CHAPTER 4
CHAPTER 4

Transfer hydrogenation reactions using prepared catalysts

Section I

Nitrobenzene reduction

Section II

Chalcone hydrogenation

Publications:

Hydrogenation of trans chalcone under transfer hydrogenation conditions using Pd on carbon catalyst prepared from agro waste material, communicated to Synthetic communications.
4.1 Introduction

Hydrogenation Reactions
A great variety of hydrogenation reactions are carried out industrially. These range from large-scale continuous catalytic operations in petroleum refineries dealing with streams of complex composition to small-scale batch operations in the pharmaceutical and fine chemical industry where a very precise hydrogenation step is often desired. Hydrogenation reactions catalysed by platinum group metals can be defined as structure sensitive or structure insensitive.

Structure sensitive reactions:
Structure sensitive reactions occur preferentially on specific metal sites and thus appear to favour particular particle sizes. For example, the hydrogenation of nitrobenzene, using methanol as a solvent, appeared to have an increased activity for catalysts exhibiting larger platinum particles compared to those with smaller particles, indicating that the reaction favours the plane surfaces of the metal rather than edge or corner sites. This has been observed to be true in case of Pd catalyst as well.

Structure insensitive reactions
Structure insensitive reactions exhibit a linear relationship between the metal dispersion and the catalyst activity, indicating that any increase in metal area provides an increase in catalytic surface for adsorption and reaction. Thus the activity does not depend on the crystal planes or particle size of the metal but only on the amount of metal exposed. Reactions including the hydrogenation of cyclohexene and cyclooctene, benzene and 1,3 butadiene are recognised as being structure insensitive. However, the rules governing the structure sensitivity or insensitivity of a reaction are not stringent and the reaction conditions, preparation method and support material have been observed to alter these properties.
In its molecular state hydrogen is unreactive in terms of a hydrogenating/reducing agent owing to the strength of the H-H bond, which has dissociation energy of 434 kJmol⁻¹. It is therefore, essential to activate the hydrogen, using a metal catalyst, by dissociative chemisorption.

**Adsorption of Hydrogen on Metal Surfaces**

The activation of hydrogen via adsorption has been well described in terms of potential energy curves (Fig 4.1)⁸.

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**Fig. 4.1**: Potential-energy curves for the adsorption of hydrogen on a metal surface with a schematic representation of the adsorbed states.
The horizontal line represents the zero of potential energy, that is, a molecule far from the surface. As a hydrogen molecule approaches the metal surface, the potential energy decreases to a shallow minimum which corresponds to the enthalpy of physisorption, which is small as there is no activation energy. The chemisorption curve, C, starts at a potential energy of 434 kJ mol\(^{-1}\), corresponding to the dissociation energy of the hydrogen molecule. The curve then drops to a minimum, corresponding to the enthalpy of chemisorption as the molecule is stabilised by the chemisorption bond. The distance from the surface is approximately 0.15 nm (that is, \(r_M + r_H\)). The activation energy for chemisorption, \(E_A\), arises because the two curves intersect above the potential energy zero and is dependent on the distance of the minima from the surface, which is approximately the atomic radii of both species. It is also evident that chemisorption can occur without providing the necessary energy to atomise the hydrogen molecule. Physical adsorption permits the hydrogen molecule to get quite close to the surface without having to acquire much energy. At the intersection of the curves, the transition from physisorption to chemisorption occurs. This is the “transition state” for chemisorption which is described (Fig. 4.2).

![Chemisorption Diagram](image)

**Fig. 4.2:** Chemisorption of hydrogen on to a metal surface.

This process occurs on numerous metals which are capable of hydrogenation reactions with a variety of reactants. The catalytic performance is determined by the metal component and a metal is chosen based on its ability to increase
the rate of reaction, which is partly determined by its ability to dissociate hydrogen, and its inability to complete unwanted reactions.

The hydrogenation activity generally decreases in the following sequence, Pd>Rh>Pt>Ru>Ni>Co>Fe>Cu. The noble metals are typically more active than the base metals and can be used at lower concentrations under milder conditions. However, specific metals are noted to be particularly useful in certain hydrogenation reactions. Palladium is typically the preferred metal for the hydrogenation of acetylenes, olefins, carbonyls in aromatic aldehydes and ketones, aromatic and aliphatic nitro compounds, reductive alkylation, hydrogenolysis and hydrodehalogenation reactions. Platinum is typically the preferred metal for selective hydrogenation of halonitroaromatics and reductive alkylations. Rhodium is used for the hydrogenation of aromatic rings and olefins whilst ruthenium is used for the hydrogenation of aromatic rings and aliphatic aldehydes and ketones. The choice of metal is also seen to cause changes in selectivity.

