

# Metal (Au, Ag and Cu) NPs in Ionic Liquid: Potential Catalytic System for Organic Reactions

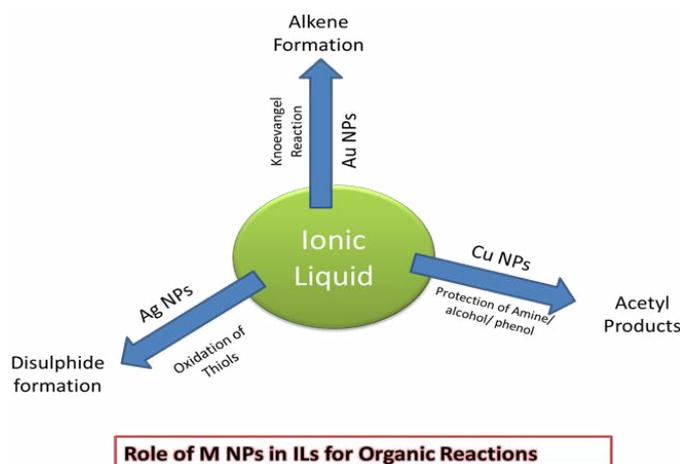
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## Abstract

Metal nanoparticles were synthesized and used to carry out organic transformation in short duration of time with excellent yield. Synthesized Au NPs in Ionic Liquid (IL) catalyzed the condensation between active methylene compounds and aldehydes in high yields and in short duration. Also, a new, simple and highly efficient methodology was described for the oxidation of thiols to form disulfides using easily recyclable silver nanoparticles to give the corresponding products in shorter duration of time with good to high yield. It was found that silver nanoparticles in ionic liquid showed the best activity. A new, simple and highly efficient methodology was described for the acetylation of alcohols, amines and thiols using easily recyclable Cu NPs to give the corresponding products in shorter duration of time with good to high yield. We found that Cu NPs in IL showed the best activity. These protocols avoid the use of expensive reagents, high temperatures and the reaction being performed in water serves as a green and efficient method. It is remarkable that the reaction in IL which makes the procedure quite simple, more convenient and environmentally benign.



Role of M NPs in ILs for Organic Reactions

**Keywords:** Metal nanoparticles; Ionic liquid; Organic transformation; Catalysis

## Introduction

Organic synthesis is routinely performed in non-aqueous solvents. Lack of solubility of generally lipophilic organic or organometallic compounds in water compelled chemists to employ non-aqueous solvents [1,2]. Current emphasis of academicians and researchers on green chemistry underscores the need for developing catalytic reactions in green solvents. One of thrust area for achieving this target is to explore alternative reaction conditions and reaction media to accomplish the desired chemical transformation with minimum by-products, waste generation as well as eliminating the use of volatile and toxic organic solvents. There are also the many feature of metal nanoparticles in the various field of science and are well established like sensitive detection of carbohydrate antigen 125 by hollow polydopamine-gold nanoparticles; deposition of gold nanoparticle on the core-shell of Fe<sub>3</sub>O<sub>4</sub> polydopamine by green method and it is recyclable; ultrasensitive detection of prostate specific antigen by Graphene oxide quantum dots based on silver core-shell nanocrystals [3-5]. It is therefore of utmost important to evolve simple and effective methodology for the synthesis of various biological or other important [3-15]. However, low solubility of reactants, incompatibility of certain intermediate or competition

between the desired reactants and hydrolysis restrict the use of water as a common solvent to carry out organic reaction, although many reactions have been studied in water using different catalyst. The use of IL, easily synthesized, non-volatile for various reactions is reclaiming its importance due to pressing environmental, economic and safety concerns [16-28].

The proposed methodology is highly economic and eco-friendly as it does not require toxic solvent, any harsh acids or bases and produces high yield with excellent chemoselectivity [28-40]. It further reduces the reaction time and is applicable to a variety of compounds. Moreover, it does not require an inert atmosphere and has an easy work

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up and product isolation from the catalyst. Metal nanoparticles (NPs) have frequently been used as efficient catalyst in place of conventional reagents/ catalysts being superior due to their extremely high surface area, reusability etc. [41-58].

In this study, application of metal NPs as potent catalyst has been reported for a variety of functional group transformations but they should be explored thoroughly for other organic reaction like Knoevenagel condensation, preparation of disulphide and acetylation of amines alcohols.

## Experimental Section

### Reagents and analysis

All reactions were carried out at ambient temperature in oven-dried glassware. The materials were purchased from Sigma-Aldrich and Merck used. All reactions were monitored by thin layer chromatography (TLC) on gel F<sub>254</sub> plates. The silica gel (250-400 meshes) for column chromatography was purchased from Spectrochem Pvt. Ltd., India.

### Au NPs in IL as efficient catalytic system for the synthesis of unsaturated compounds via reaction between active methylene compounds and aromatic aldehydes (Knoevenagel condensation)

Herein, methodology for the condensation between active methylene compounds and aromatic aldehydes using Au NPs in IL as catalyst was developed (Scheme 1).

