HIGHLY ACTIVE PANDANUS NANOCELLULOSE-SUPPORTED POLY(AMIDOXIME) COPPER (II) COMPLEX FOR ULLMANN CROSS-COUPLING REACTION

BY:
CHOONG JIAN FUI

SUPERVISED BY:

<table>
<thead>
<tr>
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</tr>
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<tbody>
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</table>
BACKGROUND
Synthesis process is necessary due to the **molecular complexity** and various type of **bond formation** through the organic transformations is being grown in parallel fashion.

C-C or C-N bonds formation (cross-coupling) reactions are **important** for the synthesis of essential chemicals such as:

1. Fine chemicals,
2. Drug and intermediate products,
3. Natural products etc.

Transition metal catalysts (Pd, Cu, Ni) are normally used for cross-coupling reactions (suzuki, heck, sonogashira, click etc.).
<table>
<thead>
<tr>
<th>Homogeneous catalyst</th>
<th>Heterogeneous catalyst</th>
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<tbody>
<tr>
<td>Expensive</td>
<td>Less expensive</td>
</tr>
<tr>
<td>Purification of product is difficult</td>
<td>Easy to purify the product</td>
</tr>
<tr>
<td>Can not be reused</td>
<td>Reusable</td>
</tr>
<tr>
<td>Environmental pollution</td>
<td>Environmental-friendly</td>
</tr>
<tr>
<td>Not stable in the reaction media</td>
<td>Stable under harsh conditions</td>
</tr>
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</table>
Price of the catalyst and catalyst market are growth year by year.

Therefore, the low cost, high activity, high stability, safe reusability, non-toxic, sustainable chemistry, and characteristic of green organic synthesis are well interest by most of the researcher.
OBJECTIVES
• To extract the cellulose from the agro-waste (pandanus fruit fibre) and utilize to synthesize a poly(amidoxime) ligand,

• To prepare heterogeneous copper catalysts from the cellulose-supported amidoxime ligands,

• To evaluate the catalytic ability and reusability of synthesize catalyst in Ullmann cross-coupling reaction.
METHODOLOGY
Filter the wood sawdust and weight 100g of fiber.

Dry the cellulose with oven at 50℃ for one day and weight the mass of cellulose obtain

(Sources: Rahman et al., 2016)
Synthesize nanocellulose

Procedure:
1. Boil the cellulose with 40% of $\text{H}_2\text{SO}_4$ for 1 hour.
2. Pour the mixture into the cool water after reaction done.
3. Neutralize the solution using $\text{NaOH}$.
4. Wash and dry.
Graft Copolymerization (Poly(acrylonitrile))

Procedure:
1. Hydrolyze cellulose react with ceric initiator in inert condition for 15 min
2. Purified monomer (methyl acrylate) is added.
3. Heat for 4 hours at 55°C.
4. Wash and dry

(Sources: Mandal et al., 2016)
Synthesis of Poly(amidoxime) Ligand

Procedure
1. Hydroxylamine hydrochloride is dissolved into 4:1 methanolic solution.
2. PMA is added into the hydroxylamine solution and heat for 6 hours at 70°C.
3. PHA ligand is washed by methanolic solution.
4. In order to cover chelating polymeric ligand into H-form ligand, the ligand was treating with 100 mL of 0.1 M of hydrochloric acid (HCl) in methanolic for five minutes.
5. Wash and dry.

(Sources: Shaheen et al., 2016)
Preparation Of Metal Catalyst (Cu\textsuperscript{2+})

Shake for 2 hours with 180 rpm Agitation speed

Wash the ligand and dry it. The ICP-OES analysis should be used to estimate the copper adsorbed

(Sources: Rahman et al., 2016)
Reaction Mechanism

Cellulose = cell

Initiation

\[ \text{Initiation} \rightarrow \text{Cell} \quad \text{Propagation} \rightarrow \text{Cell} \quad \text{Termination by combination} \]

\[ \text{Initiation} \rightarrow \text{Poly(acrylonitrile)} \quad \text{Termination by combination} \]

\[ \text{Cell} \rightarrow \text{Poly(amide oxime)} \]

\[ \text{Cell} \rightarrow \text{Cu(II)@PAM} \]
Ullmann Reactions

\[
\begin{align*}
\text{Cu(II)@PAM} \\
\text{base, heat, solvent}
\end{align*}
\]
Product

Pandanus fruit and its fibre

Cellulose from Pandanus fruit fibre

Extraction: $49.5 \pm 1.0 \text{g from 100g dried fruit fibre}$

Yield: ($\approx 50\%$)

(nanocellulose)
Physical stability of cellulose and nanocellulose

15 min String

Cellulose  | nanocellulose

Leave For 3 hour

Cellulose  | nanocellulose
Particle size and zeta potential analysis
Product

Poly(acrylonitrile)
Yield: **18.15 g** from 10g dried nanocellulose

Poly(amidoxime) Ligand
Yield: **28.50g** from 10g dried poly(acrylonitrile)

Cu(II)@PAM
ICP-OES= 0.50mmol/g of copper
FT-IR Analysis

- **Pandanus Cellulose**
- **Poly(acrylonitrile)**
- **Poly(amidoxime)**

T% (arb.units) vs. cm⁻¹

(a) Pandanus Cellulose
(b) Poly(acrylonitrile)
(c) Poly(amidoxime)

Wave numbers:
- Pandanus Cellulose: 3462, 2917, 1638, 1454, 1343, 1060, 934, 3234
- Poly(acrylonitrile): 2244, 1652, 1399, 1060, 934
- Poly(amidoxime): 2244, 1652, 1399, 1455, 934
FE-SEM Analysis

Pandanus fruit fiber

Pandanus-cellulose

Magnification: 1000X
FE-SEM ANALYSIS

nanocellulose
Magnification: 1000X

Poly(acrylonitrile)
Magnification: 5000X
FE-SEM Analysis

Poly(amidoxime)

Cu(II)@PAM

Magnification: 5000X
Energy Dispersive X-ray Diffraction (EDX Analysis)

Cu(II)@PAM

Copper = 35.4%
Carbon = 40.7%
Oxygen = 20.2%
Nitrogen = 3.8%
XRD RESULT
XPS ANALYSIS

(a) Cu2p3/2
Cu2p1/2

(i) Intensity (arb. units)

(ii) Binding Energy (eV)

(b) Cu2p1/2
Cu2p3/2

(c) O 1s
Poly(amidoxime)
Cu(II)@PAM

(d) N 1s
Poly(amidoxime)
Cu(II)@PAM

Poly(amidoxime)
CuSO4·5H2O

Cu(II)@PAM
## Optimization Of Ullmann Reaction

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cu(II)@PAM (mg)</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15</td>
<td>80</td>
<td>8</td>
<td>98</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>50</td>
<td>8</td>
<td>99</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>50</td>
<td>2</td>
<td>99</td>
</tr>
<tr>
<td>4</td>
<td>1.5</td>
<td>50</td>
<td>2</td>
<td>89</td>
</tr>
</tbody>
</table>

- Conditions: 4-nitrobenzyl bromide (1 mmol), phenol (1.2 mmol), a catalytic amount of complex copper and 3 mol equiv. of K$_2$CO$_3$ in 5 mL of acetonitrile.
REACTION

Conditions: Benzyl halide (1 mmol), phenol (1.2 mmol), ≤3.0 mg of Cu(II)@PAM and 3 mol equiv. of K2CO3 in 5 mL of acetonitrile. All the compound was determined by GC-MS and NMR.
<table>
<thead>
<tr>
<th>R₁—Ar—I</th>
<th>Ar—I</th>
<th>R₁—Ar—O—Ar₂</th>
<th>Conditions: Benzyl halide (1 mmol), phenol (1.2 mmol), ±3.0 mg of Cu(II)@PAM and 3 mol equiv. of K₂CO₃ in 5 mL of acetonitrile. All the compound was determined by using GC-MS and NMR.</th>
</tr>
</thead>
<tbody>
<tr>
<td>I= 60%; Br= 55%; Cl= 20%</td>
<td>I= 77%; Br= 69%; Cl= 51%</td>
<td>I= 90%; Br=82%; Cl= 60%</td>
<td>I= 65%; Br= 50%; Cl= 20%</td>
</tr>
<tr>
<td>I= 50%; Br= 45%; Cl= 15</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- | O₂N | NC | H₃C | H₂N | 
- | | | | |
Mechanism for Ullmann Reaction

KBr + KHCO₃

K₂CO₃ + OH

(i)

(ii)

= amidoxime

= copper (II)

= cellulose
REUSABILITY
LEACHING STUDY
CONCLUSION
Successful synthesis high active, stable and safe copper catalyst for Ullmann etherification reaction.

The synthesized copper catalyst can afford the Ullmann etherification in good to high yield of product.
FUTURE WORK
• Test the synthesize catalyst in other cross-coupling reaction (C-C, C-N, C-S, etc.)
• Utilize the Cu(II)NPs@PAM in total synthesis of natural product, medicine compound.
REFERENCES
Thank you