CHAPTER IV

One Pot Synthesis of $p$-Aminophenol from Nitrobenzene
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Introduction

In recent years, the increasing demand of new chemical processes has led to a growing need for the development of environmentally acceptable and sustainable manufacturing processes. New discoveries in the area of catalysis have improved several important reactions e.g. hydrogenation, isomerization, oxidation, acylation, reductive amination, hydroformylation etc., which are frequently used in chemical industry. The environmentally benign catalytic processes have replaced several vast generating conventional counterparts. The reduction of organic compounds via catalytic hydrogenation is one of those. The reduction of organic compounds is a key step in the synthesis of several chemicals, pharmaceuticals etc.,

Conventionally, the reduction has been carried out using stoichiometric amounts of reducing agents such as sodium borohydride, lithium aluminiumhydride, hydrazine hydrate and metal-acid. The major disadvantages of these conventional reduction processes are: (a) use of stoichiometric amounts of reducing agents posing serious waste disposal problems due to generation of large quantities of undesired inorganic salts, (b) difficulties in the separation of products from the reaction mixture and its effect on reducing the product yield, (c) non-reusability of reagents, and (d) corrosion problems. Replacement of conventional reduction methods by the catalytic hydrogenation is perhaps one of the most significant achievements of modern catalysis. Table 1. summarizes a few important examples of industrially relevant catalytic hydrogenation processes. Hydrogenation of nitro compounds to amines has wide ranging applications in the synthesis of several key intermediates and fine chemicals.
Table 1. Liquid phase hydrogenation of various functional groups under heterogeneous conditions

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Catalyst</th>
<th>Product</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2,4-dinitrotoluene</td>
<td>Pd/Alumina</td>
<td>toluenediamine</td>
<td>intermediate for TDA and pharmaceuticals</td>
</tr>
<tr>
<td>2</td>
<td>chloronitrobenzene</td>
<td>PtS/C</td>
<td>chloraanilene</td>
<td>Pharmaceutical and dyes</td>
</tr>
<tr>
<td>3</td>
<td>p-isobutylacetophenone</td>
<td>Pd/C, Ni/HY</td>
<td>p-isobutylphenyl ethanol</td>
<td>Ibuprofen intermediate</td>
</tr>
<tr>
<td>4</td>
<td>glucose</td>
<td>Raney Ni</td>
<td>sorbitol</td>
<td>pharmaceuticals</td>
</tr>
<tr>
<td>5</td>
<td>adiponitrile</td>
<td>Raney Ni</td>
<td>hexamethylene diamine</td>
<td>intermediate for Nylon 6,6</td>
</tr>
<tr>
<td>6</td>
<td>2,8-dichloroadenosine</td>
<td>Pd/BaSO₄</td>
<td>adenosine</td>
<td>CNS drug</td>
</tr>
<tr>
<td>7</td>
<td>4-chloroacetylcatechol</td>
<td>Pd/C</td>
<td>adrenaline</td>
<td>pharmaceuticals</td>
</tr>
<tr>
<td>8</td>
<td>4-aminoacetylphenol</td>
<td>Pd/C</td>
<td>Octopamine</td>
<td>pharmaceuticals</td>
</tr>
<tr>
<td>9</td>
<td>acetophenone</td>
<td>Ru/Al₂O₃</td>
<td>1-phenylethanol</td>
<td>pharmaceuticals</td>
</tr>
</tbody>
</table>

The conventional process for reduction of nitro compounds (commonly known as Béchamp process) employed stoichiometric amounts of Fe-acid as the reducing agent producing almost equivalent amount of Fe-FeO sludge as a byproduct. Apart from the serious waste disposal problems, the Béchamp process also suffers from the difficulties in the separation of desired products from the reaction mass and use of corrosive reagents like acids. The catalytic hydrogenation using supported metal catalysts (gas-liquid-solid multiphase catalytic reactions) has emerged as a cleaner alternative to the conventional Béchamp process with better selectivity and yields. Although, these novel catalytic reactions have been employed in several instances, there is still a wide scope for their extension to several other products.
However, the success of such extension will depend on proper choice of the catalyst and availability of information relevant to fundamental issues like catalysis, kinetics, mass-transfer effects, adsorption characteristics etc. Such information will not only help in the design of optimized catalysts to achieve maximum yield of the desired products with minimum side reactions, but will also be a key factor in the development of efficient catalytic processes.

