Non-phosgene method for the synthesis of Biphenyl urea using alumina based catalysts prepared by different methods
Introduction:

In recent years, replacement of mineral acid catalysts such as H$_2$SO$_4$ and HCl) and harmful reagents like COCl$_2$, R-N=C=O, Si-N=C=O, Si-N=C=S are widely used in a number of chemical processes [1]. Solid acid catalysts such as clays, zeolites, sulfated metal oxides, heteropoly acids and supported metal oxides are being employed in extensive research because of their ease of handling, greater selectivity, simple workup and non toxicity and reusability of catalyst [2-8]. Compared to conventional Lewis acids, heterogeneous catalyst has advantages over homogeneous catalysts regards low catalyst loading, moisture stability and catalyst recycling. Moreover, these systems are of practical importance as the catalytic activity in some reactions is correlated with the specific surface area and surface acidity/basicity. Amongst the solid acid catalysts, alumina and their modified forms have gained much attention due to their high strength, corrosion resistance, chemical stability and low thermal conductivity. Apart from these alumina is used as catalyst as well as catalyst supports because of its porosity and high surface area. Transition metal oxide deposited alumina on may change the crystalline nature of the material as well as acid-base properties [9-10].

The N,N'-diarylurea are useful in important medical and biological applications due to their properties [11-16]. These compounds are extensive used as agrochemicals, dyes for cellulose fibers, antioxidants in gasoline, resin precursors, and pharmaceuticals [17-22]. Apart from the above, biphenyl urea (BPU) is extensively studied in view of its application as synthetic intermediates especially for the production of carbamates and isocyanates, which are useful in industries and academic research.

According to the literature survey, biphenyl urea and its derivatives are prepared by traditional method wherein the use of toxic, hazardous, unstable, environmentally unfriendly reagents such as phosgene, isocyanates, formamides, carbamates, CO (in presence of sulphur) or carboxylic acid derivatives. During synthesis, the traditional processes liberate large amount of HCl as byproduct [23-26]. Apart from these, different transition metal catalysts such as Pd, Mn, Pt and Cu have been reported in the synthesis of Ureas by carboxylation of amines with CO.
RNH₂ + CO → (RNH)₂CO + H₂

N,N₁-asymmetric ureas are conventionally prepared starting from triphosgene (bis trichloromethyl carbonate dissolved in CH₂Cl₂ [27]. Many methods of phosgene-free synthesis for DPU have been reported in the literature. More promising routes for a large-scale production involves the catalytic oxidative carbonylation of aniline [28, 29] and the reductive carbonylation of nitro compounds [30-33]. Metal-based catalyst systems with Pt, Pd, Se and Te have been found to have good activity and selectivity by the homogeneous and heterogeneous systems [34-39].

Traditionally, BPU is manufactured by phosgenation route, but this route has severe corrosion problems. Another catalytic process for the synthesis of BPU has been developed involving a reaction of a cyclic carbonic acid ester with an amine [US Patent. 5902899, 1999] [40]. This method is very expensive for industrial production of the compound. Commercial production of BPU by this route is not recommended due to the following reasons [41].

- The process utilizes three CO molecules and the availability of CO is not economic and cost effective.
- The process utilizes precious metal catalyst such as Pd, Rh, Pt, the recycle and recovery of them is rather difficult.
- Isocyanates are highly reactive intermediates and hence their selectivity is sensitive to process parameters.

Based on our previous method for the synthesis of BPU [42, 43], here we report an effective method involving one step, non-phosgene and solvent free synthesis of BPU and its derivatives using manganese oxide (5%, 10%, 15%) supported on alumina as heterogeneous catalyst under liquid phase conditions starting from aniline and DMC/DEC (considered to be genuinely green solvent [44]. We have investigated the effect of various parameters like concentration, temperature, duration of the reaction and recyclability of the catalysts. It has been found that manganese oxide supported on
alumina catalyst is stable, efficient, ecofriendly, economic catalysts and exhibited remarkable catalytic activity with high selectivity for the synthesis of BPU and its derivatives. No byproduct has been detected in the reaction mixture at temperature below 110 °C. It can be noted here that the acidity and the phase of the prepared catalyst play a synergistic role in the synthesis of BPU’s.