Selective Hydrogenation

Selectivity to a desired product via catalysis is an important industrial application for the production of organic chemicals. In many systems the use of homogeneous catalysts is favoured as they are generally more effective. However, many heterogeneous systems are seen to provide selectivity toward desired products. In certain hydrogenation systems, for example, the selective hydrogenation of α,β-unsaturated aldehydes, the use of different noble metals is seen to alter the hydrogenation product.

The use of iridium and osmium supported catalysts for the hydrogenation of both crotonaldehyde and cinnamaldehyde yields high selectivity of the unsaturated alcohol product. The same hydrogenation reactions demonstrate only moderate selectivity when the supported metal used is platinum, ruthenium or cobalt whilst palladium, rhodium and nickel present poor selectivity to the desired product. These metal effects are a result of the expansion of their d-bands which allows for selective adsorption. The larger the d-band, the stronger is 4 electron repulsion with the C=C bond. This results
in the adsorption of the C=C bond being less favourable than C=O bond adsorption\textsuperscript{10}.

The choice of metal also affects the selectivity of the hydrogenation of buta-1,3-diene, which yields but-1-ene, but-2-ene (cis and trans) or butane. The yield of but-1-ene was determined by the electronic structure of the metal. The filling of d-bands through the metal series appears to reduce the formation of π-allylic transition states which inhibits the formation of but-2-ene favouring the production of but-1-ene\textsuperscript{11}. Thus the yield of but-1-ene follows the series Pt>Ir>Re>W>Ta.

In addition to the effect of different metals, there are also geometric effects caused by different metal surfaces which can alter the selectivity of a hydrogenation reaction.

Activity and selectivity in hydrogenation reactions may also be affected by the support material used. Different support materials exhibit different steric and electronic effects. This can affect the adsorption of reactant molecules and result in altered activity and selectivity. This is due to certain adsorbed states which are favoured and hence certain products are formed.

Simple steric effects such as pore size can promote the adsorption of the reactant on to the metal surface through a particular mode, which favours the formation of only one product. A comparison of cinnamaldehyde hydrogenation using platinum supported on activated carbon and zeolite Y revealed that the selectivity to the unsaturated alcohol product was higher in the zeolite supported catalyst than in the carbon supported platinum\textsuperscript{10}. This is the result of the narrow pore size of the zeolite, only permitting adsorption of the aldehyde via the on-top mechanism, thus favouring the C=O hydrogenation.

The variable pore size of carbon exerted no such constraints. Electronic effects, resulting from a change in charge density on the metal due to the support, may alter the favoured adsorption mode due to either repulsive interactions or backbonding interactions resulting in the formation of a favoured product. Richard \textit{et al.} demonstrated that platinum on graphite favoured the formation of the unsaturated alcohol in cinnamaldehyde hydrogenation whilst carbon supports favoured the saturated aldehyde,
despite the catalysts being prepared in the same way and exhibiting similar particle sizes\textsuperscript{10}.

The graphite support was considered to increase the electron density on the metal which decreased the likelihood of adsorption via the C=C bond unlike the carbon support. Similar findings were observed for basic zeolite supports whereby the selectivity to the alcohol was enhanced as a result of increased charge density on the metal from the basic support material\textsuperscript{10}.

The nature of the support surface has also been demonstrated to alter the selectivity of supported metal catalysts. An investigation of the hydrogenation of crotonaldehyde using platinum supported on a variety of carbon blacks, exhibiting different surface groups, revealed the selectivity towards alcohol was altered depending on the surface groups present on the carbon\textsuperscript{12}. The different nature of surface functional groups alters a polarising effect experienced by the carbonyl group of the unsaturated aldehyde. This results in the C=O bond being either more or less activated for preferential reaction, leading to an enhanced selectivity.

The most common method of altering catalyst selectivity is by the addition of a promoter. The role of a promoter is varied whereby the promotion effect can be the result of steric effects on the metal or the support or by electronic effects on the metal.

There are two mechanisms which are thought to account for the promoting effect of a second metal (promoter) in the hydrogenation of \(\alpha,\beta\)-unsaturated aldehydes. Electropositive metal \(B\) (promoter) acts as an electron-donor ligand that increases the electron density on the metal \(A\) (main metal) thus decreasing the binding energies, particularly that of the C=C bond thus favouring C=O hydrogenation.

