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Fixation of CO_2 as Carboxylic Acid Precursor by Microcrystalline Cellulose (MCC) Supported Ag NPs: A More Efficient, Sustainable, Biodegradable and Eco-friendly Catalyst

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ABSTRACT

Silver Nanoparticles supported on microcrystalline cellulose (Ag NPs@ MCC), an active catalyst has been discovered for the direct carbonylation of terminal alkynes with CO_2 in to carboxylic acid at mild and sustainable reaction conditions. The stabilized Ag NPs shows higher distribution with uniform particle size. The catalyst was characterized by PXRD, SEM, TEM, HR-TEM, EDS, EDX, ICP-AES and XPS analysis. Ag NPs@ MCC material were found to be more efficient, shows excellent dispersion in various solvents and biodegradable. The solvents effects on carbonylation of terminal alkynes were well studied by experimentally and computationally. Further, the present catalyst can be recyclable up to five catalytic cycles without significant loss in its activity and also applicable for the gram scale carbonylation of terminal alkynes.

KEYWORDS: Microcrystalline Cellulose (MCC), Carboxylic acid, CO_2

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INTRODUCTION

Carbon dioxide is an abundant greenhouse gas, renewable carbon source and an environmentally friendly chemical reagent present on earth. However, its atmospheric concentration has risen day by day which contributes in growing problems such as climate change and global warming. To mitigate the emission reduction, CO_2 capture and its utilization in to various applications is one of the best solutions. Importantly, CO_2 constitutes a highly attractive C1- building block in synthetic organic chemistry due to its abundant supply from industries and easy handling. In contrast, only few industrial-scale catalysis processes have been developed that use carbon dioxide as a carbon source.[1-6] This is attributed due to the fact that CO_2 is low in energy, thermodynamically stable, chemically inert, less reactive, highly symmetrical and more difficult to activate for bond formation. Thus, strong nucleophiles or harsh reaction conditions were usually required when carbon dioxide is utilized in organic syntheses. Significant efforts have been developed to transform carbon dioxide into high-value chemicals.[7-9]

The transition-metal-catalyzed carboxylation reactions of various carbon nucleophiles with C–C bond formation have been actively developed for the preparation of fine chemicals. In this regards, the demand of more efficient, robust and sustainable catalyst material increase due to its ability to activate as well as convert CO_2 in to some valuable organic chemicals more effectively.[10-12] Silver, is a coinage metal, which has been widely utilized in various organic syntheses. In present time, silver catalyzed activation of inactivated C-H bonds into desired functionalities has emerged as a powerful method in organic synthesis. Moreover, the transition-metal-catalyzed C-H bond functionalization could offer green and sustainable methodology to construct diverse organic molecules starting from simple and easily available compounds.[13-16]

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Propiolic acids are belongs to the more valuable intermediates and successfully applied in the various biological important molecules (Figure 1). Traditionally, the syntheses of propiolic acids carried out by the oxidation of propargylic alcohols or aldehyde, deprotonation of alkynes with strong bases such as alkali metal hydrides or organometallic reagents. However, these methods are not environmental friendly.[17-19] Literature reports indicate that different homogeneous catalysts have been well developed to afford the higher yield of Propiolic acid.[20-22] However, major bottleneck of these catalysts are its recyclability issues and its metal contamination in to the desired product that made this protocol less sustainable and applicable. To overcome this issues, metal nanoparticles (NPs) are intensely researched in the field of catalysis, as they combine the recyclability of heterogeneous catalytic systems and the activity and selectivity of homogeneous ones.[25-30] After that, several supported metal nanocatalyst (heterogeneous catalysts) have been well reported for the synthesis of Propiolic acid. In 2014, Cheng and co-worker have synthesized Ag NPs/MIL-101 (zeolite-type metal-organic framework) material and demonstrated its applicability for the synthesis of Propiolic acid. However, the need of higher loading and recyclability issues would render its applicability.[31] Previously, Huang and co-worker have developed a silica supported Schiff-base based silver catalyst and its shows higher activity towards the synthesis of Propiolic acid. However, the aggregation of silver nanoparticles that affect its catalytic performance.[32] In recent report, similar group have reported mesoporous knitting aryl network polymers supported silver nanoparticles (Ag NPs/KAPs). It has noted that the materials exhibits narrow size distribution of Ag NPs and achieved higher yield of desired product. However, this strategy required tedious workup for the preparation of the catalyst material.[33]