Author’s work

5.1 Preparation of alumina with different percentage of manganese.

Alumina support containing different percentages of manganese were prepared by a simple precipitation–impregnation method (as described in the chapter-II, section 2.1.2) and Co-precipitation method. The various percentages of manganese deposited on alumina support were 5%, 10% and 15%. The procedure for preparation of manganese oxide supported on alumina by co-precipitation method is given below.

The catalysts prepared by precipitation–impregnation method are designated as Al₂O₃-PI, 5%Mn/Al₂O₃-PI, 10%Mn/Al₂O₃-PI and 15%Mn/Al₂O₃-PI and the second set of catalyst was prepared by co-precipitation method. Manganese oxide (5% Mn) supported on alumina catalyst was prepared by co-precipitation method using manganese sulphate and aluminum sulphate as precursors. The procedure followed is as follows:

In a typical procedure for the preparation of manganese oxide supported on alumina containing 5% of manganese, 117.42 g of aluminum sulphate [Al₂(SO₄)₃] (S.D. Fine chemicals, 99% pure) was suspended in 2 L of distilled water and mixed with 3.07 g of manganese sulfate [MnSO₄. H₂O] (Merck). The suspension thus obtained was heated to 70°C on a heating Rota Mantle (Remi make). The hot solution was stirred for about one hour and liquor ammonia (28% aqueous NH₃) was added slowly from a burette with constant stirring to precipitate out manganese as its hydroxide at pH 9 as thick brown precipitate. The precipitate thus obtained was
The thick brown precipitate thus obtained was stirred for nearly 2 h at 70°C to get a homogeneous mixture which was left overnight undisturbed at room temperature. The supernatant liquid was decanted and the solid was separated by filtration using Buchner funnel fitted with Whatmann-1 filter paper. The solid was washed with deionized water until the washings were free from sulfate ions as confirmed by barium chloride test. The solid was dried in an air oven at 120°C for 12 h followed by calcination at 450°C for 5 h in a muffle furnace. The material was dried at 120°C and further calcined at 450°C. The resultant material is abbreviated as 5%Mn/Al₂O₃-CP. Similarly 10%Mn/Al₂O₃-CP and 15%Mn/Al₂O₃-CP were prepared starting from the quantities of aluminum sulphate and manganese sulphate as given in table 5.1. For reference pure alumina is obtained by precipitating aluminum sulphate at pH 9 using ammonia as precipitating agent and designated as Al₂O₃-CP.

Table 2. Amount of manganese sulphate and aluminum sulphate used in the preparation of 10%Mn/Al₂O₃-CP and 15%Mn/Al₂O₃-CP.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Al₂(SO₄)₃ in g</th>
<th>MnSO₄·H₂O in g</th>
</tr>
</thead>
<tbody>
<tr>
<td>10%Mn/Al₂O₃-CP</td>
<td>111.24</td>
<td>6.14</td>
</tr>
<tr>
<td>15%Mn/Al₂O₃-CP</td>
<td>105.06</td>
<td>9.21</td>
</tr>
</tbody>
</table>

5.2 Catalyst characterization

All the catalytic materials thus prepared above have been characterized for their surface and bulk properties by appropriate techniques such as:

- Crystallinity by Powder X-ray diffraction (PXRD).
- Functional group analysis by Fourier Transform Infrared spectrophotometry (FT-IR).
- Quality and quantity of surface acid sites by Temperature programmed desorption of ammonia (TPD-NH₃) and n-butyl amine back titration method.
• Surface morphology by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

A brief description of the experimental procedures followed in characterization of the catalysts using above techniques is given in Chapter II, section 2.2.

**Product characterization**

The melting points of products were recorded in an open capillary tube and are uncorrected. Infrared spectra were recorded as KBr pellets of the samples using Nicolet Model Impact 400D FT-IR Spectrometer with 4 cm\(^{-1}\) resolution. The mass spectra were obtained on LC-MSD-Trap-XCT-Plus instrument. \(^1\)H NMR spectrum was obtained in DMSO solution at 300 MHz using Bruker Avance NMR spectrometer. \(^1\)H NMR Spectra was referenced to transcranial magnetic stimulation (TMS).

**5.3 Catalytic activity studies**

Catalytic activity of the catalysts, manganese oxide on alumina support prepared by precipitation-impregnation method and Co-precipitation method containing different percentages of manganese, calcined at 450°C for 5 h have been investigated in a reaction between aniline and DMC/DEC for the synthesis of BPU (Scheme 1).