Electropositive metals, or oxidised metal species of \(A\) act as electrophilic or Lewis sites for the adsorption and activation of the C=O bond via the lone pair of the oxygen atom.

There is also the role of the individual reaction conditions with regards to the selectivity of a hydrogenation reaction. Factors including temperature, reaction pressure, solvent and catalyst pre-treatment have all been recognised as possible variables for the enhancement of reaction selectivity\textsuperscript{10}. 134
Transfer Hydrogenation

Molecular hydrogen, a gas of low molecular weight and therefore high diffusibility, is easily ignited and presents considerable hazards, particularly on the large scale.

In transfer Hydrogenation, use of hydrogen donors changes the scenario. Here, no gas containment is necessary, no pressure vessels are needed, and simple stirring of solutions is required\textsuperscript{13}.

Potentially, transfer methods can enhance selectivity in reduction reactions. With a catalyst and molecular hydrogen, catalyst, solvent, and temperature are possible variations. With hydrogen donors, a new dimension is opened up because the choice of hydrogen donor can affect the reaction through its competitive adsorption onto the catalyst surface. Thus, rate and specificity of reduction are amenable to control through choice of hydrogen donor.

Hydrogen donors

For suitable hydrogen-donor properties, it seems clear that compounds containing hydrogen bonded to elements or groups with similar electronegativity act as best hydrogen donors. Formic acid and formates, phosphinic acid and phosphinatea, phosphorous acid and phosphites, hydrazine, hydrides of boron, aluminum, silicon, tin, alcohol\textsc{es}, amines and hydrocarbons are all hydrogen donors in catalytic transfer reduction. An added advantage is gained when the products of the decomposing donor have large negative enthalpies of formation. Thus, CO\textsubscript{2} from formic acid and N\textsubscript{2}, from hydrazine provide added driving force to the reactivity of these substances as hydrogen donors.

Solvents

Solvents can alter the course of reaction in transfer hydrogenation. Many times solvent can work as hydrogen donors themselves. The effect of solvent on the system cinnamic acid acceptor-a-phellandrene donor was also studied\textsuperscript{25}.

The following general conclusions seem warranted. Below acritical temperature, dependent on the donor (\textit{ca.} 90\textdegree for limonene), little or no
hydrogen transfer occurs. Above this threshold temperature, the reaction rate increases rapidly and appears to be independent of the nature of the solvent as far as hydrocarbons, acids, or ethers are involved. Alcohols and amines, which have the capability of reacting themselves with the catalyst, appear to retard the reaction somewhat.

When using alcohols as solvents, it must be considered that these can also serve as hydrogen donors, especially when Raney nickel is used as catalyst. It is therefore possible that hydrogen transfer takes place from solvent to donor, thereby reducing the reaction rate. Amines are also dehydrogenated by Raney nickel and a similar problem may occur.

Catalysts

Use of both homogeneous and heterogeneous catalyst have been employed to carry out transfer hydrogenation reactions. Problem associated with homogeneous catalyst is the difficulty in their recovery from reaction products. This can be overcome by attaching some insoluble solid, mainly polymer to it. One of the advantages of homogeneous catalyst lies in use of chiral ligands to attain higher stereo selectivity.

The most active catalysts for heterogeneous transfer hydrogenation are based on palladium metal. Catalyst may be pure bulk metal, finely divided, dispersed on various supports such as carbon, Barium sulphate. A brief comparison between advantages/disadvantages of heterogeneous and homogeneous catalyst is shown:

<table>
<thead>
<tr>
<th>Heterogeneous catalyst</th>
<th>Homogeneous catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Easily separable from reaction media</td>
<td>Separation is difficult</td>
</tr>
<tr>
<td>Selectivity to particular product is obtained by changes in catalyst properties by variation in support</td>
<td>Change in ligand gives selectivity towards particular product</td>
</tr>
<tr>
<td>Need somewhat severe conditions to operate</td>
<td>Need mild conditions to operate</td>
</tr>
<tr>
<td>Catalyst loading required to carry out reaction is higher.</td>
<td>Low loadings are sufficient.</td>
</tr>
<tr>
<td>Poison tolerance is better</td>
<td>Poor poison tolerance</td>
</tr>
</tbody>
</table>
Reaction Conditions
Transfer Hydrogenation reactions are generally carried out at mild conditions as compared to pressure hydrogenation. Homogeneous catalysts require temperature between 20 and 80 °C while heterogeneous catalyst require temperature between 100 and 200 °C.