Several examples of catalytic hydrogenation studies have been published previously from catalysis and reaction engineering viewpoint, but systems involving complex multiphase catalysis (gas-liquid-liquid-solid reactions) demand further detailed investigations. One such example is the hydrogenation of nitrobenzene to \( p \)-aminophenol in a four-phase catalytic reaction system.

\( p \)-Aminophenol is a commercially important chemical intermediate used in the manufacture of several analgesic and antipyretic drugs such as paracetamol, acetaldehyde, phenacetin etc. shown in Figure 1. Apart from pharmaceuticals, \( p \)-aminophenol is also used in the manufacture of various industrial dyes. It is a strong reducing agent and is also marketed as a photographic developer under the trade names of Activol, Azol, Certinal, Citol, Paranol, Rodinol, Unal and Ursol-P, either alone or in combination with hydroquinone. The oxalate salt of \( p \)-aminophenol, marketed under a trade name of Kodelon, is used as a corrosion inhibitor in paints and anticorrosion-lubricating agent in two-cycle engine fuels. It is also used as a wood stain, imparting rose like color to timber, and as a dyeing agent. \(^{13}\)
Figure 1. Drugs and pharmaceuticals using p-aminophenol as an intermediate
Because of its industrial importance, synthesis of $p$-aminophenol has attracted considerable interest. Industrially, $p$-aminophenol is manufactured by the hydrogenation of nitrobenzene or $p$-nitrophenol. Several other methods e.g. chlorophenol amination, $^{14}$ hydroquinone amination, $^{15}$ electrolytic reduction of nitrobenzene and $p$-nitrophenol $^{16}$ etc. have also been reported, though these are not industrially practiced. Most of the information available on these reactions is patented and there are very few published papers dealing with scientific issues related to catalysis and kinetics of these reactions.

State of art

The preparation of $p$-aminophenol from nitrobenzene involves a two-step reaction carried out in a single reactor. In the first step, nitrobenzene is reduced to phenyl hydroxylamine, which undergoes a Bamberger rearrangement in the presence of an aqueous acid to give $p$-aminophenol. $^{17}$ Formation of aniline (via further hydrogenation of phenylhydroxylamine) is a major side reaction. $^{18}$

The intermediate phenylhydroxylamine can be isolated and separately subjected to the rearrangement using acid. Alternatively, both the steps (i.e. reduction and rearrangement) can also be accomplished in a single operation. Bassford $^{19}$ reported the preparation of $p$-aminophenol from nitrobenzene using a two-step process. In the first step, nitrobenzene was reduced to phenylhydroxylamine using Zn/NH$_4$Cl as the reducing agent in the aqueous phase. After the reaction, zinc hydroxide was removed by filtration and washed with warm water. In the second step, the filtrate and washings were acidified with sulfuric acid and heated to 80°C to convert phenylhydroxylamine to $p$-aminophenol. $p$-Aminophenol thus obtained remained in aqueous solution as its hydrosulfate salt. This solution was cooled and made slightly alkaline by adding aqueous ammonia and further cooled to recover solid $p$-aminophenol in 86% yield (Scheme 1).
Bean\textsuperscript{20} reported that nitrobenzene could be converted to \( p \)-aminophenol in good yields (75\%) in the presence of aluminum flakes and an aqueous solution of a mineral acid. He also observed that sulfuric acid was more effective than other acids (phosphoric acid and HCl) to get higher yields of \( p \)-aminophenol. Several other nitro compounds were also converted to corresponding 4-hydroxylamine derivatives using this procedure (Scheme 2).

Hydrogenation of \( p \)-nitrophenol to \( p \)-aminophenol is an alternative method for the preparation of \( p \)-aminophenol. The starting material i.e. \( p \)-nitrophenol is expensive.
compared to nitrobenzene, which is a drawback of this route. Nitration of chlorobenzene to 4-nitrochlorobenzene and its subsequent hydrolysis with NaOH at elevated temperatures gives 4-nitrophenol \(^{21}\) (Scheme 3).