![Scheme 1. Synthesis of BPU starting from aniline and dimethylcarbonate at 110°C.](image)

The procedure used is described as follows:

10 mmol of aniline, 20 mmol of DMC/DEC and 0.2 g of the catalyst taken in a 100 ml RB flask was heated over a mantle at 110°C for a predetermined time (4, 6, 8, 10 and 12 h). After the completion of the reaction, the RB flask containing solid BPU was removed.
from the heated mantle and cooled to room temperature. To this 10 ml of hot ethanol was added to dissolve the solid product and the catalyst was separated by filtration. The catalyst was then washed with acetone dried at 120°C and further reused for next cycles. The organic layer left behind was undisturbed for crystallization of BPU. Similar procedure was adopted for the syntheses of many substituted BPU by reaction of DMC/DEC with substituted anilines. Further, the products were characterized by M.P, FT-IR, LC-MS and 1H NMR spectral analysis studies.

**Optimization of the reaction conditions**

The effect of the reaction parameters such as temperature and duration of the reaction, amount of catalyst and different molar ratios of aniline and DMC on the percentage yield and selectivity of the product was investigated using 15%Mn/Al$_2$O$_3$-PI catalyst which exhibited the highest catalytic activity with respect to the yield and selectivity of BPU.

Further the generality of the catalyst was found out by carrying out a reaction between differently substituted anilines and DMC/DEC. The percentage yield of BPU was calculated based on aniline conversion.

**5.4 Result and discussion:**

**5.4.1 Powder x-ray diffraction (PXRD)**

PXRD patterns of the catalysts prepared from precipitation-impregnation method are given in chapter III section 3.4.3 and that of co-precipitated samples are shown in Figure 5.1. Catalysts prepared by precipitation method were more crystalline compared to those obtained from co-precipitation method. The catalysts prepared by Precipitation-impregnation method showed the presence of Boehmite (oxyhydroxy phase) of alumina and Hausmannite (crystalline phase) of Mn$_3$O$_4$. The catalysts prepared by co-precipitation method had more amorphous state. Similarly, Al$_2$O$_3$-CP and 5%Mn/Al$_2$O$_3$-CP catalysts were completely amorphous in nature. With higher percentage of manganese
oxide (10%Mn/Al$_2$O$_3$-CP and 15%Mn/Al$_2$O$_3$-CP), no peak corresponding to alumina was observed with increase in percentage of manganese. Whereas, peaks corresponding to Mn$_3$O$_4$ was observed with low intensity (Fig 5.1).

![Figure 5.1 PXRD pattern of Al$_2$O$_3$-CP, 5%Mn/Al$_2$O$_3$-CP, 10%Mn/Al$_2$O$_3$-CP and 15%Mn/Al$_2$O$_3$-CP catalysts.](image)

5.4.2 Fourier transform infrared spectrophotometer (FTIR) of catalysts

FTIR patterns of the catalysts obtained from precipitation-impregnation method are given in chapter III section 3.4.2. And co-precipitated samples are presented in figure 5.2. A weak broad band around 3600 cm$^{-1}$ and 1645 cm$^{-1}$ in the IR spectrum of all the samples are due to the stretching and bending vibrations of the -OH group respectively. Manganese oxide deposited on alumina prepared by co-precipitation method, showed a well defined band around 1076 cm$^{-1}$ is due the vibrations of Al-O-Al bonds [45] and are prominent even after 15% manganese deposition. With higher percentage of manganese,
in 15%Mn/Al₂O₃-CP, weak absorption bands at 620 cm⁻¹ and 502 cm⁻¹ characteristic of Mn₃O₄ phase is observed. This is in agreement with the reported literature [46].

![FTIR spectra](image)

Figure 5.2. FTIR spectra of Al₂O₃-CP, 5%Mn/Al₂O₃-CP, 10%Mn/Al₂O₃-CP and 15%Mn/Al₂O₃-CP catalysts.

5.4.3 Brunauer–Emmett–Teller (BET) Specific surface area determination

BET surface areas of the catalysts prepared from both precipitation-impregnation method and co-precipitation method are given in the Table 5.1. It is seen from the table 5.1 that alumina catalysts prepared by precipitation-impregnation method significantly exhibited higher surface area than catalysts prepared by co-precipitation method. Pure alumina catalysts prepared by both the methods showed highest surface area than the corresponding manganese supported alumina catalysts. With higher percentage of manganese deposition the surface area is gradually decreased. In co-precipitated sample,
the catalyst with lower percentage of manganese oxide deposition has higher surface area and 15% manganese oxide deposited sample have least surface area.