The proposed mechanism for the formation of unsaturated compounds has been explained (Scheme 2). At first, the abstraction of proton of active methylene compound (thiazolidinedione) by Au NPs

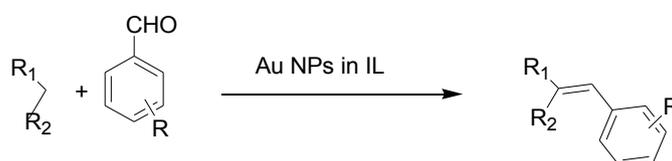
was took place, makes it nucleophilic. While, the carbonyl carbon of aromatic aldehyde behaved as electrophilic centre and was attacked by the nucleophile generated above and gave an intermediate. Further, it abstract a proton from AuNP-H, to form a stable compounds, which was went for dehydration and give the concerned product.

### Optimization of the catalytic condition for the synthesis of unsaturated compounds from thiazolidine-2,4-dione and 2,4-dichlorobenzaldehyde

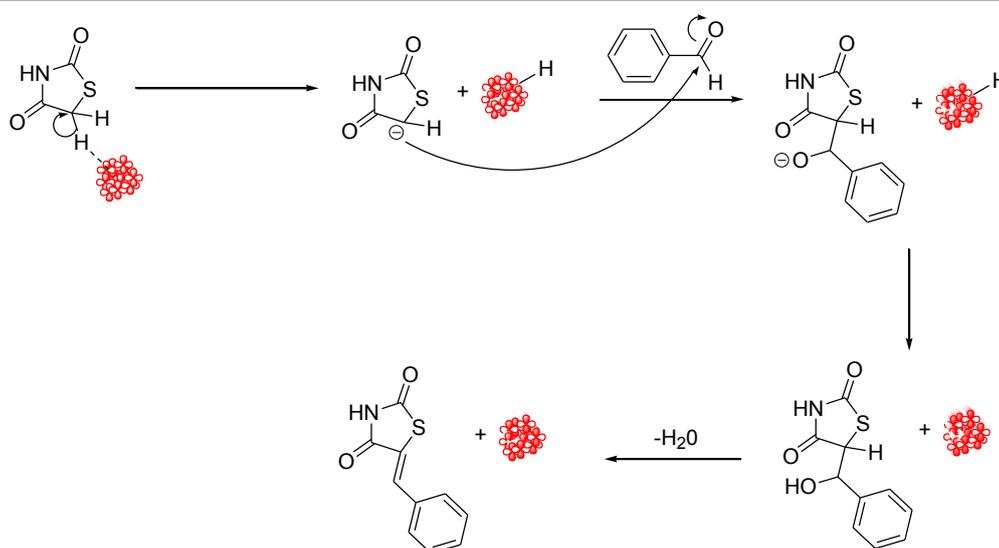
In a round bottom flask, 2,4-dichlorobenzaldehyde (10 mmol) and thiazolidine-2,4-dione (10 mmol) and catalyst were taken and was stirred at appropriate temperature for known time. The reaction was monitored by thin layer chromatography (TLC). The product was extracted in diethyl ether and solvent was evaporated to afford the product. Product was characterized by spectroscopic (FTIR, NMR and mass) techniques (Tables 1 and 2).

### General procedure for the condensation reaction between thiazolidine-2,4-dione and 2,4-dichlorobenzaldehyde using Au NPs in IL

In a round bottom flask (50 mL), 2,4-dichlorobenzaldehyde (10 mmol) and thiazolidine-2,4-dione (10 mmol) and 10 mL of Au NPs suspended in IL were taken. The reaction was stirred at appropriate temperature for known time. Completion of the reaction was checked by thin layer chromatography. Then, the reaction mixture was centrifuged at 8,000 rpm for 30 minutes. The organic compound present in the supernatant was extracted using diethyl ether. The organic layer was evaporated to afford the product and then recrystallized with ethanol. After centrifugation, the catalyst was pelleted out and washed with dilute ethanol to remove the organic impurity and the recovered



Scheme 1: Condensation reaction between active methylene compounds and aldehydes using Au NPs in ionic liquid.



Scheme 2: General mechanism of the Condensation reaction between thiazolidinedione and benzaldehyde using Au NPs in ionic liquid as a catalytic system.

Entry	Catalyst	Solvent	Temp (°C)	Time (min)	Yield (%)
1	-	THF	40	45	25
2	-	DMF	40	45	10
3	-	DMSO	40	45	-
4	-	Methanol	40	45	30
5	-	Water	40	45	25
6	-	Ionic Liquid (TAB)	40	45	35
7	-	Ionic Liquid (TAB)	55	45	60
8	-	Ionic Liquid (TAB)	70	45	70
9	-	Ionic Liquid (TAB)	80	45	75
10	-	Ionic Liquid (TAB)	100	45	60
11	-	Ionic Liquid (TAB)	120	45	50
12	Au NPs	-	80	45	95
13	Cu NPs	-	80	45	78
14	Ag NPs	-	80	45	65
15	Boric acid	-	80	45	80
16	Triflic acid	-	80	45	88
17	Indium chloride	-	80	45	80
18	Phosphotungstic acid	-	80	45	85
19	Molybdic acid	-	80	45	80
20	Au NPs	Ionic Liquid (TAB)	80	60	95
21	Au NPs	Ionic Liquid (TAB)	80	120	95
22	Au NPs	Ionic Liquid (TAB)	80	300	95

Table 1: Optimization of the condition for the reaction between thiazolidine-2,4-dione and 2,4-dichlorobenzaldehyde.