Reactions using catalyst

Nitrobenzene reduction
Nitrobenzene reduction under pressure is used as catalyst characterization test. The same conversion can be brought about by transfer hydrogenation conditions. Instead of gaseous hydrogen, ammonium formate is used as hydrogen donor. The effect of increasing catalyst loading is clearly evident with increase in rate of reduction.

Chalcone Hydrogenation
Chalcone is an aromatic ketone and an enone that forms the central core for a variety of important biological compounds, which are known collectively as chalcones or chalconoids. Benzylideneacetophenone is the parent member of the chalcone series.
Two reducible functional groups present in chalcone makes it ideal to study selectivity of catalyst towards any of it in identical conditions. This can also express relation between the parameters of the catalyst and its selectivity. Kinetic study helps in understanding various routes/ sequences taken by particular catalyst in reduction of functional groups.
Section I
Nitrobenzene reduction

4.1.2 Review of Literature

Nitrobenzene reduction under hydrogen pressure has been carried out as one of the activity test for catalyst. It is the standard test carried out by catalyst manufacturers to test activity of catalyst and to check batch to batch variations in manufacturing.

The effectiveness of catalytic transfer hydrogenation of aromatic nitro compounds to the corresponding amino compounds, utilizing unsaturated hydrocarbons as hydrogen donors, was demonstrated years ago. Subsequent general application of this mild, convenient technique in synthesis was slow. Following the earlier reported, much wider use of hydrazine as hydrogen donor for reduction of nitro groups with a variety of metal catalysts has been reviewed\(^{22,23}\) and both types of donor have been utilized. The use of cyclohexene as hydrogen donor with catalyst-to-substrate ratios of 1:100 in earlier work resulted in inordinately long reaction times and many nonspecific reductions were recorded. In a search for more active hydrogen donors for transfer hydrogenation, it was found that formic, phosphinic (hypophosphorous), and phosphorous acids or their salts in the presence of a catalyst would reduce nitro compounds to amines in high yield\(^{24}\) in short time. As compared to earlier hydrogen donors.

4.1.3 Present work

In the present work, nitrobenzene reduction was carried out using prepared catalyst viz. C800, PIP, MIP and COM1 with ammonium formate as hydrogen donor and methanol as solvent. The reaction was carried at 60 °C over 6 hrs for all the catalysts. Kinetic study was carried out by drawing samples after certain interval of time. Effect of catalyst loading was also studied. The reaction was followed by analysing the samples on gas chromatography. Aniline was the only product formed. Results of catalyst prepared on agro
waste material carbons were compared with that prepared on commercial carbon. Some catalysts show encouraging results.

4.1.4 Results and Discussion

Steady increase in reaction rate was observed with increase in catalyst loading. This confirms that nitrobenzene reaction is structure insensitive towards metal particle shape and depends upon the available flat surface of the Pd metal. Catalyst prepared on commercial catalyst COM1 was superior in performance over the prepared catalyst. It achieves ~68% conversion after 6 hr of reaction. At lower loadings (0.05 gm of catalyst), C800 shows no reaction even after 6 hrs while MIP (14.87%) and PIP (26.77%) exhibit increasing degree of activity (Fig. 4.3).

When the catalyst loading is increased to 0.1 g, C800 carbon started exhibiting activity. The order of increment in activity of catalyst is MIP, C800, PIP and COM1. The COM1 catalyst achieved 100% conversion of nitrobenzene to aniline in 6 hrs while 48.45 % conversion is observed with C800. Conversion with MIP is 30.5% and that with PIP is 60.07% (Fig 4.4). This is result of increase in available surface for reaction due to increase in catalyst loading by two times.
Increase in catalyst loading to 0.2 g improves the rate of conversion further. Catalyst PIP shows performance at par with COM1 catalyst (Fig 4.5). All the catalysts achieve conversion of more than 80 % after 6 hrs. Conversion of 82 % is achieved with C800 and MIP.
4.1.5 Conclusions
Rate of nitrobenzene reduction is directly proportional to catalyst loading. Catalyst with better dispersion of metal over support viz. PIP gives faster reaction rate compared to C800 and MIP which has larger metal particle size. 80 % of the conversion takes place in first 30 min of reaction irrespective of catalyst loading.