![Scheme 3](image)

In this conventional method, the \(p\)-aminophenol formed by reduction of \(p\)-nitrophenol is converted to the water-soluble sodium aminophenolate by adding sodium hydroxide before Fe-FeO sludge is separated from the reaction mixture. Acidification of the solution precipitates \(p\)-aminophenol, a procedure performed in the absence of air because the salts are easily susceptible to oxidation in aqueous solutions. \(^{13}\) Other reagents consisting of Zn, Al, Sn etc. \(^{22}\) have also been reported for the reduction of \(p\)-nitrophenol to \(p\)-aminophenol. The obvious drawback of these reduction processes is the formation of huge amounts of undesirable metal oxide sludge, which poses serious pollution problem. Catalytic hydrogenation of \(p\)-nitrophenol obviates the problem of sludge formation associated with the conventional reduction method. Several reports describe the preparation of \(p\)-aminophenol by catalytic hydrogenation of \(p\)-nitrophenol.
using supported metal catalysts e.g. Pd/C, Pt/C, supported Ni, and colloidal Rh, Pd and Pt catalysts.

\[
\text{Scheme 4}
\]

Goswami et al. investigated the reduction of \(\rho\)-nitrophenol using hydrazine as a reducing agent and Raney nickel catalyst in ethanol-water solvent. The effect of various reaction parameters like solvent, hydrazine hydrate and catalyst and promoter concentrations was also investigated. The reaction was reported to be first order with hydrazine and nitro compound concentration. The apparent hydrogenation rate constant was dependent on the nature of substrate, dielectric constant and ionic strength of solvent and catalyst amount (Scheme 5).
Chandalia et al. 27 investigated the hydrogenation of \( p \)-nitrophenol to \( p \)-aminophenol using 1% Pd/C catalyst in 95% ethanol solvent at 80°C. The effect of agitation frequency, catalyst loading, \( p \)-nitrophenol concentration, and temperature on the hydrogenation rate and yield of \( p \)-aminophenol was studied. It was concluded that the mass transfer of hydrogen from gas to bulk liquid phase (G-L) and liquid phase to catalyst particle (L-S) were the rate controlling steps. (Scheme 6)

Bean et al. 28 prepared several aminophenols by direct amination of hydroquinone in presence of aqueous ammonia and ammonium salts (phosphates or arsenates). In a typical procedure, the mixture of hydroquinone, diammonium phosphate, aqueous ammonia and water was heated in an autoclave at 200°C for 12 hrs. The resulting solution was filtered and treated with conc. hydrochloric acid to neutralize the mixture. After cooling, \( p \)-aminophenol crystallized out from the reaction medium. The yield of \( p \)-aminophenol was 60% (Scheme 7).
p-Aminophenol was also prepared by amination of p-chlorophenol with ammonia in the presence of CuCl and CaCl₂ as catalysts (Scheme 8). Conversion of p-chlorophenol is as high as 94.2 % could be achieved with 89.6 % selectivity to p-aminophenol. ¹⁴

The electrochemical reduction method has attracted increasing interest because it eliminates the pollution problems associated with the conventional metal-acid reduction routes. The electrolysis of nitrobenzene, phenylhydroxylamine, or azoxybenzene in deoxygenated acid solutions, using graphite or copper-mercury cathodes at potential differences of −300 to −600 mV and temperatures of 60-90°C, were reported to yield p-aminophenol in the range of 65-99 %.¹⁶ Aniline was again obtained as a major by-product. Several parameters e.g. nature of electrode, metal additives, electrolytes, agitation, flow properties through cells affected the selectivity to p-aminophenol. Electrolytic oxidation of aniline to p-aminophenol by electrochemically...
activated molecular oxygen via direct electron transfer from cathode, in the presence of iron compounds, was also reported.

The key issue in the preparation of \( p \)-aminophenol by catalytic hydrogenation of nitrobenzene was lower yield of \( p \)-aminophenol, since further hydrogenation of the intermediate phenylhydroxylamine to aniline was the main competing reaction. Formation of other side products such as \( o \)-aminophenol and \( 4,4' \)-diaminodiphenylether has also been reported. \(^{13} \) Spiegler \(^{29,30} \) reported that the use of surfactants (quaternary and non-quaternary ammonium compounds) gave enhancement in the yield of \( p \)-aminophenol during the catalytic hydrogenation of nitrobenzene. Several quaternary ammonium salts such as dodecyltrimethyl ammonium chloride, octadecyl trimethyl ammonium chloride were found to increase the yield of \( p \)-aminophenol. Non-quaternary amine compounds e.g. triethylamine sulfate, tributyl amine sulfate were also investigated. It was concluded that rate/yield obtained in the presence of quaternary ammonium compounds was higher than that with non-quaternary compounds. Brown et al. \(^{31} \) observed that certain non-ionic surfactants such as polyethers and polyols could be used instead of quaternary ammonium compounds. Use of chloride surfactants resulted in the formation of chloroanilines as impurities. This was overcome by use of sulfate salts \(^{32} \) or oxide type ammonium salts. \(^{33} \) The maximum yield of \( p \)-aminophenol obtained using quaternary ammonium compound (C-cetyl betaine) as surfactant was 98%. \(^{30} \)