Table 5.1. BET surface area of alumina catalyst containing different percentage of manganese oxide prepared by precipitation-impregnation and co-precipitation methods.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET SA (m²/g)</th>
<th>Acidity A</th>
<th>Acidity B</th>
<th>Texture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃-PI</td>
<td>262</td>
<td>1.01</td>
<td>1.34</td>
<td>Crystalline</td>
</tr>
<tr>
<td>5%Mn/Al₂O₃-PI</td>
<td>209</td>
<td>1.25</td>
<td>1.55</td>
<td>Crystalline</td>
</tr>
<tr>
<td>10%Mn/Al₂O₃-PI</td>
<td>228</td>
<td>1.32</td>
<td>1.59</td>
<td>Crystalline</td>
</tr>
<tr>
<td>15%Mn/Al₂O₃-PI</td>
<td>218</td>
<td>1.47</td>
<td>1.61</td>
<td>Crystalline</td>
</tr>
<tr>
<td>Al₂O₃-PI</td>
<td>190</td>
<td>0.48</td>
<td>-</td>
<td>Amorphous</td>
</tr>
<tr>
<td>5%Mn/Al₂O₃-CP</td>
<td>157</td>
<td>0.51</td>
<td>-</td>
<td>Amorphous</td>
</tr>
<tr>
<td>10%Mn/Al₂O₃-CP</td>
<td>134</td>
<td>0.57</td>
<td>-</td>
<td>Amorphous</td>
</tr>
<tr>
<td>15%Mn/Al₂O₃-CP</td>
<td>119</td>
<td>0.59</td>
<td>-</td>
<td>Slightly crystalline</td>
</tr>
</tbody>
</table>

BET SA: Braunner Emmett Teller Surface area.
Acidity A: Acidity (mmol/g) from n-butyl amine back titration method.
Acidity B: Acidity (TPD-NH₃) (mmol/g).

5.4.4 Total surface acidity
The amount of total surface acid sites present was investigated by n-butylamine back titration method and is given in Table 5.1 and the detailed procedure is mentioned in Chapter II, section 2.3.6. The following trends in surface acid sites of the catalysts prepared from precipitation-impregnation method and co-precipitation method have been observed.
• **Surface acidity of catalysts prepared from precipitation–impregnation method:**
  
  \[ 15\%\text{Mn/Al}_2\text{O}_3-\text{PI} > 10\%\text{Mn/Al}_2\text{O}_3-\text{PI} > 5\%\text{Mn/Al}_2\text{O}_3-\text{PI} > \text{Al}_2\text{O}_3-\text{PI} \]

  and

• **Surface acidity of catalysts prepared from co-precipitated method.**
  
  \[ 15\%\text{Mn/Al}_2\text{O}_3-\text{CP} \sim 10\%\text{Mn/Al}_2\text{O}_3-\text{CP} > 5\%\text{Mn/Al}_2\text{O}_3-\text{CP} > \text{Al}_2\text{O}_3-\text{PI}. \]

  Hence it can be inferred that the catalysts prepared by precipitation–impregnation method showed higher surface acidity than catalysts prepared from co-precipitation method. In both the methods, the total surface acidity increases with increase in manganese percentage and remains significant after 10%. It is well known that transition metal deposition increases the Lewis acidity of the supports. Of all the catalysts studied, 15% Mn/Al2O3-PI catalyst showed the highest surface acidity and catalytic activity.

5.4.5 **SEM and TEM**

The SEM and TEM micrographs of catalysts prepared by precipitation–impregnation method and co-precipitation method are shown in Figure 5.3 and Figure 5.4 respectively. The SEM and TEM images clearly showed a very widely varies distribution in morphology texture and particle size depending on the method of preparation and manganese content. SEM and TEM images clearly shows that with higher percentage of manganese oxide deposition the particle size decreases. The catalysts prepared by precipitation–impregnation method showed bigger size compared to co-precipitated samples.
Figure 5.3 SEM images of alumina and manganese oxide supported samples prepared by precipitation and co-precipitation method
Figure 5.4 TEM images of alumina and manganese oxide supported samples prepared by precipitation and co-precipitation method.
5.5 Catalytic activity studies with all the catalysts:

The catalytic activity of the catalysts prepared by precipitation–impregnation method and co-precipitation method has been investigated in the synthesis of biphenyl urea starting from aniline and dimethyl carbonate (DMC). All the catalysts showed activity in favour of formation of the product. Hence the catalysts prepared by co-precipitation method showed less activity towards the formation of biphenyl urea when compared to catalysts prepared by precipitation impregnation method. The activity of the catalysts in terms of the product yield and selectivity along with duration of the reaction is given in Table 5.2. The supports prepared by both the methods have showed less activity compared to manganese oxide deposited catalysts. The catalytic activity of alumina catalysts prepared by precipitation-impregnation increased with manganese oxide deposition. As the percentage of manganese on alumina support increases there is gradual increase in catalytic activity (47-93%). Similar observations have been noticed in case of co-precipitated samples but the yield was comparatively very low (7-21%). It may be noted that with increase in acidity of the catalysts, the catalytic activity increases. Thus, it may be inferred from the above results that reaction between aniline and DMC/DEC in the synthesis of BPU, surface acidity is one of the parameter responsible for the formation of the product. The surface area, phase of the catalyst and the acidity plays a major role in the conversion of aniline. The catalysts prepared by precipitation-impregnation method play a major role in non-phosgene route of synthesis of BPU due to the following reasons:

- Improvement in catalyst acidity upon manganese oxide deposition is observed from their acidity values.
- The higher surface area of catalysts prepared by precipitation-impregnation method.
- The presence of Boehmite phase of alumina and Hausmannite phase of manganese oxide is observed from PXRD patterns.
Table 5.2. Catalytic activity of catalysts along with their reaction temperature and duration with respect to conversion of aniline and selectivity towards BPU.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion of aniline (%)</th>
<th>Temperature (°C)</th>
<th>Duration (h)</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃-PI</td>
<td>47</td>
<td>110</td>
<td>12</td>
<td>99</td>
</tr>
<tr>
<td>5%Mn/Al₂O₃-PI</td>
<td>79</td>
<td>110</td>
<td>8</td>
<td>99</td>
</tr>
<tr>
<td>10%Mn/Al₂O₃-PI</td>
<td>87</td>
<td>110</td>
<td>7</td>
<td>99</td>
</tr>
<tr>
<td>15%Mn/Al₂O₃-PI</td>
<td>93</td>
<td>110</td>
<td>7</td>
<td>99</td>
</tr>
<tr>
<td>Al₂O₃-CI</td>
<td>7</td>
<td>110</td>
<td>12</td>
<td>57</td>
</tr>
<tr>
<td>5%Mn/Al₂O₃-CP</td>
<td>12</td>
<td>110</td>
<td>12</td>
<td>61</td>
</tr>
<tr>
<td>10%Mn/Al₂O₃-CP</td>
<td>17</td>
<td>110</td>
<td>12</td>
<td>64</td>
</tr>
<tr>
<td>15%Mn/Al₂O₃-CP</td>
<td>21</td>
<td>110</td>
<td>12</td>
<td>65</td>
</tr>
</tbody>
</table>

5.6 Optimization reactions

The best reaction conditions for synthesis of biphenyl urea with high yield and selectivity was investigated in a reaction between aniline and DMC/DEC. The effect of following reaction conditions were studied using 15%Mn/Al₂O₃-PI catalyst.

- Effect of temperature on the yield and selectivity of the product.
- Effect of molar ratio of the reactants
- Amount of catalyst and the duration of the reaction.
5.6.1 Effect of temperature on the yield and selectivity of the product.

The effect of temperature in the synthesis of biphenyl urea in presence of 15% Mn/Al₂O₃-PI was studied under solvent free conditions. The variation of catalytic activity with reaction temperature in terms of isolated yield of the product is given in Figure 5.5.

![Figure 5.5 Effect of temperature on yield and selectivity of the product.](image)

The yield of the isolated product was only 16-17%. However, the percentage aniline conversion was found to be increased with good yield and selectivity (99.7% shown in LC-MS report in the following section) with an increase in the temperature (up to 110°C). Though the conversion of aniline increased with increase in temperature, the selectivity towards the expected product BPU dropped. The byproducts obtained in the reaction at high temperature are given in Table 5.3. It is noticed here that at
110°C, 100% selectivity towards the expected product was observed. At 130-170°C byproducts such as N-methyl aniline and carbamate are observed. Therefore, 110°C was optimum temperature for the synthesis of BPU and their derivatives.

