Chapter VI

Hydrogenation of

\(m\)-chloronitrobenzene to \(m\)-chloroaniline
6.1. Introduction:
Selective hydrogenation of chloronitroaromatics give the corresponding haloanilines having wide range applications in dye industries, for the manufacture of substituted phenyl carbamates [1], drugs, herbicides, pesticides, polyanilines [2, 3], and other specialty chemicals [4-6]. Traditionally, haloanilines were synthesized by the reduction of corresponding chloronitroaromatics using Fe/HCl (Bechamp Process) or sulfide reduction method. These processes are no longer feasible due to formation of large amounts of toxic wastes, posing serious disposal problems [7]. Details of Bechamp process is discussed in chapter V, under section 5.3. Haloamines are now synthesized by liquid phase catalytic hydrogenation of corresponding chloronitroaromatics [8-19]. Major drawback of this process is formation of acid due to the dehalogenation reaction. Hence, selective hydrogenation of nitro- to amine without dehalogenation is a challenging task in the hydrogenation of halonitroaromatics. Since, this is a seminal process from both fundamental as well as industrial point of view, we have studied the liquid phase catalytic hydrogenation of $m$-chloronitrobenzene in detail.

Hydrogenation of $m$-chloronitrobenzene ($m$-CNB) to $m$-chloroaniline ($m$-CAN) involves two main reaction pathways giving rise to formation of several by products as shown in Scheme 6.1. According to the pathway A (Scheme 6.1), the hydrogenation of $m$-CNB proceeds via intermediates, $m$-nitrosochlorobenzene and $m$-(chlorophenyl)-hydroxylamine to give the desired product $m$-CAN. However, nitroso, and hydroxylamine being very reactive intermediates, can give rise to the formation of side products such as 3,3’-dichloroazobenzene (DAB) and 3,3’-dichlorohydrizobenzene (DHAB), which also subsequently undergo hydrogenation to give $m$-CAN, normally formed in basic medium. The competing pathway B, involves first the dehalogenation step to give nitrobenzene (NB) and then aniline via a nitrosobenzene intermediates. The formation of acid during dehalogenation steps either via pathway A or B, is detrimental since it deactivates the catalysts as well as produces undesired side product to a substantial extent. Further hydrogenation of $m$-CAN leads to formation of aniline and chlorobenzene along with formation of acids, (shown in red in Scheme 6.1), causing lowering yields of the desired product ($m$-CAN).
Scheme 6.1. Reaction pathway for hydrogenation of \textit{m}-CNB to \textit{m}-CAN [20-22]

Azoxy- and azo- benzene are highly toxic, hence their formation must be avoided or at least minimized by a suitable choice of catalyst and reaction conditions. The desired pathway is shown in green, which contributes to the highest productivity of \textit{m}-CAN.
6.1.1. Literature survey:

A summary of literature on hydrogenation of m-CNB to m-CAN is shown in Table 6.1. Several catalyst systems involving monometallic Ni catalyst [8, 23-27], Pd [27-29], Pt and modified Pt [12-14, 19, 27, 30, 31], and bimetallic catalysts have been reported for the hydrogenation of m-CNB to m-CAN [8, 14, 32-35]. Polymer (PVP) protected PdCl\(_2\), FeCl\(_3\), Co(Ac)\(_2\), NiCl\(_2\), RhCl\(_3\) and RuCl\(_3\) and their bimetallic catalyst systems were reported by Yu et al. in which the formation of aniline was also observed due to the competing dechlorination reaction [32]. It was found that the bimetallic PVP-PdCl\(_2\)-2RuCl\(_3\) catalyst showed 97% conversion with 95% selectivity to CAN [32]. Interestingly, the addition of sodium acetate to this system increased the catalytic activity by 40 times [32]. Palladium metal supported on anionic polymer (D) and carbon has been studied by Kratky et al. He found that the Pd/D catalyst showed more activity and selectivity (93%) towards m-CAN than Pd/C catalyst [36].