The type of the acid used for rearrangement is an important factor in the preparation of \( p \)-aminophenol by catalytic hydrogenation of nitrobenzene. The key step in this reaction is the Bamberger rearrangement of the intermediate phenylhydroxylamine. Henke \(^{34} \) reported that sulfuric acid was the most effective acid for rearrangement of phenylhydroxylamine to \( p \)-aminophenol. For example, use of hydrochloric acid and phosphoric acid gave poor yields of \( p \)-aminophenol (less than 6-
7% as compared to that obtained using sulfuric acid (57%). Lee et al.\textsuperscript{35} investigated the effectiveness of various organic acids in addition to sulfuric acid in the rearrangement step (Table 2).

Table 2: Effect of organic acid promoters on the selectivity to p-aminophenol

<table>
<thead>
<tr>
<th>Organic acid</th>
<th>Reaction time (h)</th>
<th>Selectivity (%)</th>
<th>p-aminophenol (%)</th>
<th>Aniline (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>5</td>
<td>67.8</td>
<td></td>
<td>18.6</td>
</tr>
<tr>
<td>Methane sulphonic acid</td>
<td>3</td>
<td>70.5</td>
<td></td>
<td>17.2</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>3</td>
<td>74.8</td>
<td></td>
<td>18.3</td>
</tr>
<tr>
<td>Formic acid</td>
<td>2.5</td>
<td>83.3</td>
<td></td>
<td>16.3</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>4</td>
<td>77.1</td>
<td></td>
<td>18.2</td>
</tr>
<tr>
<td>Trifluoro acetic acid</td>
<td>4</td>
<td>79.2</td>
<td></td>
<td>16.6</td>
</tr>
</tbody>
</table>

Reaction conditions: Nitrobenzene: 12.3 gm; 3\% Pt/C: 0.015gm; water: 120 gm; sulfuric acid: 13.5 \% w/w; temperature: 353 K; H2 pressure: 4.2 kg/cm2; organic acid: 0.5 gm.

Rylander\textsuperscript{36} observed that the addition of dimethylsulfoxide (DMSO) to the reaction system in the absence of any acid also increased the selectivity to phenylhydroxylamine (Scheme 9) up to 86\%. The phenylhydroxylamine accumulation was found to be much lower on Pd catalyst as compared to Pt catalyst. It had been observed that during competitive hydrogenation of nitrobenzene and hydroxylamine over Pt and Pd catalyst, nitrobenzene was reduced preferentially over Pt whereas phenylhydroxylamine over Pd.\textsuperscript{37}
Komastu et al. reported the hydrogenation of nitrobenzene to p-aminophenol in presence of zeolite and Pt/ZSM-5 catalyst under vapor phase conditions. The highest percentage of p-aminophenol obtained was 7% yield with 21% selectivity \(^{38}\) (Scheme 10).

Ahn et al. \(^{39}\) reported the hydrogenation of nitrobenzene in a biphasic system using platinum supported on mesoporous carbon and aqueous sulphuric acid with small amounts of DMSO or N,N-dimethyl-n-dodecylamine as additive (Scheme 11). N,N-dimethyl-n-dodecylamine acts as surfactant in the reaction. They achieved 84% selectivity with good conversions.
Present work

In the present chapter, the preparation and characterization of sulphated zirconia and Pt/ZrO₂ and their use in hydrogenation of nitrobenzene to p-aminophenol was described. Pt/ZrO₂ was well characterised by X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS), temperature programmed reduction (TPR) and scanning electron microscopy (SEM).