4.1.6 Materials and methods
Prepared catalysts viz. C800, PIP, MIP and COM1 were used to carryout reactions. Chemicals used were of AR grade sourced from Alfa Aiser. Reaction was carried out in Radley's carousel, simultaneously, using hard glass test tubes. Various samples drawn during the kinetic study were analysed by gas chromatography (GC).

4.1.7 Experimental
Nitrobenzene (16 ml of 6 % v/v solution of in methanol) was charged in a test test tube. Ammonium formate (0.5 g) was added. A magnetic needle was placed in the test tube. The test tube was covered with lead and placed in Radley's carousel. Stirring was carried out at 200 RPM. The temperature was increased to 60 °C. At this point 0.5 ml sample was drawn for kinetic study. This is the sample at 0 time. Catalyst was added to stirring solution in one go. Further samples were drawn at intervals of 30 min, 100 min, 180 min and 360 min. Samples drawn were first evaporated over a steam bath to dryness. 0.5 ml of DM water was added along with 0.5 ml of chloroform. Chloroform layer was separated from aqueous part to get pure organic matter. This helps in removing unreacted ammonium formate. Chloroform layer was dried over anhydrous sodium sulphate and further used for analysis on GC. Area under the curve method was utilized to find out concentration of unreacted nitrobenzene and formed aniline. The compounds were identified against retention time on GC graphs of standard nitrobenzene and aniline.
Section II
Chalcone hydrogenation

4.2.2 Review of Literature

4.2.3 Present work

Trans Chalcone was chosen as the substrate. Presence of multiple functional groups in Chalcone makes it ideal substrate to check selectivity of catalyst towards hydrogenation of particular functional group. Hydrogenation was carried out under transfer hydrogenation conditions using ammonium formate as hydrogen donor and methanol as solvent. Reaction was monitored over a two hrs by drawing samples at certain intervals. Reaction scheme is as follows –

Chalcone Hydrogenation

\[ R = \text{CH}_3, \text{OCH}_3, \text{Cl}, \text{F etc} \]

[Description of reaction scheme and product formation]

All possible products:
- a: Only \( \alpha, \beta \)-C=C get reduced to \(-\text{C}-\text{C}\)
- b: Only \( \text{C}=\text{O} \) get reduced to \(-\text{OH}\)
- c: Both \( \text{C}=\text{C} \) and \( \text{C}=\text{O} \) get reduced
- d: Both \( \text{C}=\text{C} \) and \( \text{C}=\text{O} \) get complete reduced
- e: Complete reduction of \( \text{C}=\text{C} \) and \( \text{C}=\text{O} \)
4.2.4 Results and Discussion

Increasing loadings of catalyst C600 are tried so as to find out the loading where there is reasonable conversion of feedstock i.e. trans Chalcone. This loading is used for all the other catalyst.

Purity of feedstock is determined to be 99.04 % on HPLC (Retention time 8.63 min). Two additional peaks along with main peak are observed at RT 4.21, 8.35 min with concentration of 0.21% and 0.76 % (Fig 4.6).

![HPLC graph of transChalcone](image)

Fig. 4.6: HPLC graph of transChalcone

When C600 carbon is used to carry out hydrogenation under transfer conditions, maximum conversion of chalcone is 69.42 %. Majority of the conversion takes place in first 25 min of reaction. Along with hydrogenated product, three other unknown impurities are generated viz IMP1, IMP4 and IMP5 at RT 4.02, 8.21 and 8.35 min respectively. IMP 5 at RT 8.35 has its origin in chalcone which further increased during course of reaction.

There are two reducible functional groups in Chalcone. In enone system, double bond is in conjugation with ketone. Literature survey revealed the formation of saturated alcohol in many cases. The main reason is ascertain to be electron with drawing effect of carbon support on deposited metal, reducing repulsion between metal and electron rich C=C bond. This results in
more adsorption of C=C bond on catalyst support thus resulting in its hydrogenation, which favours selective hydrogenation of test molecule. Progress of reaction is tabulated (Table 1, Fig 4.7).