During the course of reaction, the support might be attacked by hydrochloric acid formed in the reaction, causing surface modification and/or structural deformation of the catalyst. Among these metals, Pt is the first choice for hydrogenation of C-Cl due to its better activity, selectivity and stability than other metals [37]. To minimize the deactivation of catalyst, various types of supports also have been investigated for hydrogenation of m-CNB. Ma et al. prepared the novel supports for this hydrogenation reaction i.e. platinum supported on HCl-acidified attapulgite catalyst which showed very high activity and selectivity (> 99%) [38]. Han et al. studied Pt supported on series of oxides (Al\(_2\)O\(_3\), TiO\(_2\), ZrO\(_2\)), in which Pt/TiO\(_2\) showed the higher activity and selectivity towards CAN due to strong metal/support interactions [31]. A comparative study of various supports such as TiO\(_2\), SiO\(_2\) and carbon showed that Pt/C gave the highest conversion (99%) and selectivity (96%) to CAN [30]. Nomura reported the selective catalytic reduction of nitro compounds using ruthenium-carbonyl complexes under supercritical CO\(_2\)/H\(_2\)O conditions. He achieved high activity and > 99 % yield towards the haloanilines as a product [39]. Greenfield and Dovell prepared a series of selectively sulfur poisoned carbon supported catalyst systems such as Pt, Pd, Co, Rh and Ru for minimizing the...
reductive dehalogenation. In this work, complete selectivity to the haloamines was achieved using Pt-S/C catalyst [40]. The kinetic studies of the selective hydrogenation of CNB to CAN in a stirred reactor over temperature range of 313-363 K, using sulfided 1% Pt/C catalyst has been studied by Rode et al. [19].

Kosak studied the effect of various inhibitors as listed in Table 1.1 for the selective hydrogenation of halonitrobenzene to haloamines [27]. It can be seen from this Table that Pt-morpholine catalyst system showed the best results because morpholine acts as an inorganic acid acceptor to control the amount of carbon-halogen cleavage [27]. In this hydrogenation reaction morpholine acts (i) as a true suppressor to inhibit the dehalogenation reaction and (ii) as an acid acceptor when some dehalogenation occurs. He also studied various metal oxide systems, among which magnesium oxide acts only as acid acceptor, neutralizing the hydrohalide after dehydrohalogenation [27].

It is clear from the literature that obtaining the highest selectivity to chloroaniline is difficult mainly due to (i) the competing dehydrohalogenation reaction and (ii) catalyst deactivation due to carboneous deposition on the catalyst.
Table 6.1. Summary literature on hydrogenation of \textit{m}-chloronitrobenzene to \textit{m}-chloroaniline

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Catalyst</th>
<th>Conversion, %</th>
<th>Reaction conditions</th>
<th>Selectivity, %</th>
<th>Ref. No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>NanoPd/MCM</td>
<td>100</td>
<td>T=300 K; P$_H_2$=3 MPa</td>
<td>91 9</td>
<td>41</td>
</tr>
<tr>
<td>2.</td>
<td>Pt/CNT, PtM/CNT, M=La, Ce, Pr, Nd and Sm</td>
<td>99.7</td>
<td>T=303 K; P$_H_2$=0.1 MPa</td>
<td>98 0.3</td>
<td>42</td>
</tr>
<tr>
<td>3.</td>
<td>Pt/C, PtM/C, M=La, Ce, Pr, Nd and Sm</td>
<td>99.4</td>
<td>T=303K; P$_H_2$=0.1 MPa</td>
<td>95.8 2.2</td>
<td>43</td>
</tr>
<tr>
<td>4.</td>
<td>Ni/CNFs-EG-160</td>
<td>99</td>
<td>T=413 K; P$_H_2$=2MPa</td>
<td>98 -</td>
<td>36</td>
</tr>
<tr>
<td>5.</td>
<td>Pt/HCl-acidified attapulgite</td>
<td>100</td>
<td>T=323 K; P$_H_2$=2 MPa</td>
<td>100 -</td>
<td>38</td>
</tr>
<tr>
<td>6.</td>
<td>Pd (II) chelates</td>
<td>100</td>
<td>T=318 K; P$_H_2$=0.1 MPa</td>
<td>90</td>
<td>45</td>
</tr>
<tr>
<td>7.</td>
<td>PVP-M- Pt catalyst, M=La, Ce, Pr, Nd and Sm</td>
<td>100</td>
<td>T=303 k; P$_H_2$=0.1 MPa; NaOH</td>
<td>97.2 2.1</td>
<td>46</td>
</tr>
<tr>
<td>8.</td>
<td>Ionic liquid Trans PtCl$_2$; [BMIM] [BF4]</td>
<td>100</td>
<td>T=383 K; P$_H_2$=2 MPa</td>
<td>0.5</td>
<td>8</td>
</tr>
<tr>
<td>9.</td>
<td>Ni/Al$_2$O$_3$</td>
<td>100</td>
<td>T=393 K; P$_H_2$=0.1 MPa (gas phase hydrogenation)</td>
<td>100</td>
<td>47</td>
</tr>
<tr>
<td>10.</td>
<td>Pd/D, Pd/C</td>
<td>100</td>
<td>T=298 K; P$_H_2$=0.5 MPa</td>
<td>100</td>
<td>36</td>
</tr>
<tr>
<td>11.</td>
<td>Pt/C</td>
<td>100</td>
<td>T=363K; P$_H_2$=3.45 MPa; Morpholine and</td>
<td>95</td>
<td>35</td>
</tr>
<tr>
<td>Other Inhibitor</td>
<td>Temperature</td>
<td>Pressure</td>
<td>Conversion</td>
<td>Yield</td>
<td></td>
</tr>
<tr>
<td>----------------</td>
<td>-------------</td>
<td>----------</td>
<td>------------</td>
<td>-------</td>
<td></td>
</tr>
<tr>
<td>Pd/C</td>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni/Kieselguhr</td>
<td>25</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVP-Pt</td>
<td>48</td>
<td>T=303; P(_H_2)=0.1 MPa</td>
<td>99</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt/ZrO(_2), PtM/ZrO(_2), (Sm, Pr, Ce, Nd, and La)</td>
<td>49</td>
<td>T=303; P(_H_2)=0.1 MPa</td>
<td>95</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-M-P</td>
<td>50</td>
<td>T=303K; P(_H_2)=</td>
<td>99</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(M = Cu, Ca, Zn, Sn, Co)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PtM/TiO(_2), M=La, Ce, Pr, Nd and Sm</td>
<td>51</td>
<td>T=303K; P(_H_2)=</td>
<td>96</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1% Pt-S/C</td>
<td>19</td>
<td>T=363 K; P(_H_2)=0.1 MPa</td>
<td>99</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co/C</td>
<td>52</td>
<td>T=413 K; P(_H_2)=2.0MPa</td>
<td>99</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 6.2. Inhibitors for selective hydrogenation of CNB to CAN [32].