RESULTS AND DISCUSSION
Catalyst preparation

A series of sulphated zirconias were investigated. Among them, two zirconia samples (references 1077-30 and 0999) supplied by MEL Chemicals, U.K were sulphated. These are designated as MEL-XZ0707 and MEL 999/1 respectively. Another zirconia sample obtained from LOBA Chemie was sulphated and this sample was designated as Loba -S. A lab-made zirconia was prepared by hydrolysis of ZrOCl₂ (LOBA Chemie, India.) at a pH=10. The solid obtained after filtration was sulphated by treatment with a 1 N solution of sulphuric acid, followed by drying and calcination at 650°C (denoted as ZrSAD1). Another sulphated catalyst, ZrSAD3, was prepared by dissolving the hydrous gel in sulphuric acid, followed by drying to obtain a hydrated zirconium sulphate. The sulphated zirconia (ZrSAD3) was calcined in air at different temperatures between 550°C and 650°C. The catalysts, Loba -S, Sulphonated silica, MEL-XZ0707 and MEL 999/1 were used after calcination in air at 625°C. The final calcination temperature was obtained with a linear programming rate of 2 °C/min. ⁴⁰

Supported Pt catalysts were prepared using zirconia, sulphated zirconia, titania or a MgLaO mixed oxide described elsewhere ⁴¹ as carrier. 2% or 1%Pt were introduced using the method of impregnation at incipient dryness, from aqueous solutions of
chloroplatinic acid. The resulting solids were dried overnight at 110°C, calcined in air at 400°C, then reduced in an H₂ flow at 250°C. A commercial 1% Pt/C was also used as received.

Characterization of the catalysts

The XRD pattern of ZRSAD1 and ZRSAD3 were similar. ZRSAD3 exhibits the composition and the XRD pattern of zirconium sulphate up to 600°C. The characterization of the acidities of the solid acids has been reported in chapter II. 42,43 The modification of the parameters of the preparation allows to tune the surface properties of sulphated zirconias. The X-ray diffraction pattern of the calcined sample (Figure 2) shows the presence of an intense peak at 2θ=30 characteristic of the tetragonal structure, and the absence of any peak at 2θ=28.2 characteristic of a monoclinic structure.44

Figure 2. X-ray diffraction pattern of the sulphated zirconia used as catalyst
The solid used as support is zirconia, as evidenced from the XRD spectrum (Figure 3a). After loading with Pt, an amorphous phase was observed by XRD (Figure 3b), after reduction the original pattern of zirconia was restored (Figure 3c). The XPS analysis of the unreduced Pt/ZrO₂ sample by XPS gave a spectrum containing a doublet at 73.6 (Pt 4f₁/₂) and 77 ev (Pt 4f₃/₂) (Figure 4a), characteristic of cationic Pt, while after reduction the presence of the doublet at 71.4 and 74.7 (Figure 4b) may be attributed to metallic platinum. The TPR data shows the cationic platinum species converted to metallic platinum at 250 °C (Figure 5). The electron micrographs of the Pt/ZrO₂ catalysts show a relatively homogeneous distribution of particles of about 3 nm. (Figure 6)
Figure 4a: XPS of Pt 4f for unreduced Pt/ZrO₂.

Figure 4b: XPS of Pt 4f for reduced Pt/ZrO₂.
Figure 5: TPR profile of unreduced Pt/ZrO$_2$

Figure 6. Electron micrographs Pt/ZrO$_2$ catalysts.
Figure 7. Schematic diagram of hydrogenation of nitrobenzene to p-aminophenol and aniline

Exploratory study of the reaction

An exploration was first performed on the possible substitution of sulphuric acid by solid acids using ZRSAD1, sulphated zirconia calcined at 650°C, and DMSO as promoter and the results are reported in Table 3. In the presence of DMSO, PAP is formed both on Pt/C and Pt/TiO2, showing that these supports indeed exhibit some acidity. The selectivity is significantly increased on Pt/TiO2, and PHA is also detected with a selectivity of about 12%, which indicates that the overall process is controlled by the acid catalysed rearrangement of PHA. The number of acid sites can be increased adding a solid acid in a mechanical mixture. Using DMSO as additive, the reaction is promoted by the addition of an acidic zeolite such as BEA. The interesting point is that
using a sulphate as solid acid, DMSO can be omitted. As illustrated in the Table 3 the conversion and selectivity then increase and the yield in PAP is significantly improved. Due to the coupling of reactions, the balance of the two functions has to be respected: the comparison of the results with different amounts of Pt catalyst shows that a large amount of Pt favours the hydrogenation of NB to aniline, with a large loss of selectivity to PAP. The support of Pt has little importance, as long as Pt is dispersed. It can be chosen in a large variety of supports, either hydrophobic such as carbon, acidic or basic.