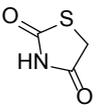
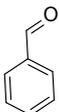
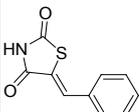
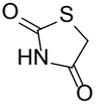
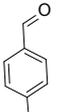
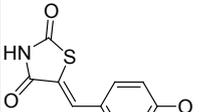
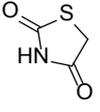
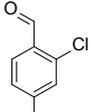
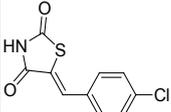
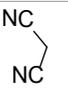
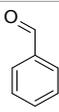
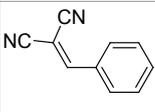
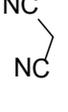
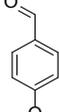
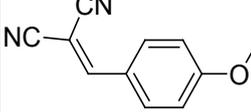
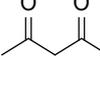
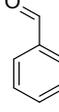
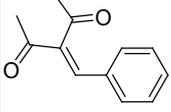
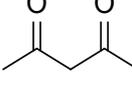
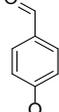
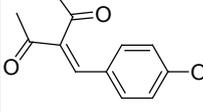
Entry	Reactant 1	Reactant 2	Product	Compound No.	Time (min)	Yield (%)
1				1	50	90
2				2	60	88
3				3	45	93
4				4	60	90
5				5	90	88
6				6	75	90
7				7	95	88

Table 2: Condensation reaction between various active methylene compounds and aldehydes using Au NPs in IL.

catalyst was dispersed in IL and reused for evaluating the performance in the next cycle. The structures of the compounds were confirmed by FTIR, NMR and mass spectroscopic techniques.

### Silver Nanoparticles in ionic liquid as an Efficient Catalytic System for the oxidative coupling of thiols

Herein, a methodology for the oxidation of thiols to prepare disulphide using Ag NPs in IL has been developed (Scheme 3).

Mechanism for the formation of disulphide from thiol has been explained (Scheme 4). Thiol was exposed to Ag NPs and forms alkylthiolated silver and silver hydride. Then, alkylthiolated silver was converted into disulphide and bare silver. Further, silver hydride on arial oxidation gave bare silver and water.

### Optimization of the catalytic system for the oxidation of thiophenol

Herein, thiophenol was treated with different catalytic system as in Table 3 for appropriate time and temperature. Completion of reaction was monitored by thin layer chromatography (TLC) and after completion of the reaction. The product was extracted by ethyl acetate and then, the organic layer was evaporated to afford the compound. Synthesized product was characterized by spectroscopic (FTIR, NMR and mass) techniques.

### General procedure for the oxidation of thiophenol using Ag NPs in IL

In a round bottom flask (50 mL), Ag NPs (5 mol%) was dispersed in the synthesized IL (10 mL) at 30°C and then thiophenol (10 mmol) was added. Completion of the reaction was monitored with thin layer chromatography (TLC). After the completion of reaction, the reaction mixture was centrifuged at 7,000 rpm for 30 minutes. Centrifuged pallet was washed with ethanol and redispersed in IL for other reactions. The supernatant obtained after centrifugation was taken in ethyl acetate (50 mL). Further, the organic layer was washed with water

(3x10 mL) and then with brine solution (3x10 mL), dried over sodium sulfate and the ethyl acetate was evaporated under reduced pressure to afford the product. Structural assignment of the product is based on their <sup>1</sup>H-NMR and <sup>13</sup>C-NMR, IR and Mass spectrum. Similarly, different derivatives have been synthesized (Table 4) and the spectral data revealed the formation of corresponding products.

### Cu NPs in IL as an efficient catalytic system for the Acetylation of alcohols, amines and thiols

Herein, application of Cu NPs in IL as potential catalyst in the protection of thiols, alcohols and amines has been explored (Scheme 5).

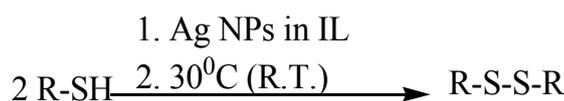
The proposed mechanism for the acetylation or protection of aniline has been explained (Scheme 6). Acetic anhydride was exposed to Cu NPs and the lone pair of electrons present in oxygen of the carbonyl was donated to Cu NPs and acquired positive charge with the formation of an intermediate. It was further, reacted to aniline and forms a transition compound and then proton was abstracted. It finally gave acetic acid phenyl ester or acetyl derivative of aniline.