<table>
<thead>
<tr>
<th>Inhibitors, catalyst</th>
<th>Dechlorination, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morpholine, Pt/C</td>
<td>0.5</td>
</tr>
<tr>
<td>5% Morpholine Pd/C</td>
<td>~30</td>
</tr>
<tr>
<td>25% Morpholine, Pd/C</td>
<td>~30</td>
</tr>
<tr>
<td>1% Morpholine Ni/Kieselguhr</td>
<td>&gt;25</td>
</tr>
<tr>
<td>N-Methylmorpholine Pt/C</td>
<td>1</td>
</tr>
<tr>
<td>N-Ethylmorpholine Pt/C</td>
<td>1.5</td>
</tr>
<tr>
<td>3,5-Dimethylmorpholine Pt/C</td>
<td>2.5</td>
</tr>
<tr>
<td>Piperazine Pt/C</td>
<td>1</td>
</tr>
<tr>
<td>Dimethylformamide, Pt/C</td>
<td>&gt;5.0</td>
</tr>
<tr>
<td>Piperidine Pt/C</td>
<td>2</td>
</tr>
<tr>
<td>Pt-S₂/C</td>
<td>0.1</td>
</tr>
<tr>
<td>Triphenyl phosphite Pt/C</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Pd-S/C</td>
<td>96</td>
</tr>
<tr>
<td>Morpholine Pt/C + Ni(II) + Cr (III)</td>
<td>0.19</td>
</tr>
<tr>
<td>Ca(OH)₂, Rh/Al₂O₃</td>
<td>?</td>
</tr>
<tr>
<td>Ca(OH)₂, Raney Ni</td>
<td>?</td>
</tr>
<tr>
<td>MgO, Pt/C</td>
<td>0.3</td>
</tr>
</tbody>
</table>

6.1.2. Objectives:
The main objectives of this work were (i) to develop supported mono and bimetallic catalyst systems for selective hydrogenation for \( m \)-chloronitrobenzene (ii) study of effect of reaction parameters such as effect of substrate concentration, temperature, hydrogen pressure, catalyst loading on conversion of \( m \)-chloronitrobenzene and selectivity to \( m \)-chloroaniline. The stability of the catalyst was also studied by catalyst recycle experiments.
6.2. Experimental:

6.2.1. Catalyst preparation:
Details of preparation of 1% Pt/C, 10% Ni supported on carbon and Al₂O₃, and 10% Ni-
1% Pt/C catalyst are described in chapter II, section 2.2.

6.2.2. Catalyst Characterization:
The details of catalyst characterization are described in chapter II, section 2.3.

6.2.3. Catalyst activity testing:
The experimental batch setup used for the hydrogenation reaction and experimental
procedure is described in chapter II, section 2.4.2.