Table 5.3. Percentage yield of byproducts obtained at higher temperatures.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Conversion of aniline (%)</th>
<th>BPU (%)</th>
<th>NMA (%)</th>
<th>Carbamate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>93</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>130</td>
<td>95</td>
<td>77</td>
<td>8</td>
<td>15</td>
</tr>
<tr>
<td>150</td>
<td>97</td>
<td>65</td>
<td>7</td>
<td>28</td>
</tr>
<tr>
<td>170</td>
<td>97</td>
<td>5</td>
<td>12</td>
<td>43</td>
</tr>
</tbody>
</table>

NMA : N methyl aniline

5.6.2 Effect of molar ratio of the reactants

Since the catalysts prepared by precipitation impregnation method showed a higher catalytic activity than co-precipitated catalysts, the former catalysts were selected to study other reaction parameters at 110°C. Effect of molar ratio of the reactants with the catalysts prepared by precipitation-impregnation method is given in Figure 5.6.

The appropriate molar ratio necessary for the conversion of aniline to biphenyl urea was studied. The experiment with molar ratios 1:1, 1:2 and 1:3 of aniline and dimethyl carbonate was selected and the reaction was carried out with all the four catalysts prepared by Precipitation-impregnation method. With increase in molar ratio of the reactants, the conversion of aniline increased from 31% to 47% in case of Al₂O₃-PI catalyst, 63-79 in case of 5%Mn/Al₂O₃-PI catalyst, 61-87% in case of 10%Mn/Al₂O₃-PI and 62 to 93% in case of 15%Mn/Al₂O₃-PI catalyst. The excess dimethylcarbonate remaining is drained off from the flask by filtration. The solid product obtained was dissolved using hot ethanol and filtered through whatmann no 1 filter paper to remove the
catalyst from the reaction mixture and the product was recrystallized which gave fine shiny crystals.

![Figure 5.6](image)

**Figure 5.6** Effect of molar ratio of the reactants with the catalysts prepared by precipitation-impregnation method.

### 5.6.3 Amount of catalyst and duration of the reaction

The catalyst 15% Mn/Al$_2$O$_3$-PI was chosen to study the effect of amount of catalyst on the yield and selectivity of the product. The catalyst amount was varied starting from 0.05-1 g. With increase in the amount of the catalyst (0.05 to 0.2 g), the catalytic activity also increased. With further increase in catalyst amount, no significant increase in catalytic activity was observed. When the catalyst amount was greater than 0.5 g, the selectivity of the reaction in the formation of the product BPU was decreased.
and the yield of carbamate was increased. This might be due to the increase in acidity of the catalysts.

The time required by 15%Mn/Al₂O₃-PI catalyst for maximum conversion of aniline to BPU was found to be good in yield and selectivity was carried out in a range 2-9 h. Initially the yield of BPU was increased with increase in duration of the reaction until 7 h. Fine needles like shiny crystals of BPU were formed in the RB flask. The amount of BPU crystals obtained was maximum, when the reaction was carried out for 5-7 h depending on the active mass of the reactants used. With further increase in duration the selectivity towards BPU decreases and the color of the crystals inside RB flask used changes from creamish white to brown and the selectivity of the product was decreased.

5.6.4 Generality of the catalysts

The utility of 15%Mn/Al₂O₃-PI catalyst which exhibited good catalytic activity and selectivity towards the product BPU was evaluated in the synthesis of BPU derivatives starting from substituted anilines and DMC/DEC using 0.2 g of 15%Mn/Al₂O₃-PI catalyst at 110°C for about 7 h. The result of the effect of substituted anilines in BPU derivative synthesis is summarized in Table 5.4.

When secondary substituted anilines like N-methylaniline and N-propylaniline were used in the reaction, the conversion of aniline is very low. Primary substituted anilines such as 4-chloroaniline, 3-chloroaniline 2-toluidines, 3-toluidine and 4-toluidine, when employed in a reaction, 90% aniline was converted to the expected product with good selectivity. The solid product obtained was of high purity and separated from the solid catalyst by dissolving the product mixture in hot ethanol, followed by filtration to remove the catalyst. The filtrate was recrystallized which gave fine silky, needle like crystals.
Table 5.4. Synthesis of biphenyl urea derivatives using 15% Mn/Al\textsubscript{2}O\textsubscript{3}-PI catalyst at 110°C for 7 h with various substitutes anilines.