### Optimization of the catalytic system for the acetylation of aniline

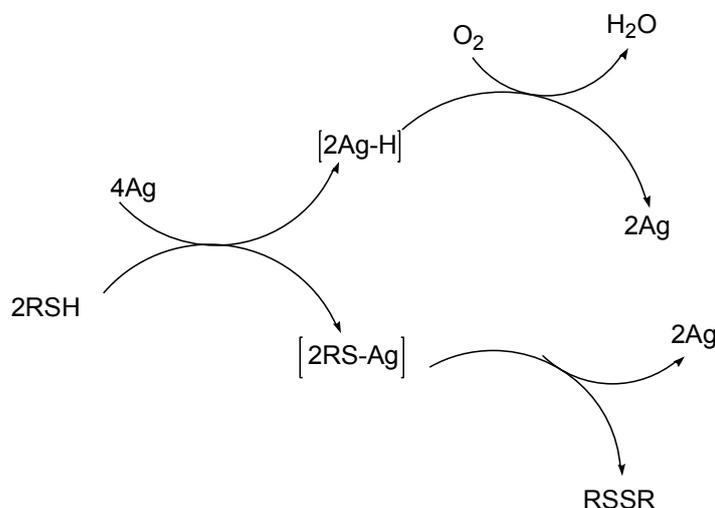
Aniline (1 mmol) and acetic anhydride (1.3 mmol) were taken to the flask and then different solvent, catalyst were added. The reaction mixture was stirred in different catalytic system for appropriate times at a temperature (Table 5). The completion of the reaction was checked by thin layer chromatography (TLC). After completion of the reaction, the product was extracted from reaction mixture using diethyl ether and then the diethyl ether was evaporated under reduced pressure to obtain the required product. Synthesized product was characterized by spectroscopic (FTIR, NMR and mass) techniques.

### General procedure for the acetylation of aniline using Cu NPs in IL

In this typical experiment, Cu NPs (0.05 mmol) was suspended in



Scheme 3: Oxidation of thiols into disulfides using Ag NPs.



Scheme 4: Mechanism for oxidation of thiols into disulfides using Ag NPs.

Entry	Catalyst	Solvent	Temperature (°C)	Time (min)	Yield (%)
1	-	THF	30	20	30
2	-	DMF	30	20	-
3	-	DMSO	30	20	-
4	-	Methanol	30	20	45
5	-	Water	30	20	-
6	-	Ionic Liquid (TAB)	30	20	75
7	-	Ionic Liquid (TAB)	40	20	75
8	-	Ionic Liquid (TAB)	50	20	75
9	-	Ionic Liquid (TAB)	60	20	75
10	-	Ionic Liquid (TAB)	75	20	75
11	Au NPs	-	30	20	45
12	Cu NPs	-	30	20	70
13	Ag NPs	-	30	20	98
14	Iodine	-	30	20	92
15	Sodium persulphate	-	30	20	85
16	FeCl <sub>3</sub>	-	30	20	88
17	H <sub>2</sub> O <sub>2</sub>	-	30	20	90
18	Br <sub>2</sub>	-	30	20	85
19	Ag NPs	Ionic Liquid (TAB)	30	60	98
20	Ag NPs	Ionic Liquid (TAB)	30	90	98
21	Ag NPs	Ionic Liquid (TAB)	30	120	98

Table 3: Optimization of catalyst for the oxidation of thiophenol using different catalyst.

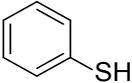
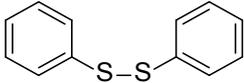
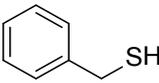
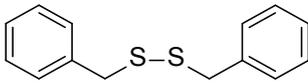
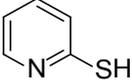
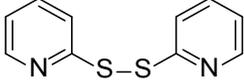
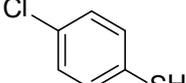
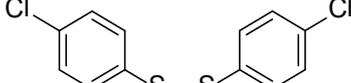
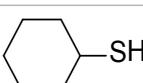
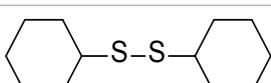
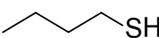
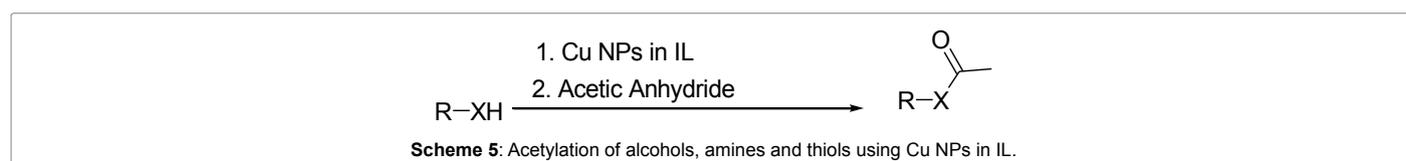
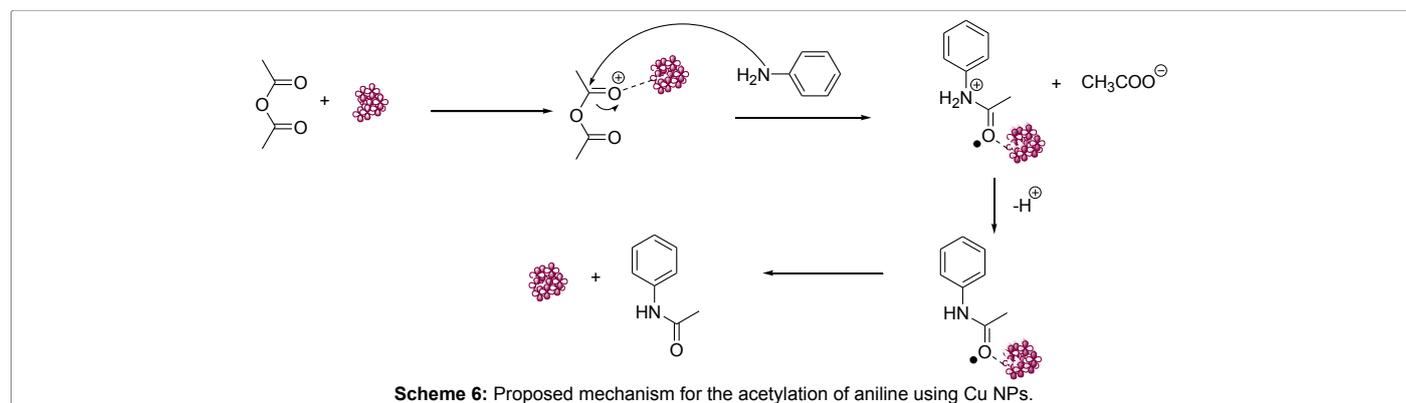
Entry	Reactant	Product	Compound No.	Time (min)	Yields (%)
1			8	20	98
2			9	15	96
3			10	16	91
4			11	25	85
5			12	20	92
6			13	22	90