6.2.4. Analytical methods:
The quantitative analysis of liquid samples was performed by Hewlett-Packard GC model
6890 gas chromatograph equipped with FID. Other details of temperature programming
method (80°C → 5 min $\frac{200°C}{min}$ → 300°C → 5 min etc.) are described in chapter II,
section 2.5. Product identification was carried out by using GC and GCMS spectra as
shown in Figures 6.1 and 6.2 respectively.
Figure 6.1. Standard gas chromatograph of the reaction crude of hydrogenation of *m*-CNB

Figure 6.2. (a) GCMS spectra of Aniline
Figure 6.2. (b) GCMS spectra for nitrosochlorobenzene

Figure 6.2. (c) GCMS spectra for m-chloronitrobenzene
Figure 6.2. (d) GCMS spectra of \( m \)-chloroaniline

Figure 6.2. (e) GCMS spectra of 3,3’-dichloroazobenzene
6.3. Results and discussion:

6.3.1. Catalyst characterization:

6.3.1.1. XPS study:
Surface composition of 1% Pt/C fresh (PtF), 1% Pt/C used (PtU) and 1% Pt/C catalyst used in presence of sodium carbonate (PtUS) were characterized by XPS. The composition of various species was calculated using the intensity of an appropriate line and atomic sensitivity factor (as given by Sconfiled) [53]. Table 6.3 shows the comparison of fresh and used catalysts samples. It was observed that chlorine and nitrogen were absent in case of a fresh 1% Pt/C catalyst while, PtU and PtUS catalysts showed the presence of chlorine and nitrogen along with oxide species formation higher than that observed for fresh catalyst indicating oxidation of Pt species to some extent due to nitro compound. The used catalyst (PtU) also showed 1.65 and 3.5 times higher composition of chlorine and nitrogen respectively, than the fresh catalyst. The higher
surface concentration of chlorine species in PtU could be due to HCl formed during hydrodechlorination reaction. For the PtUS catalyst, surface concentration of chlorine has reduced substantially as compared to the PtU catalyst since the extent of dehydrohalogenation was reduced due to sodium carbonate addition.

Table 6.3. Surface compositions of catalyst (atom%) estimated by XPS for PtF, PtU used and PtUS catalysts

<table>
<thead>
<tr>
<th></th>
<th>Platinum</th>
<th>Oxygen</th>
<th>Chlorine</th>
<th>Carbon</th>
<th>Nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtF</td>
<td>0.40</td>
<td>7.70</td>
<td>0.180</td>
<td>91.72</td>
<td>-</td>
</tr>
<tr>
<td>PtU</td>
<td>0.38</td>
<td>12.94</td>
<td>2.07</td>
<td>78.28</td>
<td>5.95</td>
</tr>
<tr>
<td>PtUS</td>
<td>0.39</td>
<td>10.31</td>
<td>1.247</td>
<td>86.36</td>
<td>1.68</td>
</tr>
</tbody>
</table>

PtF : 1% Pt/C fresh catalyst  
PtU: 1% Pt/C used catalyst  
PtUS: 1% Pt/C catalyst used in presence of sodium carbonate

Figure 6.3 presents XPS spectra of PtF, PtU and PtUS catalysts in which Pt4f spectrum shows Pt in different oxidation states. For PtF and PtUS catalysts (Figure 6.3 (a) and (b)) the most intense doublet for Pt 4f7/2 and Pt 4f5/2 (71.8 and 75.1 eV) is due to metallic Pt. The second set of doublets for Pt 4f7/2 and Pt 4f5/2 (73.6 and 76.9 eV) could be assigned to the Pt (II) due to PtO or Pt(OH). The third doublet of Pt is the weakest in intensity, and was observed due to the binding energies for Pt 4f7/2 and Pt 4f5/2 (75.8 and 79.1 eV) assigned to Pt (IV) due to PtO2[54-56]. The XPS spectra of PtU catalyst (Figure 6.3 (c)) showed binding energies of 72.5 and 75.8 eV for Pt 4f7/2 and Pt 4f5/2 assigned to Pt (II) species in (NH4)2 Pt(II) Cl4 [57]. This was consistent with the activity studies in which the deactivation of the catalyst was observed hence, the formation of (NH4)2 Pt(II) Cl4 species could be due to interaction of the catalyst with the amine formed in the reaction. The second set of doublets for Pt 4f7/2 and Pt 4f5/2 (73.6 and 76.9 eV) corresponds to PtO, which could be due to mild oxidation of Pt in presence of nitro compound [55]. It was interesting to note that the peak corresponding to metallic Pt was
not observed for PtU catalyst (Table 6.4), which was also consistent with the fact that this catalyst deactivated during the 1st use.