Another aspect was the choice of the solvent: the original work of Rylander et al on the hydrogenation of nitrobenzene to phenylhydroxylamine was performed in ethanol as solvent, and this solvent was therefore investigated. The results were very poor, since the conversion in a mixture methanol/water = 70:30 reached only 6.6% after 1 h of reaction, with a selectivity to PAP of 77 %, compared to 30% of conversion and 83% selectivity in pure water. The isomerization of PHA is therefore slower in methanol, and this inhibition is attributed to the fact that water is required to maintain the solid acid in the protonic form, which is needed for the Bamberger rearrangement.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Without DMSO</th>
<th>With DMSO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conv (%)</td>
<td>PAP sel</td>
</tr>
<tr>
<td>1%Pt/C (0.1g)</td>
<td>27.4^a</td>
<td>0</td>
</tr>
<tr>
<td>Pt/TiO_2 (0.1g)</td>
<td>36^a</td>
<td>27</td>
</tr>
<tr>
<td>Pt/C (0.13g) + BEA zeolite (1g)</td>
<td>17.8^a</td>
<td>86</td>
</tr>
<tr>
<td>1%Pt/C (0.01g) + ZRS(0.5g)</td>
<td>62^b</td>
<td>98</td>
</tr>
<tr>
<td>2%Pt/ZrO_2 (0.01g)+ZrS(0.5g)</td>
<td>85^b</td>
<td>83</td>
</tr>
<tr>
<td>2%Pt/TiO_2 (0.01g) +ZrS (0.5g)</td>
<td>78^b</td>
<td>82</td>
</tr>
<tr>
<td>2% Pt/MgLaO (0.05g )+ZrS(0.5g)</td>
<td>98.6^b</td>
<td>7.9</td>
</tr>
<tr>
<td>2% Pt/MgLaO (0.01g )+ZrS(0.5g)</td>
<td>75^b</td>
<td>77</td>
</tr>
</tbody>
</table>

Conversions after a- 7h or b-6h of reaction, with 0.01 g of Pt catalyst.
Effect of the amount of Pt on the catalytic properties

If the type of support has little influence on the catalytic results, the balance between hydrogenating/acid sites is very important. The Pt loading on the support has been changed from 0.1% to 0.5% using cationic exchange from Pt ammonia complex, and the activity measured at 80°C, 3.8 bars, with different amounts of Pt/ZrS catalyst (0.01, 0.1 and 0.3g) keeping the amount of ZrS constant (0.1g). The catalytic results after 1h of reaction are reported in Table 4. Decreasing the amount of Pt from 1% to 0.5 has no effect either on rate or selectivity. Increasing the amount of Pt catalyst from 0.01 to 0.03 g increases the conversion by 3, as expected, with a constant selectivity. A decrease of the Pt loading to 0.1% induces an increase of activity. This increase is linked to a better dispersion of Pt at low loading. This proposal is consistent with the observation of a low activity of the catalyst prepared by wet impregnation from the chloride salt. The comparison of last two experiments shows that the amount of ZrS cannot be decreased below 0.1g without loss of conversion and selectivity. With the lower amount of acid catalyst, PHA appears in the products; therefore isomerisation is not fast enough to convert all the intermediate.

Table 4. Effect of the amount of Pt in the mechanical mixture on the distribution of products.

<table>
<thead>
<tr>
<th>Pt catalyst (g)</th>
<th>% Pt/ZrO₂</th>
<th>ZrSAD-3A (g)</th>
<th>NB Conv</th>
<th>PHA</th>
<th>PAP</th>
<th>AN</th>
<th>PAP Sel</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>2.0</td>
<td>0.5</td>
<td>13.7</td>
<td>0.0</td>
<td>12.2</td>
<td>1.5</td>
<td>88.9</td>
</tr>
<tr>
<td>0.01</td>
<td>1.0</td>
<td>0.1</td>
<td>6.0</td>
<td>0.0</td>
<td>5.8</td>
<td>0.2</td>
<td>97.4</td>
</tr>
<tr>
<td>0.01</td>
<td>0.5</td>
<td>0.1</td>
<td>5.2</td>
<td>0.0</td>
<td>5.1</td>
<td>0.1</td>
<td>97.2</td>
</tr>
<tr>
<td>0.03</td>
<td>0.5</td>
<td>0.1</td>
<td>17.8</td>
<td>0.0</td>
<td>17.4</td>
<td>0.4</td>
<td>97.9</td>
</tr>
<tr>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>17.8</td>
<td>0.0</td>
<td>17.3</td>
<td>0.3</td>
<td>97.2</td>
</tr>
<tr>
<td>0.1</td>
<td>0.1</td>
<td>0.05</td>
<td>12.9</td>
<td>0.1</td>
<td>10.9</td>
<td>1.5</td>
<td>84.5</td>
</tr>
</tbody>
</table>
Kinetics of the reaction

Effect of the concentration of nitrobenzene

It has been reported earlier that the hydrogenation of chloronitrobenzene obeyed a Langmuir-Hinshelwood mechanism in which both reactants competed for adsorption. The rate as a function of concentration then goes through a maximum. It is tried to check this mechanism for the present reaction, measuring the initial rate as a function of the concentration of nitrobenzene. The results, reported in Figure 8, indeed agree with those of chloronitrobenzene. In both cases a maximum is observed and a clear decrease of activity is noticed at the higher concentrations.
Figure 8. Variation of the initial rate as a function of the initial concentration, for reactions at 80°C and 10 bars of hydrogen.

Comparison of different solid acids

It was reported earlier that the Bamberger rearrangement was very sensitive to the nature of the solid acid; therefore an influence could be expected for the hydrogenation of nitrobenzene to PAP. The comparison of a series of solids is reported on Table 4. The results are given after 4 h at 80°C, using a reaction mixture consisting of NB 3.0 mL, water 75.0 mL, and 0.01g of 2% Pt/MgLaO mixed with 0.5 g of solid acid. As illustrated in this Table, the temperature of calcinations has a significant influence on the catalytic
properties. In particular, high temperature calcinations, which induces strong acid properties is here unfavourable since an increase of conversion is observed but the selectivity drops down. The low selectivity of sulphated titania and EA zeolite was expected from their behaviour in Bamberger rearrangement.

Table 4. Comparison of different solid acids used in mechanical mixture with Pt/MgLaO.

<table>
<thead>
<tr>
<th>Solid acid</th>
<th>NB conv.</th>
<th>PHA</th>
<th>PAP</th>
<th>AN</th>
<th>PAP select.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO₂ 922/1</td>
<td>28.2</td>
<td>5.6</td>
<td>2.2</td>
<td>20.3</td>
<td>7.9</td>
</tr>
<tr>
<td>ZrSAD-3A calc 700°C</td>
<td>75.6</td>
<td>13.9</td>
<td>2.2</td>
<td>20.3</td>
<td>2.2</td>
</tr>
<tr>
<td>ZrSAD-3A calc 675°C</td>
<td>25.3</td>
<td>5.0</td>
<td>5.6</td>
<td>14.7</td>
<td>22.2</td>
</tr>
<tr>
<td>ZrSAD-3A calc 650°C</td>
<td>43.0</td>
<td>0.4</td>
<td>36.0</td>
<td>6.4</td>
<td>83.6</td>
</tr>
<tr>
<td>ZrSAD-3A calc 550°C</td>
<td>20.9</td>
<td>0.0</td>
<td>19.7</td>
<td>1.1</td>
<td>94.1</td>
</tr>
<tr>
<td>TiO₂ sulf</td>
<td>62.5</td>
<td>5.2</td>
<td>0.5</td>
<td>56.8</td>
<td>0.9</td>
</tr>
<tr>
<td>Sulf 922-1</td>
<td>31.2</td>
<td>3.6</td>
<td>7.1</td>
<td>20.5</td>
<td>22.8</td>
</tr>
<tr>
<td>HBEA zeol</td>
<td>23.7</td>
<td>2.1</td>
<td>2.7</td>
<td>18.8</td>
<td>11.5</td>
</tr>
<tr>
<td>ZrS999/1</td>
<td>81.1</td>
<td>13.6</td>
<td>0.4</td>
<td>66.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Using the best catalyst, ZrSAD-3A calcined at 550°C, the conversion varies as a function of time as reported in Figure 9. The final result is comparable to those reported with sulphuric acid as acid catalyst.
Figure 9. Variations of conversion and selectivity of PAP as a function of time for a mechanical mixture of Pt/ZrO₂ (0.01 g) and ZrSAD-3A (0.5 g). Reaction conditions: 3.0 mL of nitrobenzene in 75.0 mL of water, 80°C, hydrogen pressure 10 bars.

Table 5. Hydrogenation of Nitrobenzene to p-aminophenol using various supported Pt catalysts and zirconium sulphate.

<table>
<thead>
<tr>
<th>ExpNo</th>
<th>Catalyst</th>
<th>H₂, bar</th>
<th>Conv NB</th>
<th>Sel PAP</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2% Pt/ZrO₂ + ZRS-AD3A</td>
<td>10</td>
<td>97</td>
<td>76</td>
</tr>
<tr>
<td>2</td>
<td>1% Pt/C + ZRS-AD3A</td>
<td>20</td>
<td>62</td>
<td>98</td>
</tr>
<tr>
<td>3</td>
<td>2% Pt/MgLaO + ZRS-AD3A</td>
<td>20</td>
<td>75</td>
<td>77</td>
</tr>
</tbody>
</table>

CONCLUSIONS

An all heterogeneous process for the bi-functional conversion of nitrobenzene into p-aminophenol has been described, using the combination of zirconium sulphate and supported platinum. This system requires only very small amounts of Pt (a few mg of a 2%Pt catalyst). The support of Pt is not critical and any industrial support can probably be used. The most critical point is the choice of the solid acid, which must be selective for the Bamberger rearrangement. This rearrangement has been shown before to be
very demanding and the strong effect of the calcinations temperature illustrates this point. Strong solid acids are not good catalysts for this process.

Experimental

Preparation of the catalyst

A series of sulphated zirconias were investigated. Among them, two zirconia samples (references 1077-30 and 0999) supplied by M/s MEL Chemicals, U.K were sulphated. These are designated as MEL-XZ0707 and MEL 999/1, respectively. Another zirconia sample obtained from M/s LOBA Chemie was sulphated and this sample was designated as Loba –S. A lab-made zirconia was prepared by hydrolysis of ZrOCl₂ (M/s LOBA Chemie, India.) at a pH of 10. This solid was sulphated by treatment with a 1 N solution of sulphuric acid, followed by drying and calcination at 898 or 923 K (denoted as ZrSAD1). Another sulphated catalyst, ZrSAD3, was prepared by dissolving the hydrous gel in sulphuric acid, followed by drying to obtain a hydrated zirconium sulphate. The ZrSAD3 was calcined in air at 625°C or 650°C. The catalysts, Loba –S, sulphonated silica, MEL-XZ0707 and MEL 999/1 were used after calcination in air at 625°C.

Pt(0)/ZrO₂ was prepared by the following procedure. Zirconium hydroxide was precipitated from ZrOCl₂ (Loba, L.R grade) at constant pH 10 with the help of NH₄OH. The precipitate was aged at 80°C for 12 h, filtered and washed several times with deionized water until free from chloride ions and dried at 120°C for 24 h and calcined at 500°C. The ZrO₂ thus obtained showed a surface area of 105 m²g⁻¹. To prepare Pt(II)/ZrO₂, 0.2708 g of H₂PtCl₆ was dissolved in 50 distilled water, then 5 g of calcined ZrO₂ added, then the beaker was placed on the hot plate, stirred thoroughly with a glass rod. Water was evaporated on the hot plate, yielding the Pt²⁺/ZrO₂ as light yellow powder. The final catalyst Pt(0)/ZrO₂, a grey colour solid, was obtained after hydrogenation at 250°C for 3h under the hydrogen flow (30 ml min⁻¹) and from the
elemental analysis the Pt content in the catalyst was 0.102 mmol/g (Pt content: 2 wt%). Same impregnation procedure for the preparation of platinum supported on titania, lanthanum magnesium oxide, sulfated zirconia etc.,

**General procedure of hydrogenation of nitrobenzene**

In a 100mL autoclave engineers pressure reactor, 3.0mL nitrobenzene, 75.0mL water, and 0.01gms of Pt/support were mixed with 0.5g of ZRS-AD3A and purged with nitrogen and then by hydrogen at 80°C. Reaction was carried out for 7 hours at 10 atm. The autoclave is allowed to cool to room temperature and then back to atmospheric pressure. The reaction mixture was removed, catalyst was filtered off and the reaction mixture was homogenized by adding 20.0 mL methanol and subjected to high performance liquid chromatography using a UV detection (Figure 10).

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Chapter IV


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Figure 10. HPLC diagram of nitrobenzene reduction to p-aminophenol using Pt/ZrO₂ and sulphated Zirconia.