**Table 1:** Progress of reaction using C600 catalyst

<table>
<thead>
<tr>
<th>Retention time (min)</th>
<th>RM (%)</th>
<th>Hydrogenated product (%)</th>
<th>IMP1 (%)</th>
<th>IMP4 (%)</th>
<th>IMP5 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>99.04</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.76</td>
</tr>
<tr>
<td>25</td>
<td>22.56</td>
<td>28.73</td>
<td>2.47</td>
<td>19.31</td>
<td>26.93</td>
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<tr>
<td>60</td>
<td>22.44</td>
<td>35.29</td>
<td>7.96</td>
<td>28.11</td>
<td>6.12</td>
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<tr>
<td>90</td>
<td>25.31</td>
<td>44.20</td>
<td>4.48</td>
<td>18.00</td>
<td>8.01</td>
</tr>
<tr>
<td>120</td>
<td>29.62</td>
<td>51.10</td>
<td>3.41</td>
<td>12.41</td>
<td>3.46</td>
</tr>
</tbody>
</table>

**Fig. 4.7:** Progress of reaction using C600 catalyst

Data clearly indicates that the catalyst is not effective in converting the chalcone fully. Also many side reactions are taking place indicating unselective nature of the catalyst.

When C800 catalyst is used to carry out reaction, great improvement in the catalyst activity is observed with 100 % conversion of chalcone within first 25 min of reaction. Hydrogenated product ketone (RT 8.71 min) is the major product (99.04 %) with formation of two impurities at RT 8.35 min (IMP5) and
at RT 9.31 min (IMP7) towards end of the reaction. Progress of reaction is tabulated (Table 2, Fig 4.8).

**Table 2**: Progress of reaction using C800 catalyst

<table>
<thead>
<tr>
<th>Retention time (min)</th>
<th>RM (%)</th>
<th>Hydrogenated product (%)</th>
<th>IMP5 (%)</th>
<th>IMP7 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>99.04</td>
<td>0.00</td>
<td>0.76</td>
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</tr>
<tr>
<td>25</td>
<td>0.00</td>
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<td>60</td>
<td>0.00</td>
<td>99.60</td>
<td>0.40</td>
<td>0.00</td>
</tr>
<tr>
<td>90</td>
<td>0.00</td>
<td>97.37</td>
<td>0.00</td>
<td>0.41</td>
</tr>
<tr>
<td>120</td>
<td>0.00</td>
<td>99.04</td>
<td>0.51</td>
<td>0.45</td>
</tr>
</tbody>
</table>

**Fig. 4.8**: Progress of reaction using C800 catalyst

With PIP catalyst, hydrogenated product ketone (RT 8.71 min) is again the major product with concentration of 77.23% after 120 minutes of reaction as compared to 51.1 % with that of C600 catalyst. This shows improvement in catalyst activity when the support used for catalyst preparation is activated with phosphoric acid as against carbon support obtained by only carbonization. There is increment in the concentration of IMP 5 (RT 8.35 min) which is present in RM, along with hydrogenated product ketone. Progress of reaction is tabulated (Table 3, Fig. 4.9).
Table 3: Progress of reaction using PIP catalyst

<table>
<thead>
<tr>
<th>Retention time (min)</th>
<th>RM (%)</th>
<th>Hydrogenated product (%)</th>
<th>IMP5 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>99.04</td>
<td>0.00</td>
<td>0.76</td>
</tr>
<tr>
<td>25</td>
<td>22.46</td>
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<td>60</td>
<td>12.35</td>
<td>71.07</td>
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<td>10.88</td>
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<td>120</td>
<td>11.65</td>
<td>77.23</td>
<td>11.12</td>
</tr>
</tbody>
</table>

Fig. 4.9: Progress of reaction using PIP catalyst

MIP catalyst shows improved activity over PIP catalyst with 100 % of the chalcone getting converted in 60 min of reaction. The hydrogenated product ketone is the major product (RT 8.71 min). One more impurity is formed at RT 7.27 min at proportion of 1.64 %.

So there is improvement in activity and selectivity in catalyst prepared on mid impregnated carbon over catalyst made from pre impregnated carbon. Treatment with acid improves the selectivity of catalyst towards hydrogenated product (RT 8.71 min) when comparison is made in C600 and PIP, MIP. All these catalysts are prepared from carbon which are carbonized to 600 °C maximum but treatment with activating agents help in improving selectivity. Progress of reaction is tabulated (Table 4, Fig. 4.10).
Table 4: Progress of reaction using MIP catalyst

<table>
<thead>
<tr>
<th>Retention time (min)</th>
<th>RM (%)</th>
<th>Hydrogenated product (%)</th>
<th>IMP7 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
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<td>0.00</td>
</tr>
<tr>
<td>25</td>
<td>3.14</td>
<td>84.83</td>
<td>1.05</td>
</tr>
<tr>
<td>60</td>
<td>0.00</td>
<td>97.75</td>
<td>1.54</td>
</tr>
<tr>
<td>90</td>
<td>0.00</td>
<td>98.46</td>
<td>1.54</td>
</tr>
<tr>
<td>120</td>
<td>0.00</td>
<td>98.36</td>
<td>1.64</td>
</tr>
</tbody>
</table>

Fig. 4.10: Progress of reaction using MIP catalyst

Catalyst prepared from potassium hydroxide treated carbon MIK shows selectivity towards hydrogenated product ketone (RT 8.71 min) but the impurities generated during the reaction are different from those generated by catalyst prepared from phosphoric acid treated carbons as described for PIP and MIP catalysts (IMP 5 and IMP 7 at RT 8.35 min and 9.31 min respectively). During first 25 minutes, 100 % conversion of the chalcone is observed with hydrogenated product ketone as major product (80.23 %) with formation of two impurities at RT 4.02 min (IMP1), 8.21 min (IMP4). It is observed that the hydrogenated product subsequently gets converted into these two impurities increasing their proportion. This is indication of higher
activity of catalyst which subsequently results into initiation of side reactions decreasing selectivity. Progress of reaction is tabulated (Table 5, Fig 4.11).

Table 5: Progress of reaction using MIK catalyst

<table>
<thead>
<tr>
<th>Retention time (min)</th>
<th>RM (%)</th>
<th>Hydrogenated product (%)</th>
<th>IMP1 (%)</th>
<th>IMP4 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>99.04</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
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<td>0.00</td>
<td>80.09</td>
<td>4.87</td>
<td>15.05</td>
</tr>
<tr>
<td>60</td>
<td>0.00</td>
<td>65.67</td>
<td>7.59</td>
<td>26.74</td>
</tr>
<tr>
<td>90</td>
<td>0.00</td>
<td>64.97</td>
<td>6.92</td>
<td>28.11</td>
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<tr>
<td>120</td>
<td>0.00</td>
<td>59.78</td>
<td>8.19</td>
<td>32.03</td>
</tr>
</tbody>
</table>

Fig. 4.11: Progress of reaction using MIK catalyst

When catalyst made from commercial carbon is used, it is observed that, many impurities are formed along with hydrogenated product ketone (RT 8.71 min). Hydrogenated product ketone is subsequently converted to another product (RT 7.95 min). Impurities at RT 5.6 min (IMP10), 6.43 min (IMP3), 8.21 min (IMP4), 8.98 min (IMP6), 9.65 min (IMP11) and 10.34 min (IMP12) are formed along with 8.35 min originating from Chalcone (IMP5), during the reaction and their proportion keeps on fluctuating suggesting them to be inter convertible.
It appears that the catalyst is too active and leads to multiple side reactions upon passage of time. This could also be because of high loading of catalyst for reaction. Progress of reaction is tabulated (Table 6, Fig. 4.12).

**Table 6:** Progress of reaction using MIK catalyst

<table>
<thead>
<tr>
<th>Retention time (min)</th>
<th>RM (%)</th>
<th>Hydrogenated product (%)</th>
<th>MW212</th>
<th>IMP3</th>
<th>IMP4</th>
<th>IMP5</th>
<th>IMP6</th>
<th>IMP10</th>
<th>IMP11</th>
<th>IMP12</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>99.04</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.76</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>25</td>
<td>0.00</td>
<td>80.23</td>
<td>9.55</td>
<td>2.74</td>
<td>1.77</td>
<td>2.46</td>
<td>3.26</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>60</td>
<td>0.00</td>
<td>11.01</td>
<td>41.68</td>
<td>7.76</td>
<td>5.78</td>
<td>6.75</td>
<td>11.42</td>
<td>8.2</td>
<td>0.06</td>
<td>7.4</td>
</tr>
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<td>90</td>
<td>0.00</td>
<td>0.00</td>
<td>39.48</td>
<td>9.52</td>
<td>7.34</td>
<td>8.16</td>
<td>14.07</td>
<td>10.71</td>
<td>1.12</td>
<td>8.56</td>
</tr>
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<td>120</td>
<td>0.00</td>
<td>6.05</td>
<td>42.07</td>
<td>7.68</td>
<td>5.81</td>
<td>7.22</td>
<td>12.19</td>
<td>9.15</td>
<td>1.17</td>
<td>7.96</td>
</tr>
</tbody>
</table>