Table 4: Synthesis of disulfides using the Ag NPs in IL as catalytic system.



the synthesized ionic liquid (5ml) and was stirred. Aniline (1 mmol) and acetic anhydride (1.5 mmol) were added to the above flask and then the reaction mixture was stirred for appropriate time. The completion of the reaction was checked by thin layer chromatography (TLC). After completion of the reaction, the reaction mixture was taken in diethyl ether. Then the reaction mixture was centrifugated and the supernatant was taken in a flask and it was dried over sodium sulphate. Further, the

organic solvent was washed with brine solution and then the organic layer was evaporated under reduced pressure to obtain the required product. Structural assignments of the products are based on their IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and Mass spectroscopic techniques. Formation of acetyl derivatives of different thiols, alcohols and amines is in good to high yield as mentioned in Table 6. Centrifuged pallet i.e. Cu NPs were



Entry	Catalyst	Solvent	Temperature (°C)	Time (min)	Yield (%)
1	-	THF	30	5	-
2	-	DMF	30	5	-
3	-	DMSO	30	5	-
4	-	Methanol	30	5	-
5	-	Water	30	5	75
6	-	Ionic Liquid (TAB)	30	5	80
7	Au NPs	-	30	5	50
8	Cu NPs	-	30	5	96
9	Ag NPs	-	30	5	88
10	CoCl <sub>2</sub>	-	30	5	88
11	ZnCl <sub>2</sub>	-	30	5	85
12	RuCl <sub>3</sub>	-	30	5	75
13	LiClO <sub>4</sub>	-	30	5	85
14	Mg(ClO <sub>4</sub> ) <sub>2</sub>	-	30	5	80
15	Zn(ClO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	-	30	5	84
16	Cu NPs	Ionic Liquid (TAB)	30	15	96
17	Cu NPs	Ionic Liquid (TAB)	30	30	96
18	Cu NPs	Ionic Liquid (TAB)	30	45	96

**Table 5:** Optimization of the catalyst for synthesis of acetyl derivative of aniline.

S. No.	Reactant	Product	Compound No.	Time (min)	Yield (%)
1			14	5	95
2			15	5	90
3			16	10	85
4			17	5	87
5			18	5	85
6			19	4	93
7			20	5	90

**Table 6:** Acetylation of different compounds by using Cu NPs in IL.

washed with ethanol and dispersed in ionic liquid to be used as the catalytic system to carry out other reactions.

## Results and Discussion

### Impact of Au NPs in IL as efficient catalytic system for the synthesis of unsaturated compounds (Knoevenagel condensation)

To carry out the synthesis of unsaturated compounds via the reaction between active methylene compounds and aromatic aldehyde, an efficient catalytic system was used via optimizing different parameters.

Herein, the reaction was carried out between thiazolidine-2,4-dione and 2,4-dichlorobenzaldehyde using different solvent (THF, DMF, DMSO, methanol, water and ionic liquid), catalyst (Au NPs, Ag NPs, Cu NPs, triflic acid, indium chloride, phosphotungtic acid) and further, temperature was varied to obtain maximum yield in minimum duration of reaction. As per Table 1, during the optimization of solvent, it was observed that maximum yield was obtained in case of ionic liquid. DMSO is the only in which no product was formed while using other solvent, a small amount of product was obtained. But for getting maximum yield, temperature was varied. It was observed that initially we obtained increases in yield and maximum was obtained when the temperature was 80°C. On further increases in temperature, yield decreases and it is because of the stability factor of the ionic liquid as the ionic liquid starts decomposing at 90°C and the same was confirmed through thermo-gravimetric analysis of the ionic liquid. To further increase the yield of the product, different catalysts were introduced and the maximum yield was obtained in case of gold nanoparticles dispersed in the ionic liquid. Also, the effect of time was studied and it was observed that with increase in duration of the reaction, no increase in the yield was observed.

Powder X-ray diffraction pattern of the sample showed signature for gold nanoparticles. The peaks found at two theta value of 37.54, 43.98 and 66.45 confirmed the presence of Au NPs in the sample. The size of Au nanoparticles was determined by Using Scherrer formula and no change in particle size was found after recycle. No change in the nanoparticles size showed the potential of the gold nanoparticles. It is a sign of the stability of Au NPs (Figure 1). A series of unsaturated

compounds have been synthesized using the active methylene compounds and the aromatic aldehyde as mentioned in Table 2.

Recycling of catalyst a control experiment for the coupling of TZD and 2,4-dichlorobenzaldehyde was conducted for showing potential of catalyst up to six cycles and only a little decrease in activity of Au NPs in IL was found (Graph 1). The recyclability of Au NPs was also surveyed thoroughly. After completion of the reaction, Au NPs were isolated from the reaction mixture via at 8,000 rpm for 10 minutes. Further, the centrifuged pallet was washed with ethanol to remove all the organic impurities and dispersed in IL to be used as catalytic system for next cycles for evaluating the performance. It was found that a slight decreases in the yield of the product which showed the slight loss in the activity of catalyst.

### Impact of Ag NPs in IL as an efficient catalytic system for the oxidative coupling of thiols

To carry out the synthesis of disulphides compounds via the oxidation reaction of thiols, there is need to find an efficient catalytic system. To find out the optimum condition for the oxidation reaction in thiols to obtain the disulphide, various parameters were optimized. Herein, the reaction was carried out using different solvent (THF, DMF, DMSO, methanol, water and ionic liquid), catalyst (Au NPs, Ag NPs, Cu NPs, iodine, sodium persulphate, ferric chloride, hydrogen peroxide, bromine water) and further, temperature was varied to obtain maximum yield in minimum duration of reaction. As per Table 3, first of all for the optimization of solvent, it was observed that maximum yield was obtained in case of ionic liquid. No product was formed when DMF or DMSO were used as solvent for the synthesis of disulphides via the oxidation of thiols. But for getting maximum yield, the temperature of reaction mixture was varied. It was observed that no increase in yield was found. For further enhancement in the yield of the product, different catalysts were used and the maximum yield was obtained in case of Ag NPs dispersed in the IL. Also, the effect of time was studied and it was observed that with increase in duration of the reaction, no increase in the yield was observed.

Powder X-ray diffraction pattern of the sample showed signature for silver nanoparticles. The peaks found at two theta value of 37.35 and 44.65 confirmed the presence of silver nanoparticles in the sample. The size of silver nanoparticles was determined by Using Scherrer

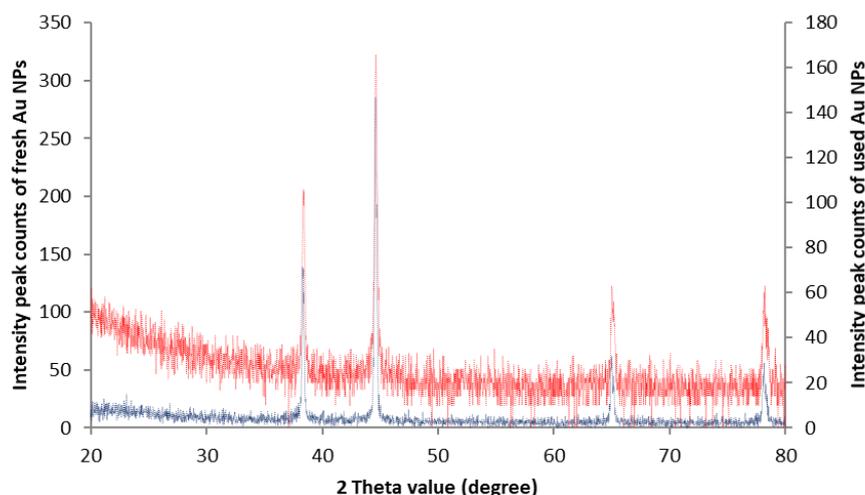
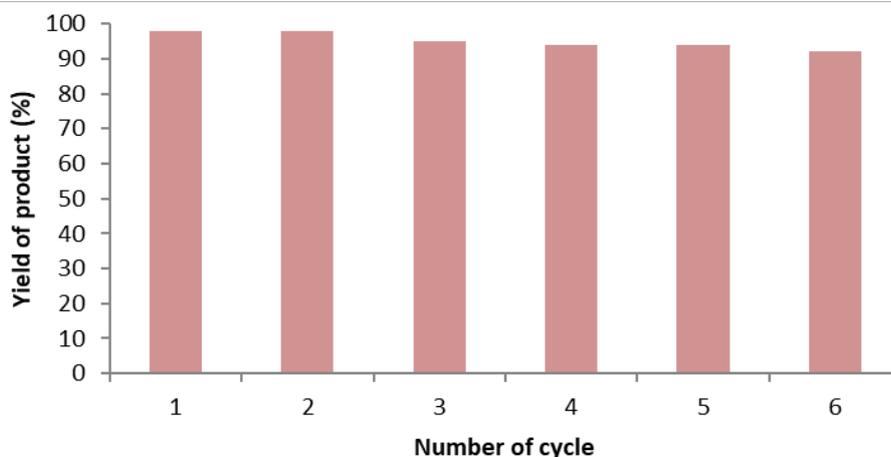


Figure 1: Powder X-ray diffraction of fresh and used Au NPs.



Graph 1: Potential of Au NPs after recyclability from the reaction.

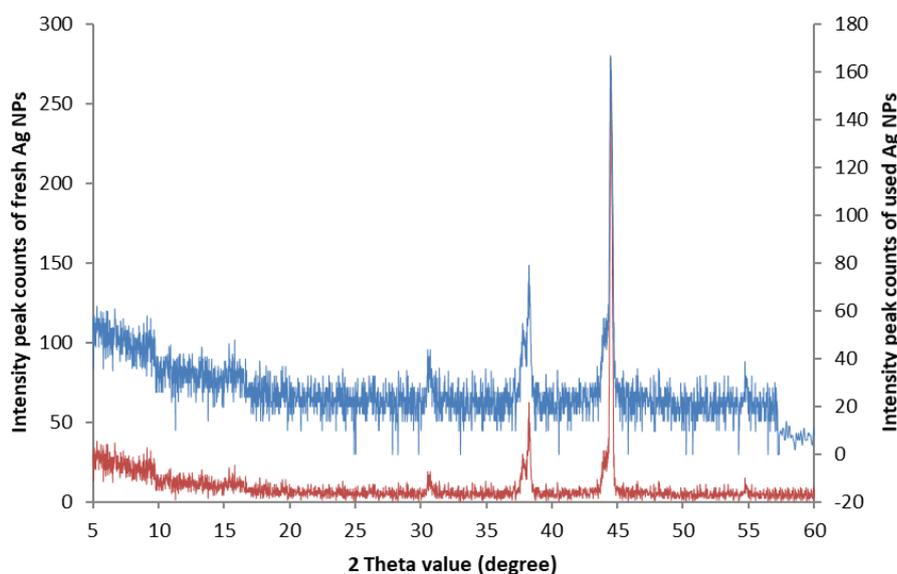


Figure 2: Powder X-ray diffraction of fresh and used Ag NPs.

formula and no change in particle size was found. No change in the nanoparticles size showed the potential of the silver nanoparticles. It is a sign of the stability of silver nanoparticles (Figure 2). A series of disulphides have been synthesized via the oxidation of thiols as mentioned in Table 4.

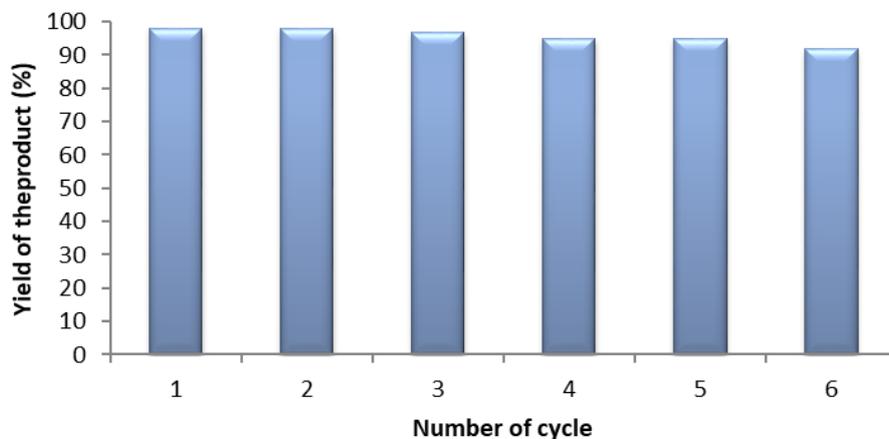
Recycling of catalyst a control experiment of coupling of thiophenol was conducted for showing recycling potential of catalyst for six cycles (Graph 2). The data show a slight loss of activity of catalyst used in experiment with cycle. Recycling of the catalyst was done by centrifugation on the reaction mixture after the completion of the reaction mixture. The supernatant was taken and the pallet was washed and stored. Ionic liquid was recovered from the supernatant and used to disperse the Ag NPs for further reactions.

### Impact of Cu NPs in IL as efficient catalytic system for the acetylation of alcohols, amines and thiols

To carry out the acetylation of phenol via the reaction of aniline

with acetic anhydride in an efficient catalytic system was used. To find out the optimum condition for the acetylation reaction of phenol using acetic anhydride to obtained acetyl or protected phenols, various parameters were optimized i.e. solvent, catalyst, temperature, time etc. Herein, the acetylation reaction was carried out using different solvent (THF, DMF, DMSO, methanol, water and ionic liquid), different catalysts (Au NPs, AgNPs, Cu NPs,  $\text{CoCl}_2$ ,  $\text{ZnCl}_2$ ,  $\text{RuCl}_3$ ,  $\text{LiClO}_4$ ,  $\text{Mg}(\text{ClO}_4)_2$ ,  $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ) to obtain maximum yield in minimum duration of reaction. As per Table 5, during the optimization of solvent, it was observed that product was formed only when water and ionic liquid were used as solvent while in other cases no product was formed. But for maximum yield, different catalysts were used for obtaining maximum yield and the maximum yield was obtained in case of Cu NPs dispersed in the ionic liquid. To further increase the yield of the product, duration of the reaction was optimized and found no change in yield with increase in time period.

Powder X-ray diffraction pattern of the sample showed signature



Graph 2: Potential of Ag NPs after recyclability from the reaction.

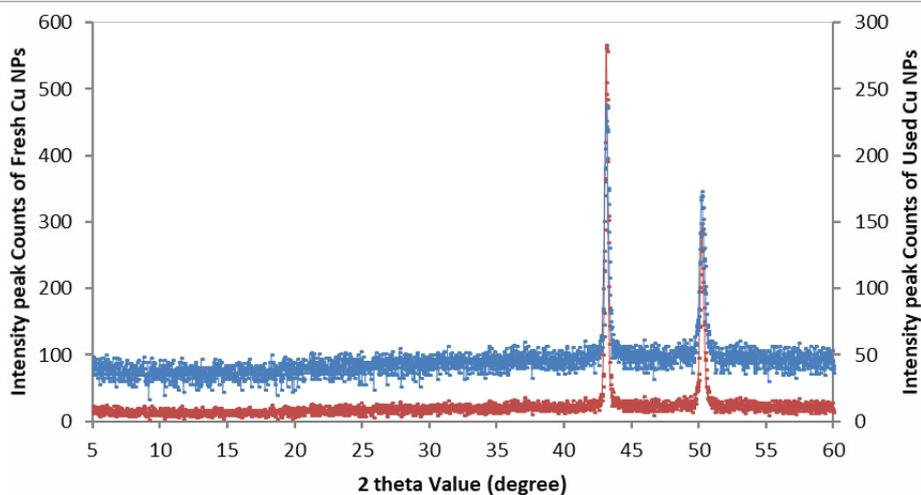
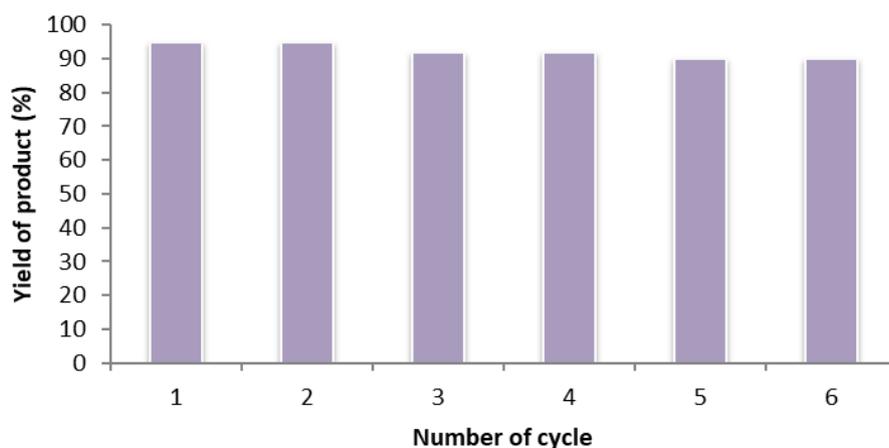


Figure 3: Powder X-ray diffraction of fresh and used Cu NPs.



Graph 3: Potential of Cu NPs after recyclability from the reaction.

for copper nanoparticles. The peaks found at two theta value of 42.06 and 49.54 confirmed the presence of copper nanoparticles in the sample. The size of copper nanoparticles was determined by Using Scherrer formula and no change in particle size was found after recycle.

No change in the nanoparticles size showed the potential of the copper nanoparticles. It is a sign of the stability of Cu NPs (Figure 3). A series of acetyl derivatives of the compounds have been synthesized using acetic anhydride as acetylating agent as mentioned in Table 6.

## Recycling of catalyst

A control experiment of acetylation of aniline was conducted for showing recycling potential of catalyst for six cycles. It was observed that a slightly gradual loss of activity of catalyst used in experiment (Graph 3). Data showed a minor loss of activity of Cu NPs in IL used in organic reaction. Recycling of the catalyst was done by centrifugation on the reaction mixture after the completion of the reaction mixture. The supernatant was taken and the pallet was washed and stored. Ionic liquid was recovered from the supernatant and used to disperse the Cu NPs for further reactions.

## Conclusion

It was observed that the synthesized Au NPs in IL catalyzed the condensation between active methylene compounds and aldehydes and gave products with high yields in short duration. Present methodology avoids the use of expensive reagents, very high temperatures and the reaction being performed in ionic liquid serves as a green and efficient method. It is remarkable that the reaction carried out using Au NPs in IL which makes the procedure quite simple, more convenient and environmentally benign. Further, it was found that Ag NPs in ionic liquid showed the best activity for the formation of disulphides. Further, a simple and highly efficient methodology was developed for the formation of disulfides using Ag NPs to give the corresponding disulphides in shorter duration of time with good to high yield. It was found that Ag NPs can be recycled and reused for other reaction, which makes it cheap or economical. Then, an easy and rapid procedure for the acetylation of alcohols, amines and thiols using easily recyclable Cu NPs in ionic liquid was determined. This catalytic system gave the corresponding products in shorter duration of time with good to high yield. Several catalytic systems were studied and out of those Cu NPs in IL showed the best activity as acetylation agent. Further, it was found that Cu NPs can be recycled and reused for other reaction, which makes it cheap or economical.

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