<table>
<thead>
<tr>
<th>Anilines</th>
<th>DMC/DEC</th>
<th>Product</th>
<th>M.P (°C)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{NH}_2\text{C}_6\text{H}_4\text{NH}_2)</td>
<td>DMC (DEC)</td>
<td><img src="image1.png" alt="Image" /></td>
<td>241-243 (239-241)</td>
<td>89 (93)</td>
</tr>
<tr>
<td>(\text{ClC}_6\text{H}_4\text{NH}_2)</td>
<td>DMC (DEC)</td>
<td><img src="image2.png" alt="Image" /></td>
<td>&gt;300</td>
<td>87 (93)</td>
</tr>
<tr>
<td>(\text{ClC}_6\text{H}_4\text{Cl})</td>
<td>DMC (DEC)</td>
<td><img src="image3.png" alt="Image" /></td>
<td>-</td>
<td>45 (57)</td>
</tr>
<tr>
<td>(\text{ClC}_6\text{H}_4\text{CH}_3)</td>
<td>DMC (DEC)</td>
<td><img src="image4.png" alt="Image" /></td>
<td>282-284 (283-285)</td>
<td>91 (95)</td>
</tr>
<tr>
<td>(\text{ClC}_6\text{H}_4\text{CH}_3)</td>
<td>DMC (DEC)</td>
<td><img src="image5.png" alt="Image" /></td>
<td>254-256 (254-256)</td>
<td>93 (93)</td>
</tr>
</tbody>
</table>
5.6.5 Analysis of BPU crystals by Single crystal X-Ray diffraction method.

The crystal obtained from the reaction was r-Ray diffraction studies recrystallized and suitable for BPU crystals obtained after recrystallization were shiny and transparent. The second time slow crystallized crystals were subjected to Single crystal X-Ray diffraction studies and the following structures were obtained and the R factor which corresponds to the purity of the compound was < 6. This indicates that the obtained crystals are of high purity. The ORTEP view of 1,3 Diphenyl urea and 1,3-bis(4-chlorophenyl)urea are shown in Figure 5.7.

**ORTEP view of the compound showing 100% probability to the expected product**

![ORTEP view of the compound showing 100% probability to the expected product](image)

(a) 1,3 Diphenyl urea
Figure 5.7 ORTEP view of 1,3 Diphenyl urea (a), 1,3-bis(4-chlorophenyl)urea (b), .
The spectral data of some of the BPU derivatives synthesized are given below.

Entry 1. in Table 5.4 1,3-biphenyl urea: White crystalline shiny solid, M.P 239-241 °C. IR (KBr) 3291 cm\(^{-1}\) (N-H), 1635 cm\(^{-1}\) (C=O). \(^1\)HNMR (300 Hz, DMSO), \(\delta\): 6.52-7.4 (Ar-H, m, 10H), 8.2 (N-H, s, 2H). Ms: \(M^+\)=213.2.

Entry 2. in Table 5.4 1,3-bis (2-amino phenyl)urea: yellow crystalline compound. IR (KBr) 3291 cm\(^{-1}\) (N-H), 3347 cm\(^{-1}\) and 3169 cm\(^{-1}\) (-NH\(_2\)), 1629 cm\(^{-1}\) (C=O). \(^1\)HNMR (300 Hz, DMSO), \(\delta\): 6.72-7.34 (Ar-H, m, 8H), 8.34 (N-H, s, 2H). Ms: \(M^+\)=241.

Entry 3. in Table 5.4 1,3-bis (4-chloro phenyl)urea: white crystalline shiny solid. IR (KBr) 3297 cm\(^{-1}\) (N-H), 1637 cm\(^{-1}\) (C=O), 877 cm\(^{-1}\) (C-Cl). \(^1\)HNMR (300 Hz, DMSO), \(\delta\): 7.32-7.51 (Ar-H, m, 8H), 8.85 (N-H, s, 2H). Ms: \(M^+\)=283.

Entry 5. in Table 5.4 1,3-dio-tolyl urea: pale yellow crystalline solid. M.P 283-285°C. IR (KBr) 3307 cm\(^{-1}\) (N-H), 2935 cm\(^{-1}\) (C-H) 1641 cm\(^{-1}\) (C=O). \(^1\)HNMR (300 Hz, DMSO), \(\delta\): 6.92-7.79 (Ar-H, m, 8H), 8.24 (N-H, s, 2H), 2.50 (-CH\(_3\), s, 3H). Ms: \(M^+\)=241.