**Fig. 4.12:** Progress of reaction using COM1 catalyst
The major product formed during reaction is hydrogenated product (RT 8.71) which is formed by reduction of double bond. It is characterised by LC-MS where molecular wt of the product is found to be higher than RM by 2. LC-MS (Fig.4.34) exhibits a molecular ion peak at m/z 268 [M+1]⁺. The hydrogenated ketone product is characterized using spectral techniques. ^1H-NMR spectrum (Fig. 4.35) illustrates a most down field merged doublet at δ 7.95(d, J= 8 Hz, 2H) for aromatic H1 and H5 protons which are at ortho position to carbonyl group. Another downfield doublet of doublet is noticed at δ 7.55 (dd, J= 8 and 7.96Hz, 1H) for H3 proton. Another aromatic protons indicate a doublet of doblet at δ 7.42 (dd, J= 8 and 1 Hz, 2H) for H4 and H2 protons.

Other five aromatic protons viz. H6, H7, H8, H9, and H10 appear as cluster between δ7.27 to δ 7.35. Up field methylene protons have indicated a triplateat δ 3.28 (t, J= 6 Hz, 2H) for aliphatic H11, another upfield triplate is noticed at δ 3.05 (t, J= 6 Hz, 2H) for H12 methylene protons.

4.2.5 Conclusions

All carbons show electron with drawing effect on the deposited metal by which C=C is attracted towards the metal surface and is predominantly hydrogenated (hydrogenated product ketone RT 8.71 min). It also appears that it is kinetically preferred product as it is readily formed with all the catalyst in the beginning of the reaction. If catalyst is highly active e.g. COM1, MIK and MIP, this products gets converted to other impurities.

Catalyst prepared with carbons prepared at lower temperature viz. C600, PIP, MIP, are less active as compares catalyst prepared with carbons prepared at higher temperature viz. C800, MIK.

Excess loading of catalyst during reaction can reduce selectivity of highly active catalyst when contact time with reactants is increased.
4.2.6 Materials and methods

Trans Chalcone used for the reaction was sourced from Alfa Aiser. All the solvents used were of AR grade sourced from Alfa Aiser. The reaction was initially traced on TLC and then on HPLC.

4.2.7 Experimental

0.050 g Chalcone was weighed and transferred to 25 ml round bottom flask with magnetic needle. 0.235 g Ammonium formate was added to it followed by 16 ml of AR grade methanol. The flask was placed in oil bath kept on magnetic stirrer cum heater. Water condenser was attached on top of the flask. The temperature was set at 60 °C and stirring was initiated.

When temperature was reached, Chalcone and ammonium formate were dissolved, 1 ml of sample was drawn and kept in glass vial. This is sample at zero time. 0.4 g of catalyst (on dry basis) was added to the reaction flask and stop watch started.

1 ml sample was drawn at the interval of 25 min, 60 min, 90 min and 120 min. The sample was filtered through Whatman filter paper no 42. The filtrate was evaporated to dryness on water bath. 1 ml of DM water was added to it. The product was extracted using 2 portions of ethyl acetate and these portions were subjected to HPLC analysis. Identification of the hydrogenated product ketone was done by LC-MS. Various HPLC graphs are shown below (Fig 4.13 to 4.33).
Fig. 4.13: HPLC graph C600 25 min

Fig. 4.14: HPLC graph C600 60 min
Fig. 4.15: HPLC graph C600 90 min

Fig. 4.16: HPLC graph C600 120 min
Fig. 4.17: HPLC graph C800 25 min

Fig. 4.18: HPLC graph C800 60 min
Fig. 4.19: HPLC graph C800 90 min

Fig. 4.20: HPLC graph C800 120 min
Fig. 4.21: HPLC graph PIP 25 min

Fig. 4.22: HPLC graph PIP 60 min
Fig. 4.23: HPLC graph PIP 90 min

Fig. 4.24: HPLC graph PIP 120 min
Fig. 4.25: HPLC graph MIP 25 min

Fig. 4.26: HPLC graph MIP 60 min
Fig. 4.27: HPLC graph MIP 90 min

Fig. 4.28: HPLC graph MIP 120 min
Fig. 4.29: HPLC graph COM1 25 min

Fig. 4.30: HPLC graph COM1 60 min
Fig. 4.31: HPLC graph COM1 90 min

Fig. 4.32: HPLC graph COM1 120 min
Fig. 4.33: HPLC graph Hydrogenated product ketone
Spectral data

Fig. 4.34: Mass Spectrogram of triazole product

Fig. 4.35: NMR of hydrogenated ketone product
References