Table 6.4. Percentage of the Pt metal species.

<table>
<thead>
<tr>
<th>Binding energy, eV</th>
<th>71.8, Pt&lt;sup&gt;0&lt;/sup&gt;</th>
<th>72.5, Pt (II)</th>
<th>73.6, Pt (II)</th>
<th>75.8, Pt (IV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtF, %</td>
<td>40.5</td>
<td>-</td>
<td>27</td>
<td>32.5</td>
</tr>
<tr>
<td>PtUS, %</td>
<td>37.21</td>
<td>-</td>
<td>32.3</td>
<td>30.47</td>
</tr>
<tr>
<td>PtU, %</td>
<td>-</td>
<td>74.3</td>
<td>25.7</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 6.3. (a) XPS of PtF catalyst
Figure 6.3. (b) XPS of PtUS catalyst

Figure 6.3. (c) XPS of PtU catalyst

Figure 6.3. XPS spectra of PtF, PtU and PtUS catalysts
The XPS spectrum of N 1s was also studied for PtU and PtUS catalysts. In both PtU and PtUS catalysts, peak at 400.5 eV corresponding to nitrogen of amine was observed. In addition to this, in case of PtU (Figure 6.4) catalyst, a peak at 404 eV was also observed which could be due to the N-O species [58].

![PtU](image)

**Figure 6.4. XPS of nitrogen spectra for PtU catalyst.**

The deposition of carbonaceous material on the catalyst surface was studied by comparing the intensity area ratio of carbon peaks of the PtF, PtU, and PtUS samples. The XPS study of carbon spectra for PtF, PtU, and PtUS catalysts showed marginal deposition of carbonaceous material in PtU catalyst as compared with the PtUS catalyst. The intensity area ratio of $I_{PtU}/I_{PtF}$ and $I_{PtUS}/I_{PtF}$ was found 1.07 and 1.01 respectively.

6.3.1.2. X-ray diffraction study:

X-ray diffraction patterns for the monometallic 10% Ni/C and bimetallic 10%Ni-1%Pt/C catalysts are presented in Figure 6.5. It could be seen that Ni/C and Ni-Pt/C catalysts exhibited the comparable diffraction patterns. For the Ni/C catalyst, typical diffraction peaks centered at $2\theta = 43.5$ (NiO), $44.5^\circ$ (Ni$^0$) were observed, which agrees well with the
face-centered cubic nickel phase [59] however, no diffraction peaks corresponding to platinum were observed due to its low concentration in the bimetallic system. By addition of Pt as a co-metal in monometallic Ni/C catalyst, the peak at 43.5° corresponding to NiO disappeared and a peak at 40° appeared indicating the stabilization of completely reduced Ni⁰ as was observed by Telkar et al. [63]. It also indicated that the catalyst Ni-Pt/C combined the crystals features of Ni and Pt, indicating the co-existence of both of them [61, 62].

![X-ray spectra of 10% Ni/C and 10%Ni-1%Pt/C catalysts](image)

**Figure 6.5. X-ray spectra of 10% Ni/C and 10%Ni-1%Pt/C catalysts**

6.3.1.3. *BET surface area measurement*:

The specific surface areas of the PtF, PtU and PtUS (after recycling tests) catalysts were determined by BET method and the results are shown in Table 6.5. A decrease in surface area of PtU and PtUS catalysts was observed as compared with PtF catalyst. A substantial decrease in surface area of the used catalyst samples could be attributed to the agglomeration and/or deposition of carbonaceous species on the catalyst surface.
Table 6.5. BET surface area of PtF, PtU and PtUS catalyst

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>PtF</th>
<th>PtU</th>
<th>PtUS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface area, m²/g</td>
<td>1087</td>
<td>513.11</td>
<td>802.13</td>
</tr>
</tbody>
</table>

6.3.2. Preliminary hydrogenation experiments:

Some initial experiments on hydrogenation of m-CNB without any additives gave several by products along with the desired product m-CAN, as per the Scheme 6.1. In these experiments, the hydrogenation reaction was monitored by hydrogen absorption as well as liquid-phase analysis as a function of time, and the various intermediates and products formed were identified as I. 3,3’-dichloroazoxybenzene, II. 3,3’-dichlorobenzene, III. 3,3’-dichlorohydrazobenzene IV. aniline and, V. m-chloroaniline. In each experiment, the final sample was analyzed by GC to calculate the conversion of m-CNB and selectivity to m-CAN. In order to achieve the highest selectivity to m-CAN, role of an additive, sodium carbonate was studied and the results are discussed below.