Entry 8. in Table 5.4 1,3-bis(2-nitrophenyl)urea: yellow crystalline solid. M.P 235-237 °C. IR (KBr) 3347 cm\(^{-1}\) (N-H), 1328 cm\(^{-1}\) (N=O) 1649 cm\(^{-1}\) (C=O). \(^1\)HNMR (300 Hz, DMSO), \(\delta\): 6.92-7.59 (Ar-H, m, 8H), 8.54 (N-H, s, 2H). Ms: \(M^+\)=303.2.

5.6.6 Recyclability of the catalyst

Recyclability of 15%Mn/Al\(_2\)O\(_3\)-PI catalyst was investigated in a reaction between aniline and DMC in the molar ratio 1:3 at 110°C for 5 h. Once the solid product was obtained, the catalyst was separated from the reaction mixture by adding 10 ml of hot ethanol followed by filtration. The solid catalyst thus obtained was washed with acetone to remove any organic moieties adsorbed onto the surface of the catalyst and dried in hot air oven at 120°C for 4 h. The catalyst thus obtained was used in next cycle for its catalytic activity. The catalyst could be easily separated from the reaction mixture and reused for three cycles more. After three cycles the catalytic activity of the catalyst was decreased indicating that leaching of manganese from the catalyst occurred (as indicated by ICP-OES) and results of this are given in Table 5.5.
Table 5.5 Amount of manganese (%) in 5%Mn/Al₂O₃-PI, 10%Mn/Al₂O₃-PI and 15%Mn/Al₂O₃-PI catalysts after three recycles.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Actual amount of Mn (%)</th>
<th>Mn after 1st cycle</th>
<th>Mn after 2nd cycle</th>
<th>Mn after 3rd cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%Mn/Al₂O₃-PI</td>
<td>4.32</td>
<td>4.11</td>
<td>3.93</td>
<td>3.67</td>
</tr>
<tr>
<td>10%Mn/Al₂O₃-PI</td>
<td>8.91</td>
<td>8.79</td>
<td>8.44</td>
<td>7.89</td>
</tr>
<tr>
<td>15%Mn/Al₂O₃-PI</td>
<td>13.73</td>
<td>13.55</td>
<td>13.26</td>
<td>12.45</td>
</tr>
</tbody>
</table>

CONCLUSION

Manganese oxide modified alumina catalyst is successfully prepared by precipitation–impregnation and co-precipitation methods and well characterized for their physico-chemical properties. Manganese oxide modified alumina catalyst prepared by precipitation–impregnation method has been found to be active in a non-phosgene and solvent free synthesis of biphenyl urea and their derivatives starting from aniline and dimethyl carbonate. About 99% selectivity with good catalytic activity towards BPU formation is obtained in single step at 110°C for 7 h. The enhancement of catalytic activity clearly observed with varying percentage of manganese oxide on alumina support. The synergistic role is played by both acid sites of the catalyst and the phase of manganese oxide and alumina. The catalyst is ecofriendly and recycled for three cycles in a reaction carried out without deactivation.
$^1$HNMR spectra of BPU


Table 5.4 1,3-biphenyl urea

Table 5.4 1,3-bis(2-nitrophenyl)urea
Entry 2. in Table 5.4, 1,3-bis (2-amino phenyl)urea

Entry 5. in Table 5.4 1,3-dio-tolyl urea
Entry 3. in Table 5.4: 1,3-bis (4-chloro phenyl)urea:

LC-MS data of BPU obtained from aniline and DMC showing 99.71% selectivity
LC-MS data of BPU obtained from 4-chloroaniline and DMC showing 99.45% selectivity

<table>
<thead>
<tr>
<th>Peak</th>
<th>RT</th>
<th>Area</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>13.868</td>
<td>1.868e+003</td>
<td>99.455</td>
</tr>
<tr>
<td>12</td>
<td>14.344</td>
<td>4.658e+000</td>
<td>0.248</td>
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<tr>
<td>13</td>
<td>14.497</td>
<td>5.582e+000</td>
<td>0.297</td>
</tr>
</tbody>
</table>

LC-MS data of BPU obtained from OPDA and DMC showing 99.45% selectivity
References:


