to minimise the use of solvents and to reduce the temperature we had synthesised nano Pd/CeO<sub>2</sub> and explore its catalytic activity for the reduction of aromatic nitro compounds. The catalyst was characterized by using various analytical techniques. The present work also contributes towards heterogeneous catalysis with respect to recovery and reuse of the noble metal catalyst which is extremely important for industrial application.

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## 6.2 Experimental

### 6.2.1 Materials

Cerium nitrate, Palladium acetate and CTAB were purchased from M/S S.D. Fine Chemical, Mumbai, India. All the chemicals were purchased from firms of repute with their highest purity available and were used without further purification.

### 6.2.2 Methods

#### 6.2.2.1 Synthesis of nano Pd/CeO<sub>2</sub>

Pd/CeO<sub>2</sub> nanoparticles were prepared by adding palladium acetate in cerium hydroxide. Ce(OH)<sub>4</sub> was prepared as discussed in the method used chapter 4, section 4.2.2.

Palladium acetate (13 mg) was dissolve in hot 20 mL methanol. Cerium hydroxide (120 mg) was added in the Pd-methanol solution. The mixture was then stirred at 50°C for 5 h. Brown powder of Pd-Ce(OH)<sub>4</sub> was obtained after evaporation of excess of solvent. It was then dried at 120°C and subsequently calcined at 500 °C for 3 h. The prepared Pd/CeO<sub>2</sub> was then characterized with various techniques such as X-ray diffractograms (XRD), EDAX, Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM).

#### 6.2.2.2 General procedure for reduction of nitrobenzene

##### Method A

Nitrobenzene (1 mmol, 123 mg), hydrazine hydrate (3 mmol, 150 mg), 2 mL solvent and 10 mg of Pd/CeO<sub>2</sub> catalyst were taken in a 10 mL round bottom flask. The reaction mixture was stirred at 80 °C for 1 h.

##### Method B

Nitrobenzene (1 mmol, 123 mg), hydrazine hydrate (3 mmol, 150 mg), potassium hydroxide (1 mmol, 56 mg), 2 mL solvent and 10 mg of Pd/CeO<sub>2</sub> catalyst was taken in a 10 mL round bottom flask. The reaction mixture was stirred at room temperature for 1 h.



After completion of the reaction, as indicated by TLC, catalyst was separated by centrifugation and subsequently washed with dichloromethane. The reaction mixture was diluted with water and product was extracted with dichloromethane ( $2 \times 10$  mL). The organic layer was dried over anhydrous sodium sulphate and evaporated under reduced pressure to afford the crude product. The crude product was isolated by column chromatography using petroleum ether / ethyl acetate (9:1) as an eluent. The isolated yield was reported in this chapter. Quantitative and qualitative analysis of all amines were done by GC, GC-MS and identified by comparison with authentic samples.

**Following parameters were optimized for method A**

- 1) Temperature : RT to 80 °C
- 2) Effect of Solvents : Ethanol, Water, Toluene, IPA, ACN, EA, Hexane
- 3) Effect of Catalyst conc. : 0 to 10 mg
- 4) Effect of Hydrazine : 1 to 3 mmol  
Hydrate conc.

**Following parameters were optimized for method B**

- 1) Temperature : RT to 80 °C
- 2) Effect of Solvents : Ethanol, Water, Toluene, IPA, ACN, EA, Hexane
- 3) Effect of base : KOH, NaHCO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, N(Et)<sub>3</sub>, NH<sub>3</sub>
- 4) Effect of Base conc. : 0.25 to 1 mmol
- 5) Effect of Hydrazine : 1 to 3 mmol  
Hydrate conc.

The optimised reaction conditions are summarised in table 6.5

## 6.2.3 Characterization of Nano Pd/CeO<sub>2</sub>

### 6.2.3.1 X-Ray Diffraction

The X-ray diffractograms were obtained (XRD, MINI FLEX RIGAKU MODEL) with Cu K- radiation (1.5418 Å) with scanning rate of 2° per min from 2° to 80°. The X-ray diffraction spectrum (XRD) of the prepared PdCeO<sub>2</sub> is shown in figure 6.1. The fluorite phase of ceria was observed. The diffraction peaks displayed almost all the characteristic diffractions corresponding to the face-centred cubic (FCC) CeO<sub>2</sub>, matching with the JCPDS pattern (Powder Diffraction File No 34-394). This spectrum did not show distinct peaks corresponding to either PdO or Pd. It may be due to the low concentration of the Pd on CeO<sub>2</sub>. It was found that the prepared nanoparticles show good crystallinity. The crystallite size of catalyst was around 5-10 nm, calculated from the X-ray line broadening by applying full width half maximum (FWHM) of characteristic peak (111) to the Scherrer equation.

$$D = 0.9 / \cos$$

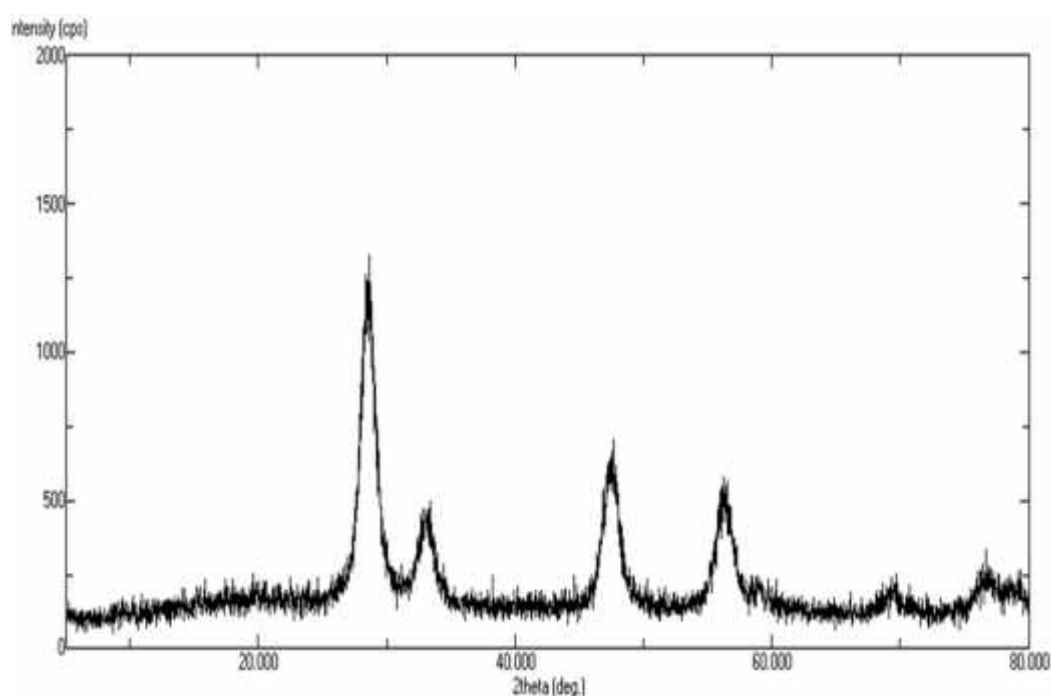
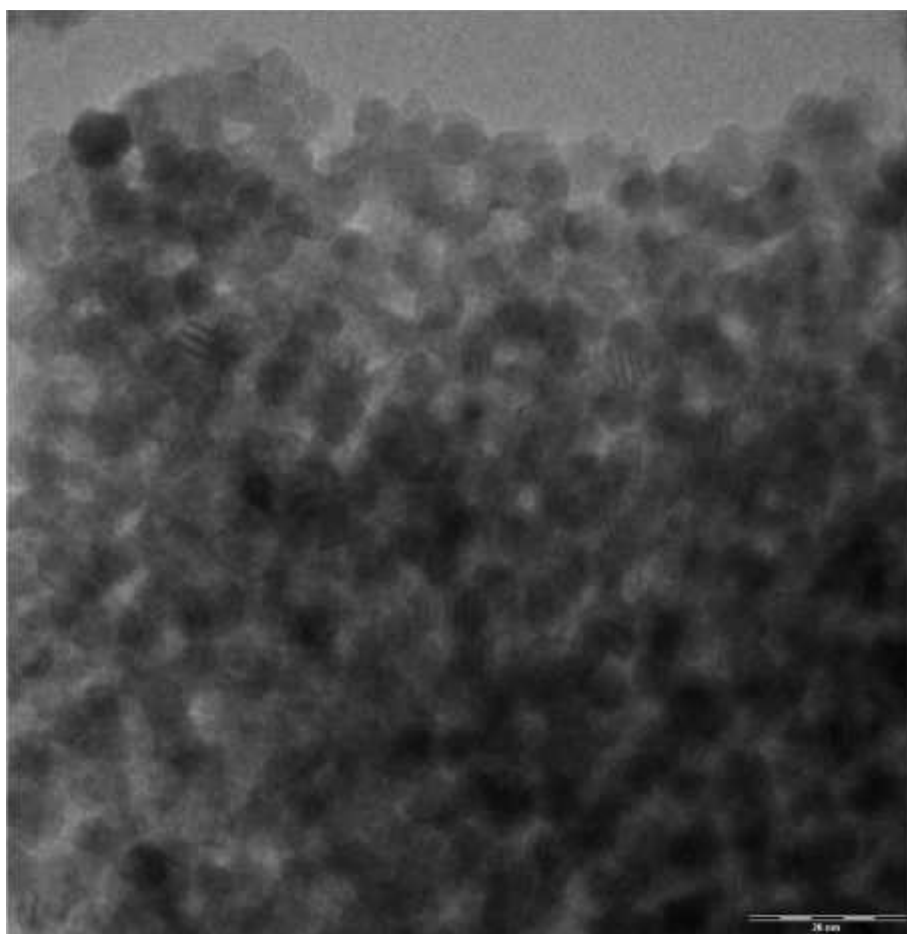


Figure 6.1 XRD of Nano Pd/CeO<sub>2</sub>

### 6.2.3.2 Transmission Electron Microscope

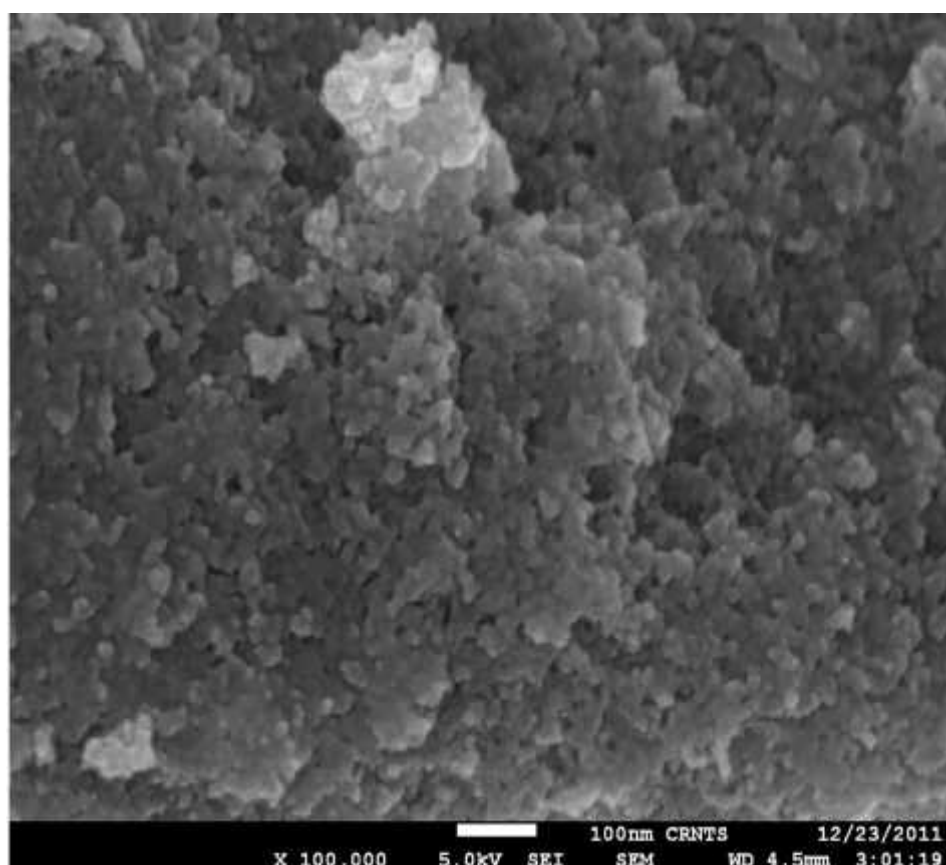
Particle size and external morphology of the prepared particles were observed on a Transmission Electron Microscope (TEM) (Philips CM 200, operating at 20 – 200 kV accelerating voltage and having resolution upto 2.4 Å). It can be seen from figure 6.2 that the size of CeO<sub>2</sub> nanoparticles was in the range of 4 -5 nm (scale bar of 20 nm) and the shape of the particles was mostly spherical. The size of nano CeO<sub>2</sub> obtained from TEM was in well agreement with the crystal size from the XRD data



**Figure 6.2** TEM of Nano Pd/CeO<sub>2</sub>

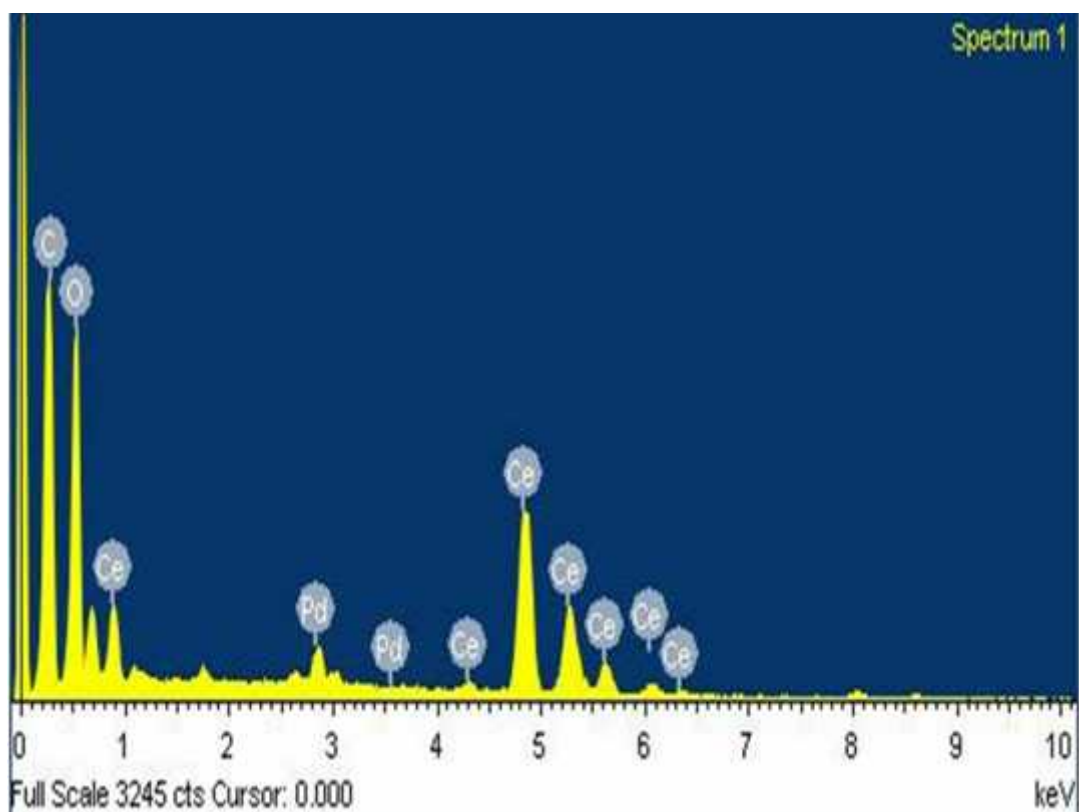
### 6.2.3.3 Scanning Electron Microscope and EDAX

Surface morphology and EDAX (Energy Dispersive X-Ray Spectroscopy) analysis was done by using Field Emission Gun-Scanning Electron Microscopes (FEG-SEM) JSM-7600F model operating at accelerating voltage 0.1 to 30 kV, Magnification x25 to 1,000,000 and having resolution 1.0 nm - 1.5 nm (15kV). SEM image of CeO<sub>2</sub> (figure 6.3) shows the result in support of TEM image having agglomerated spherical particles.



**Figure 6.3** SEM of Nano Pd/CeO<sub>2</sub>

The resultant EDAX image of Pd/CeO<sub>2</sub> (figure 6.4) shows presence of only palladium, cerium and oxygen elements in prepared Pd/CeO<sub>2</sub> and loading of approximately 5% (actual 4.89%) of palladium on CeO<sub>2</sub>.

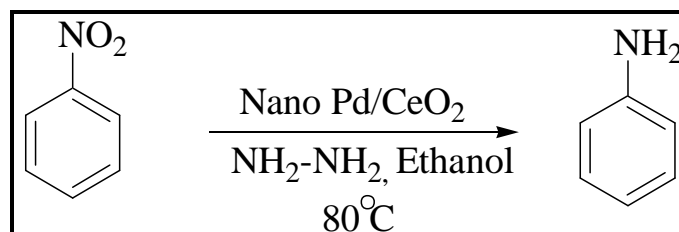


**Figure 6.4** EDAX of Nano Pd/CeO<sub>2</sub>

### 6.3 Result and Discussion

#### Method A

The present work reports an efficient protocol for reduction of nitrobenzene to aniline by using nano Pd/CeO<sub>2</sub> catalyst at 80 °C for 1 h.



**Scheme 6.9** Reduction of nitrobenzene by using nano Pd/CeO<sub>2</sub>

Nitrobenzene was chosen for model reaction to test the catalytic activity of Pd/CeO<sub>2</sub>. Table 6.1 gives the details about the comparison of the catalytic activity of Pd catalysts on different supports. The reaction was carried out with the Pd/CeO<sub>2</sub>, Pd/ZnO and Pd/C as a catalyst. We observed that the nano Pd/CeO<sub>2</sub> gave maximum yield of the desired product than Pd/C and Pd/ZnO. Hydrazine hydrate was used as a reducing agent. It was reported that the presence of base like CaCO<sub>3</sub> was useful for generation of molecular hydrogen required for reduction reaction [32]. Since CeO<sub>2</sub> has shown basic characteristics [33], Pd/CeO<sub>2</sub> demonstrates better catalytic activity than Pd/C and Pd/ZnO.

**Table 6.1** Catalyst optimisation by method A<sup>a</sup>

Sr. No.	Catalyst	Reaction Condition	Conversion in %	Yield <sup>b</sup> in %
1	Pd/C	80 °C /1h	100	34
2	Pd/ZnO	80 °C/1h	100	19
<b>3</b>	<b>Pd/CeO<sub>2</sub></b>	<b>80 °C /1h</b>	<b>100</b>	<b>90</b>

<sup>a</sup> Reaction conditions: Nitrobenzene (1 mmol), hydrazine hydrate (3 mmol), solvent (2 mL) and 10 mg catalyst for 1 h. <sup>b</sup> Isolated Yields.

Influence of various parameters such as temperature, solvents and catalyst loading were studied for the optimisation of the reaction conditions. The details are given in the table 6.2. Initially 10 mg of catalyst was used for optimizing the temperature and solvent. It was found that 90% of the product was formed at 80 °C in 1h. The temperature below 80 °C lowers the yield. Ethanol was found to be the best solvent after screening various solvents. It was also interesting to note that the 85% yield of the product was obtained in aqueous medium. The catalyst loading of 10 mg was sufficient to give maximum yield of the required product.

**Table 6.2** Influence of temperature, solvent and catalyst loading by method A<sup>a</sup>

Sr. No.	Catalyst (mg)	Hydrazine Hydrate (mmol)	Solvent	Temp In °C	Yield <sup>b</sup> (%)
1	10	3	Ethanol	RT	5
2	10	3	Ethanol	40	13
3	10	3	Ethanol	60	33
<b>4</b>	<b>10</b>	<b>3</b>	<b>Ethanol</b>	<b>80</b>	<b>90</b>
5	10	3	Water	80	85
6	10	3	Toluene	80	50
7	10	3	IPA	80	87
8	10	3	ACN	80	1
9	10	3	EA	80	11
10	10	3	Hexane	80	16
11	7.5	3	Ethanol	80	82
12	5	3	Ethanol	80	67
13	2.5	3	Ethanol	80	48
14	0	3	Ethanol	80	0
15	10	2.5	Ethanol	80	72
16	10	2	Ethanol	80	58
17	10	1.5	Ethanol	80	46
18	10	1	Ethanol	80	19

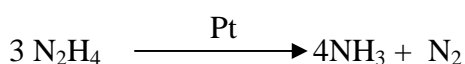
<sup>a</sup> Reaction conditions: Nitrobenzene (1 mmol), hydrazine hydrate (3 mmol), solvent (2 mL) for 1 h. <sup>b</sup> Isolated Yields.



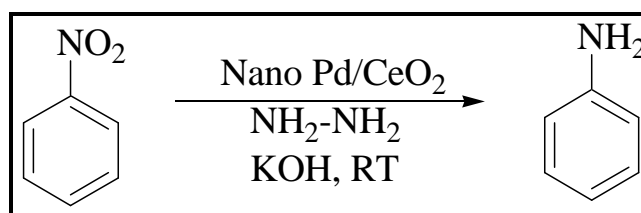
## Method B

The catalytic hydrogen transfer reaction involves addition and abstraction of hydrogen. It is well known that hydrazine hydrate gets converted into hydrogen and nitrogen gas in presence of platinum and hydroxyl ion [32]. Though the presence of hydroxyl ion increases the rate of formation of molecular hydrogen, it cannot be used for reduction reaction in presence of platinum catalyst.

Gutbier and Neundlinger proved that



The present work reports an efficient protocol for reduction of nitrobenzene to aniline by using nano Pd/CeO<sub>2</sub> catalyst at room temperature.



**Scheme 6.10** Reduction of nitrobenzene by using nano Pd/CeO<sub>2</sub> at room temperature

Nitrobenzene (1 mmol) and 10 mg of Pd/CeO<sub>2</sub> catalyst was chosen for model reaction to check feasibility of the reaction at milder conditions. Table 6.3 gave the details about influence of optimised reaction conditions on catalytic activity of nano Pd/CeO<sub>2</sub>. All the reactions were performed in presence of different bases and in different solvents. Table 6.3 clearly indicates that 95% yield was obtained by using water as a solvent in presence of 1 mmol of the KOH at room temperature. Here we observed that Pd/CeO<sub>2</sub> in presence of hydroxyl ions reduces nitrobenzene to aniline.

**Table 6.3** Influence of temperature, solvent and base by method B<sup>a</sup>

Sr. No.	Catalyst (mg)	Solvent	Base	Temp (°C)	Yield <sup>b</sup> (%)
1	10	Ethanol	KOH	80	90
2	10	Ethanol	KOH	60	88
3	10	Ethanol	KOH	40	86
4	10	Ethanol	KOH	RT	80
<b>5</b>	<b>10</b>	<b>Water</b>	<b>KOH</b>	<b>RT</b>	<b>95</b>
6	10	Toluene	KOH	RT	47
7	10	IPA	KOH	RT	81
8	10	ACN	KOH	RT	2
9	10	EA	KOH	RT	4
10	10	Hexane	KOH	RT	25
11	10	Water	NaHCO <sub>3</sub>	RT	6
12	10	Water	K <sub>2</sub> CO <sub>3</sub>	RT	61
13	10	Water	NEt <sub>3</sub>	RT	53
14	10	Water	NH <sub>3</sub>	RT	19

<sup>a</sup> Reaction conditions: Nitrobenzene (1 mmol), hydrazine hydrate (3 mmol), base (1 mmol) and solvent (2 mL) for 1 h. <sup>b</sup> Isolated Yields.

The feasibility of the reaction at the room temperature in aqueous medium is in accordance with green concept which underlines the importance of the Pd/CeO<sub>2</sub> catalyst. The reaction was then optimized with respect to concentrations of base and hydrazine hydrate. The results are summarized in table 6.4. It clearly indicates that 1 mmol of KOH and 3 mmol of hydrazine hydrate were required to get maximum yield of the product.

**Table 6.4** Effect of concentration of base and concentration of hydrazine hydrate on reduction reaction by method B<sup>a</sup>.

Sr. No.	Conc. of Base in mmol	Conc. of Hydrazine hydrate in mmol	Yield <sup>b</sup> in %
<b>1</b>	<b>1</b>	<b>3</b>	<b>95</b>
2	0.75	3	87
3	0.5	3	78
4	0.25	3	68
5	1	2.5	86
6	1	2	70
7	1	1.5	54
8	1	1	28

<sup>a</sup> Reaction condition: Nitrobenzene (1mmol), 10 mg of catalyst (0.5 mmol% Pd) and 2 mL water at RT, <sup>b</sup> Isolated yield.

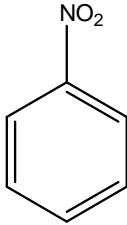
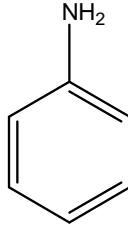
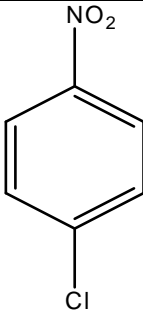
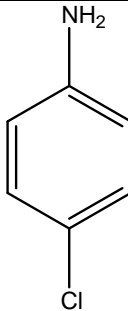
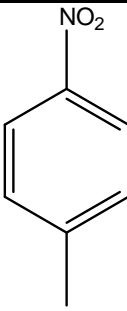
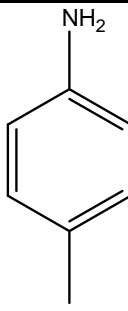
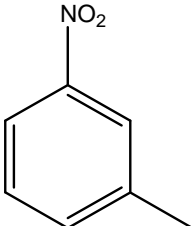
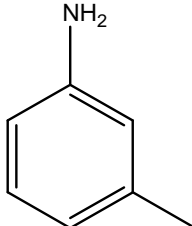
**Table 6.5** Optimized reaction conditions for method A and B are

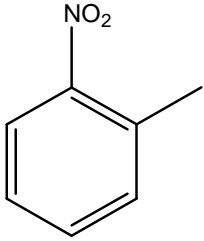
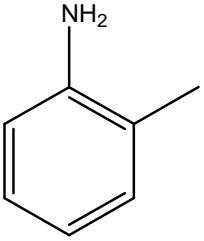
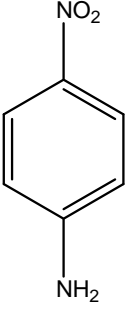
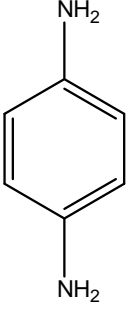
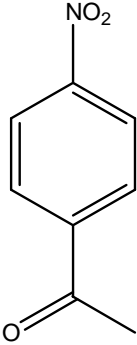
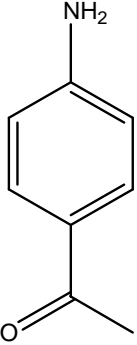
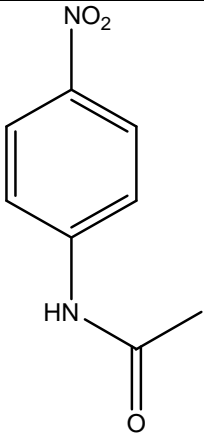
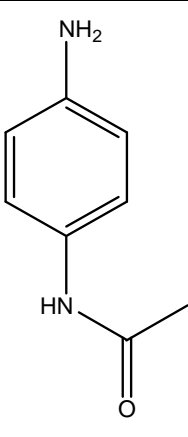
<b>Conditions</b>	<b>Method A</b>	<b>Method B</b>
Temperature	80 °C	RT
Solvent	Ethanol	Water
Catalyst Concentration	10 mg	10 mg
Hydrazine Hydrate	3 mmol	3 mmol
Base	Not Applicable	KOH (1 mmol)

To study the scope and applicability of the developed protocol by method A and method B, reactions of various substituted nitrobenzenes were investigated. The results are shown in table 6.6 (method A) and table 6.7 (method B). Excellent yields of desired products were obtained with different substituted nitrobenzenes. The presence of electron withdrawing or electron donating groups at para position did not have any significant effect on the yield of the product with or without KOH.

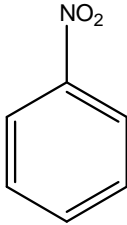
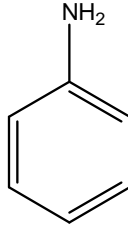
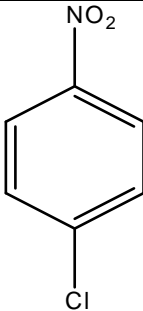
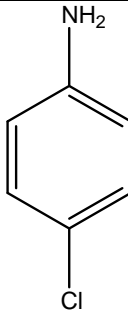
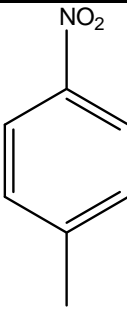
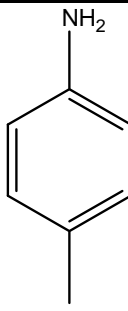
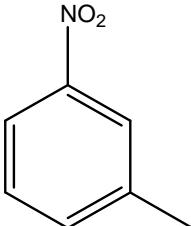
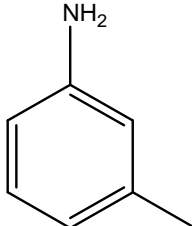
Hence the Pd/CeO<sub>2</sub> can efficiently catalyze the reduction of nitro aryls at 80 °C by using ethanol as solvent and at room temperature in alkaline medium. Yields were determined by GC-FID and compared with authentic samples. Quantitative and qualitative analysis of all amines were made by GC, GC-MS and identified by comparison with authentic samples.

**Table 6.6** Nano Pd/CeO<sub>2</sub> catalyzed reduction of different nitrobenzene (method A)

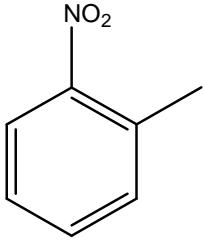
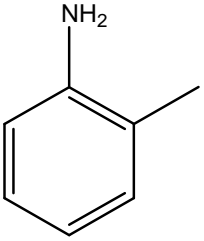
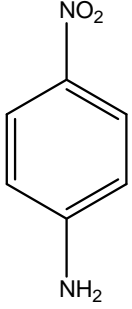
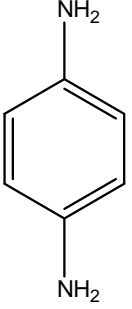
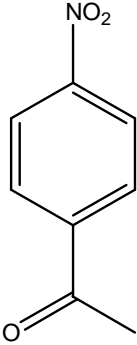
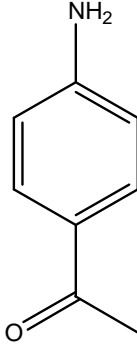
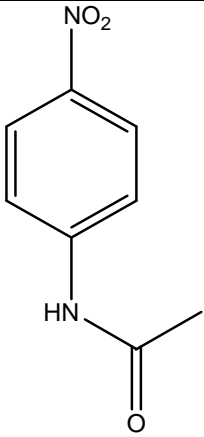
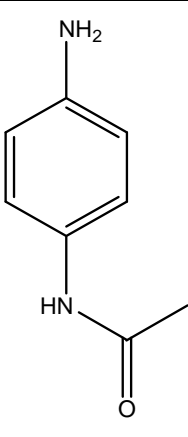
Entry	Amine	Amine	Time (h.)	Yield <sup>b</sup> (%)
1			1	90
2			1	90
3			1	91
4			1	89

5			1	87
6			1	85
7			3	85
8			1	85

**Table 6.7** Nano Pd/CeO<sub>2</sub> catalyzed reduction of different nitrobenzene (method B)

Entry	Amine	Amine	Time (h.)	Yield <sup>b</sup> (%)
1			1	95
2			1	91
3			1	93
4			1	92



5			1	90
6			1	90
7			3	88
8			1	89

### Catalyst Reusability

The recyclability of the catalyst is checked after completion of the reaction. The catalyst was separated by centrifugation, washed with water and subsequently with acetone for three times. The catalyst was then dried at 120 °C and reused for next cycle. The reusability of the catalyst was checked for three cycles. It was found that the catalyst showed good recyclability for consecutive runs. The results were shown in Table 6.8.

**Table 6.8** Recyclability of nano Pd/CeO<sub>2</sub> by methos B<sup>a</sup>

Run	Fresh	Run 1	Run 2	Run 3
% Yield <sup>b</sup>	95	93	90	90

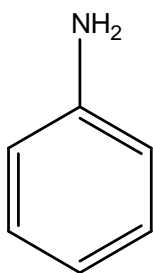
<sup>a</sup> Reaction condition: 1 mmol Nitrobenzene, 3 mmol hydrazine hydrate, 1 mmol KOH and 2 mL water for 1 h at room temperature, <sup>b</sup> Isolated yield.

## 6.4 Conclusion

- We have prepared nano Pd/CeO<sub>2</sub> catalyst for catalytic transfer hydrogenation by using hydrazine hydrate as hydrogen donor.
- The given methodology can also be applied in alkaline medium at room temperature.
- This recyclable catalyst offers advantages like simple work-up and high yields.
- The developed concept is expected to be more general and easily applicable.
- The Pd/CeO<sub>2</sub> catalyst is environmentally benign and can be used for reduction of nitro aryls to corresponding amines.
- Hence the protocol fits into various green chemistry concepts such as use of non toxic solvent, atom economy, ambient reaction temperature and recyclable, non hazardous catalyst.

## 6.5 Spectral Data

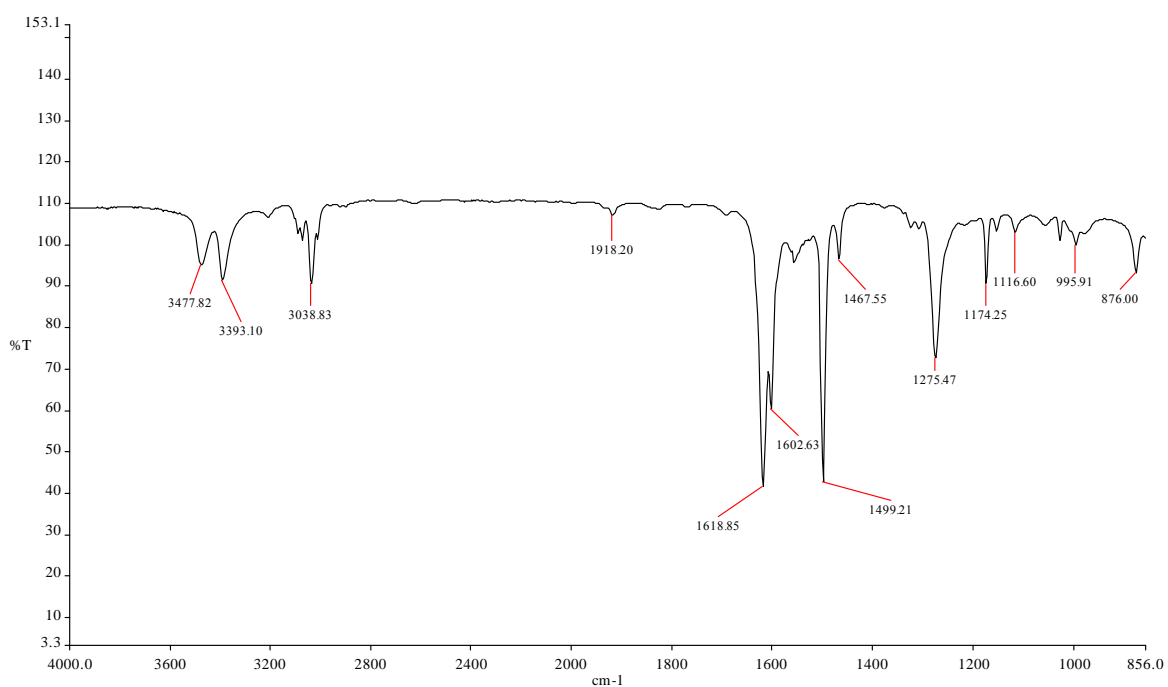
IR, Mass and  $^1\text{H}$ -NMR of entry 1, Table 6.6 and 6.7



Aniline

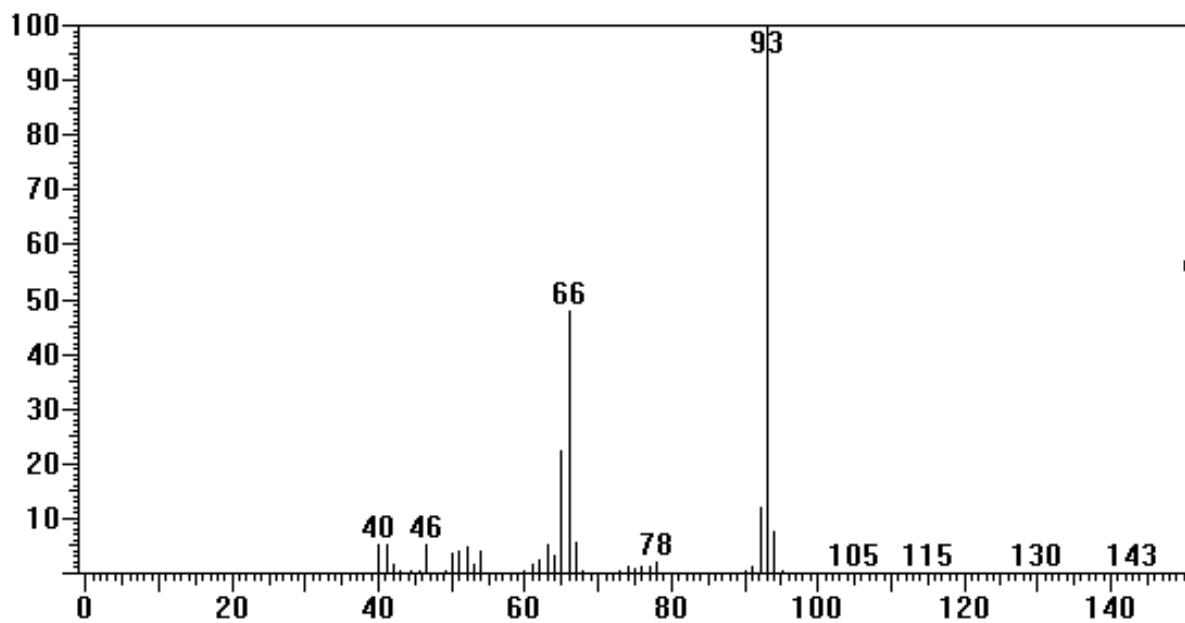
### IR Spectra

IR (KBr)  $\text{cm}^{-1}$ : 3477 and 3393 ( $-\text{NH}_2$ ), 3038 ( $-\text{CH}$ ), 1174 (C-N), 1103–997.



## Mass Spectra

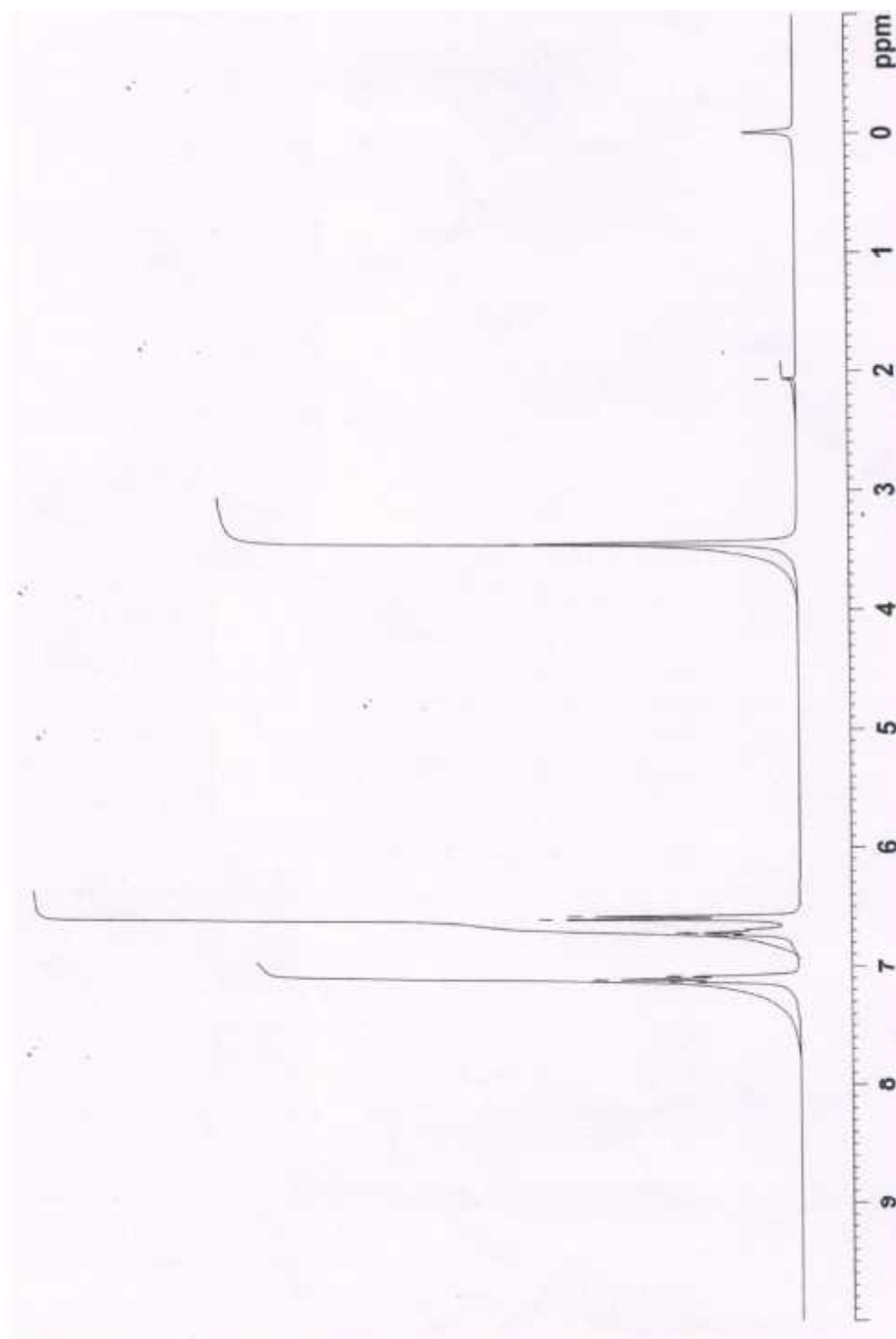
GC-MS (EI, 70 eV):  $m/z$  (%) = 93 (100%)  $[M]^+$ .



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 **$^1\text{H}$ -NMR Spectra (300 MHz,  $\text{CDCl}_3$ ):**

3.4 (s, 2H,  $\text{NH}_2$ ), 6.6 (d, 1H, ortho H of phenyl ring), 6.8 (t, 1H, para H of phenyl ring), 7.15 (t, 1H, meta H of phenyl ring) ppm.



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