6.3.2.1. Catalyst performance study:

Initially the catalyst activity and stability was studied by repeated use of 1% Pt/C catalyst without using any additive, at 358 K temperature and 1.03 MPa hydrogen pressure and results are presented in Figure 6.6. As it can be seen from Figure 6.6, initially at 0.25 h of the reaction, m-CAN selectivity was found to be 42% and DAB was the major competing side product (35%), along with formation of DHAB and aniline with 45% conversion of m-CNB. As reaction proceeded, DAB undergoes further hydrogenation and selectivity to m-CAN increased 74%. Almost complete conversion of m-CNB was obtained after 0.9 h with 74% selectivity towards m-CAN. After complete conversion of m-CNB the reaction was kept for 5-10 min for complete conversion of the intermediates DAB and DHAB which showed 84% selectivity towards the m-CAN. During the recycle study, loss of catalyst activity was observed. XPS study (section 6.2.2.1) clearly showed the presence of amine, N-O and chloride species on the surface of the PtU catalyst. N-O species have higher affinity towards the metal surface [47] and it may remain on the active sites of Pt metal surface due to which catalyst activity was retarded. Another
possibility of catalyst deactivation is change in Pt\(^0\) active species (71.8 eV) to Pt (II) (72.5 eV) for PtU, which may be due to the formation of (NH\(_4\))Pt(II)Cl\(_4\) species during the reaction.

![Graph showing the conversion and selectivity of m-CNBr, m-CAN, Aniline, DHAB, and DAB over time.](image)

**Figure 6.6. Hydrogenation of m-CNBr to m-CAN**

Reaction conditions: m-CNBr, 0.0317 mol; temperature, 358 K; hydrogen pressure, 1.03 MPa; 1% Pt/C catalyst, 0.050 g; MeOH, 95 mL; agitation speed, 1000 rpm.

The liquid phase hydrogenation of m-CNBr was then carried out using Pt/C catalyst in presence of sodium carbonate as an additive by keeping the reaction conditions same as in case of Pt/C without additive. Figure 6.7 clearly shows the increase in selectivity from 84 to 93% as compared to the hydrogenation carried out in absence of an additive. The catalyst activity and stability was studied by repeated use of 1% Pt/C catalyst at 358 K and 1.03 MPa hydrogen pressure and the results are presented in Figure 6.8. After
completion of the reaction, reactor was cooled down to room temperature and stirring was stopped for 10 min to settle down the catalyst. Reaction crude from upper layer was taken out from liquid sampling valve by ensuring the catalyst remained in the reactor and then fresh charge was added to continue to the next reaction. The catalyst activity was found to be consistent even after third recycle.

Figure 6.7. Hydrogenation of $m$-CNB to $m$-CAN in presence of sodium carbonate

Reaction conditions: $m$-CNB, 0.0317 mol; temperature, 358 K; hydrogen pressure, 1.03 MPa; 1%Pt/C catalyst, 0.050 g; water, 0.5 mL; sodium carbonate, 0.02%; MeOH, 95mL; agitation speed- 1000 rpm.
Figure. 6.8. Catalyst recycle study in hydrogenation of m-CNB to m-CAN

Reaction conditions: m-CNB, 0.0317 mol; temperature, 358 K; hydrogen pressure, 1.03 MPa; 1%Pt/C catalyst, 0.050 g; MeOH, 95 mL; sodium carbonate, 0.02%; water, 0.5 mL; agitation speed- 1000 rpm.

6.3.3. Effect of reaction parameters:
Further work on effects of various reaction parameters on conversion of m-CNB and selectivity to m-CAN was studied over 1% Pt/C catalyst. Table 6.6 shows the range of various process parameters studied in the present work.
Table 6.6. Range of operating conditions

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Partial pressure of hydrogen</td>
<td>1.03-2.06 MPa</td>
</tr>
<tr>
<td>2</td>
<td>Temperature effect</td>
<td>338 – 378 K</td>
</tr>
<tr>
<td>3</td>
<td>Substrate concentration</td>
<td>0.317- 0.952 mol</td>
</tr>
<tr>
<td>4</td>
<td>Catalyst loading</td>
<td>0.025-0.100 g</td>
</tr>
<tr>
<td>5</td>
<td>sodium carbonate concentration</td>
<td>0.02 -0.08 %</td>
</tr>
<tr>
<td>6</td>
<td>Total reaction volume</td>
<td>$1.0 \times 10^{-4}$ m$^3$</td>
</tr>
<tr>
<td>7</td>
<td>Agitation speed</td>
<td>1000 rpm</td>
</tr>
</tbody>
</table>

6.3.3.1. Effect of substrate concentration:
Effect of concentration of $m$-CNB was studied in the range of 0.317 to 0.952 mol by keeping constant hydrogen pressure, temperature and catalyst loading and the results are shown in Figure 6.9. With increase in concentration of $m$-CNB from 0.317 to 0.952 mol, the catalytic activity expressed in TOF, decreased from 1.4 to $1.1 \times 10^6$ h$^{-1}$, while selectivity to $m$-CAN remained almost the same at 94-93% with 6% formation of aniline. The linear decrease in TOF with increase in substrate concentration indicates a negative order dependence with respect to the substrate.
Figure 6.9. Effect of substrate concentration

Reaction conditions: temperature, 358 K; hydrogen pressure, 1.03 MPa; 1%Pt/C catalyst, 0.050 g; MeOH, 85 mL; sodium carbonate, 0.02%; water, 0.5 mL; agitation speed, 1000 rpm.

6.3.3.2. Effect of temperature:
Effect of temperature on the selectivity to m-CAN was studied by varying the temperature from 338 to 378 K by keeping constant hydrogen pressure and catalyst loading and the results are shown in Figure 6.10. It was observed that increase in temperature from 338 K to 378 K led to the increase in formation of aniline from 6 to 8% along with decrease in selectivity to m-CAN from 94 to 90%. It was also observed that as temperature increased, catalytic activity also increased from 0.573 to 1.77 x 10^6 h⁻¹.
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Figure 6.10. Effect of temperature

Reaction conditions: \( m \)-CNB, 0.0317 mol; hydrogen pressure, 1.03 MPa; 1\%Pt/C catalyst, 0.050 g; MeOH, 95mL, sodium carbonate, 0.02 \%; water, 0.5 mL; agitation speed, 1000 rpm.

6.3.3.3. Effect of pressure:
The effect of hydrogen pressure on activity and selectivity in hydrogenation of \( m \)-CNB was studied by varying the hydrogen pressure from 1.03 to 2.03 MPa, keeping constant temperature, substrate, catalyst loading and the results are presented in Figure 6.11. It was observed that \( m \)-CAN selectivity decreased from 94 to 90 \% with increase in hydrogen pressure from 1.03 to 2.06 MPa, with simultaneous increase in the formation of aniline from 5 to 8\%. It was also found that as pressure increased from 1.03 to 2.06 MPa, the catalytic activity also increased by almost two folds i.e. from 1.4 to 2.66 \( \times 10^6 \) h\(^{-1} \).
6.3.3.4. Effect of catalyst loading:

Effect of catalyst loading on selectivity to \( m \)-CAN was studied by varying the catalyst loading in a range of 0.025 g to 0.1 g at 358 K and 1.03 MPa hydrogen pressure and the results are shown in Figure 6.12. It was found that at lower catalyst loading (0.025 g) the selectivity towards the \( m \)-CAN was 96 % and as the catalyst loading increased from 0.050 to 0.100 g, the selectivity towards \( m \)-CAN decreased from 94 to 88% with increase in AN selectivity. TOF also increased from 0.38 to \( 7.5 \times 10^6 \) h\(^{-1}\) with increase in catalyst loading.
Figure 6.12. Effect of catalyst loading

Reaction conditions: \( m\)-CNB, 0.0317 mol; temperature, 358 K; hydrogen pressure, 1.03 MPa, water, 0.5 mL; sodium carbonate, 0.02 %; MeOH, 95 mL; agitation speed, 1000 rpm.

6.3.3.5. Effect of concentration of sodium carbonate:
To minimize the dehalogenation and to increase the selectivity towards the \( m\)-CAN the effect of concentration of sodium carbonate in hydrogenation of \( m\)-CNB was studied by varying the concentration of sodium carbonate in a range of 0.02 to 0.08% (w/w) while keeping other reaction parameters constant. As can be seen from Figure 6.13, with increase in concentration of sodium carbonate from 0.02 to 0.06%, selectivity to \( m\)-CAN also increased from 93 to ~96% while it remained same with further increase in sodium carbonate concentration upto 0.08%.
Selectivity  

TOF  

Sodium bicarbonate concentration, %  

Selectivity, %  

TOF, (10^6), h⁻¹  

0.02 0.04 0.06 0.08  

80 82 84 86 88 90 92 94 96  

Figure 6.13. Effect of concentration of sodium carbonate  

Reaction conditions: \( m \)-CNB, 0.0317 mol; temperature, 358 K; hydrogen pressure, 1.03 MPa; 1% Pt/C catalyst, 0.050 g; water, 0.5 mL; MeOH, 95 mL; agitation speed, 1000 rpm.  

Role addition of a co-metal (Pt) to monometallic Ni/C catalyst in increasing the selectivity by minimizing the dechlorination was also studied and the results are discussed below.  

6.3.4. Supported nickel mono and bimetallic catalysts:  

Effect of supported mono- and bimetallic nickel catalysts on the selectivity to \( m \)-CAN was studied at 358 K temperature and 1.03 MPa hydrogen pressure and the results are presented in Figure 6.14. A dramatically different activity and selectivity trends were observed for mono- and bimetallic supported nickel based catalysts for the hydrogenation of \( m \)-CNB. Monometallic Ni supported on alumina and carbon catalysts showed 50 and 70% conversion with 78 to 82% selectivity respectively towards the \( m \)-CAN. While, for a bimetallic 10% Ni-1% Pt/C catalyst more than 99% selectivity to \( m \)-CAN was achieved.
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with complete conversion of \( m \)-CNB. Based on XRD results (section 6.2.2.2) it was concluded that the catalytic activity was affected by the change in electronic structure of the nickel metal by addition of co-metal i.e. Pt. The addition of Pt to Ni/C catalyst caused the stabilization of completely reduced Ni\(^0\) which is mainly responsible for the hydrogenation reaction. It is important to note that nitro compounds are known to be good oxidants hence, stabilization of Ni\(^0\) phase is critical in the catalytic hydrogenation nitro compounds.

![Figure 6.14. Activity, selectivity performance of nickel based mono and bimetallic catalysts](image)

**Figure 6.14. Activity, selectivity performance of nickel based mono and bimetallic catalysts**

Reaction conditions: \( m \)-CNB, 0.0317 mol; hydrogen pressure, 1.03 MPa; temperature, 358 K; catalyst loading, 0.050 g; MeOH, 95 mL; agitation speed, 1000 rpm; water, 0.5 mL.

### 6.3.5. Hydrogenation of substituted chloronitrobenzene:

Hydrogenation of substituted chloronitrobenzene like \( o \)-, \( p \)-, \( m \)-CNB were also studied using 10%Ni-1%Pt/C catalyst at 358 K and 1.03 MPa hydrogen pressure and the results are shown in Figure 6.15. It can be seen from Figure 6.15 that the selectivity to CAN of
all substrates was found to be >99% but as the substrate varied from \(o-, p-, m\)-CNB the catalytic activity also varied i.e. from 7.5 to 3.5 \(x \times 10^{-1} \text{ h}^{-1}\) due to the induction effect of –Cl at various positions of nitrobenzene.

![Figure 6.15. Effect of substituted chloronitrobenzene](image)

Reaction conditions: CNB, 0.0317 mol; temperature, 358 K; hydrogen pressure, 1.03 MPa; 10%Ni-1%Pt/C catalyst, 0.050 g; MeOH, 95 mL; water, 0.5 mL; agitation speed, 1000 rpm;

6.4. Conclusion:
The liquid phase hydrogenation of \(m\)-CNB to \(m\)-CAN carried at 358K and 1.03 MPa pressure using 1% Pt/C catalyst without any additive gave 84% selectivity to \(m\)-CAN due to the dehydrohalogenation reaction. During the catalyst recycle study, activity was lost due to the formation of \((\text{NH}_4)\text{Pt(II)}\text{Cl}_4\), amine and N-O species on the surface of catalyst which was observed by XPS study. The improvement in selectivity \(m\)-CAN from 84 to 94% was observed by addition of sodium carbonate in Pt/C catalyst. Bimetallic 10%Ni-1% Pt/C catalyst also showed the two fold enhancement in the activity and gave 99%
selectivity to \textit{m}-CAN. This was due to the stabilization of Ni$^{\circ}$ state by incorporation of co-metal, platinum. The order of hydrogenation rate of substituted CNB is \textit{m} - \textit{p} - \textit{o} - with >99\% selectivity towards the CAN.
6.5. References:

49. X. C. Meng, Y. J. Cheng, S. X. Cai, F. Y. Zhao in 2nd international IUPAC conference on green chemistry, Russia, 14-19 September (2008).