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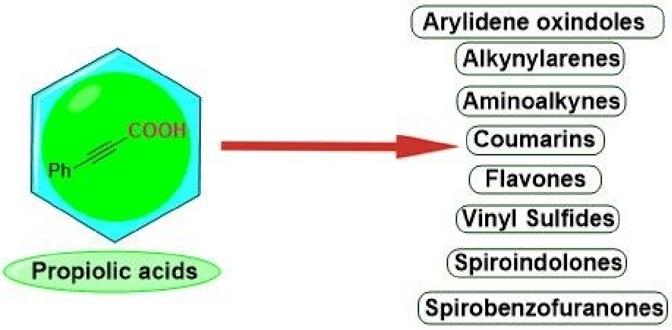

Figure 1. Various important organic molecules synthesis from the Propiolic Acids.

Thus, the development of a more efficient, sustainable, low cost, easily available and bio-degradable supported silver nanocatalyst is must require for the fixation of CO_2 into corresponding to Propiolic acid under milder and greener reaction conditions. In the present work, we have synthesized Ag NPs supported on MCC (Ag NPs/MCC) and investigated its performance towards the fixation of CO_2 via C-H bond activation of terminal alkyne. The present catalyst shows excellent dispersion, higher activity, scalability, and recyclability. Importantly, the solvents effects on carbonylation of terminal alkynes were well studied by experimentally and computationally. Further, the applicability of the Propiolic acid was exploded for the synthesis of aminoindolines, pyrrolo [1,2a] quinoline and arylacetylenic sulfones.

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RESULT AND DISCUSSION

Synthesis and Characterization of Ag NPs/MCC material

Microcrystalline Cellulose (MCC) is an interesting conjugated polymer and composed of glucose units connected with a 1, 4-β glycosidic bond. It exhibits unique properties including such as renewable, biodegradable, non-toxic, thermally stable, superior mechanical strength, inexpensiveness, excellent dispersion, controllable surface chemistry and environmental sustainability made this material highly favourable for the catalysis support. [34-35] The catalyst was synthesized by sorption reduction method. After impregnation of Ag NPs the colour of support material changed from white to light reddish brown. The catalyst was centrifuged, washed with water, dried and isolated as a light reddish brown coloured powder. The catalyst system was characterize by different sophisticated analytical techniques such as energy dispersive X-ray spectroscopy (EDS), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), powder X-ray diffraction (PXRD), inductively coupled plasma atomic emission spectrometry (ICP-AES), and transmission electron microscopy (TEM) and high-resolution-transmission electron microscopy (HR-TEM).

The crystalline phase of the Ag NPs/MCC was characterized by powder XRD. The finely amorphourous powdered MCC did not show any peak, only a broad hump was observed at 2θ value at 15.73˚ and 22.61˚ which indicated the amorphous nature of the carbon matrix. (**Figure S_1**). When this MCC material was impregnated with silver nanoparticles, it showed four characteristic peaks at 38.37˚, 44.51˚, 64.69 ˚ and 77.61˚ in the XRD spectrum and conferring (111), (200), (220) and (311) facets of the face centered cubic (fcc) symmetry. It confirmed Ag NPs pattern agreed as per JCPDS card no. 04-0783 and suggesting that the Ag NPs were crystalline in nature as represented in **Figure 2 (A)**.[36] The

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average particles size of Ag NPs calculated from the Scherrer's equation was found to be 5-10 nm. The oxidation state and surface property of silver nanoparticles supported on MCC was also investigated by X-ray photoelectron spectroscopy. The 3d orbital of silver clearly resolved in to Ag $3d_{5/2}$ and Ag $3d_{3/2}$ contributions centred at 368.4 eV and 374.4 eV respectively depicted in **Figure 2 (B),** which are in good agreement with the binding energies of metallic silver Ag (0).[37]

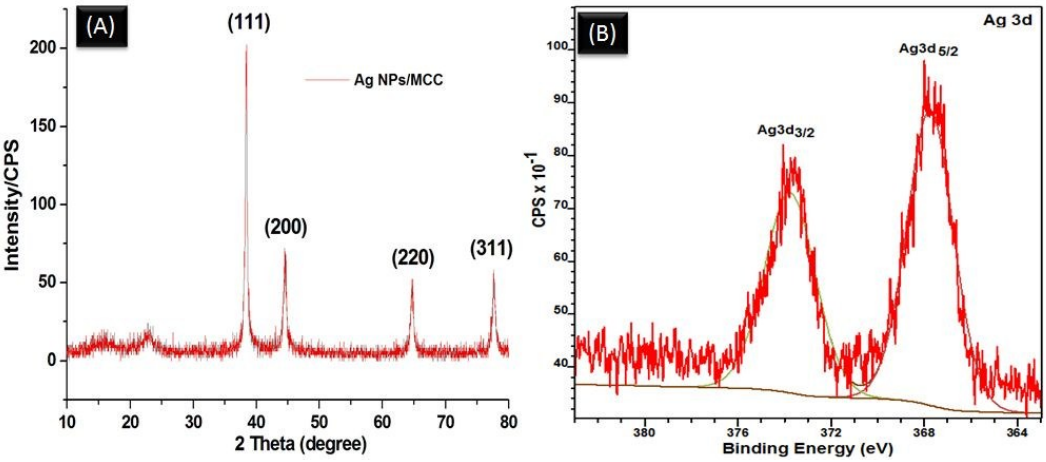

Figure 2. PXRD of Ag NPs/MCC (A) and deconvoluted XPS spectra of Ag3d (B).

The FT-IR spectra shown in **Figure 3** exhibit the patterns of the functional groups present in both MCC and Ag NPs/MCC. The observed peaks in the range of 3660-2900 cm^{-1} is characteristic peak for stretching vibration of O-H and C-H bonds present in polysaccharides. In addition, the broad peak observed at 3331 cm^{-1} is the characteristic for the confirmation of the stretching vibration of the hydroxyl group present in polysaccharides. The band observed at 2864 cm^{-1} is mainly attributed due to the C-H stretching vibration of all hydrocarbons in polysaccharides. The peaks found at 1633 cm^{-1} correspond to the vibration of water molecules that absorbed in micro crystalline cellulose. Apart from that, the absorption bands observed at 1428, 1367, 1334, 1027 cm^{-1} and 896 cm^{-1} belong to stretching and bending vibrations of $-CH_2$, -CH, -OH and C-O bonds in micro crystalline cellulose. The band around 1420-1430 cm^{-1} is associated due to the amount of the crystalline structure of the

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cellulose, while the band at 897cm^{-1} is assigned to the amorphous region in cellulose.[38-39] After impregnation of MCC with Ag NPs, all absorption peak positions are almost similar to those present in the case of MCC, which indicated that the structure of MCC is not much changed after the impregnation with Ag NPs.

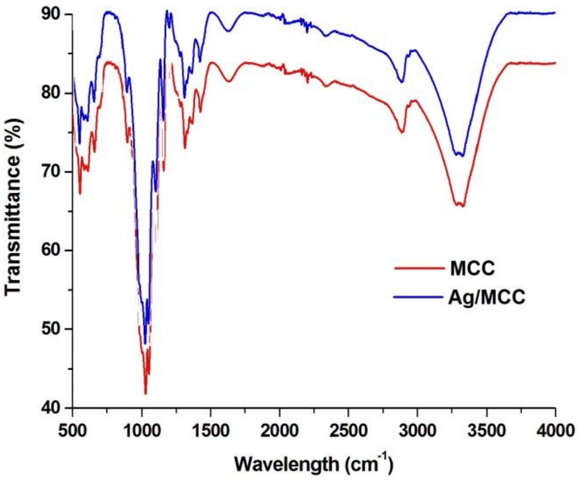

Figure 3. FT-IR spectrum of MCC and Ag NPs/MCC.

Scanning electron microscopy (FE-SEM) was used to study the composition and surface morphology of Ag NPs/MCC. The results clearly show that there is a no change in the morphology of Ag NPs/MCC shown in **Figure 4** as compared with MCC (**Figure S_2**). The EDS mapping (**Figure 5**) and EDX spectra (**Figure 6**) evaluated the presence of Ag and also indicate the homogenous distribution of Ag NPs. Total quantity of Ag loaded on to MCC was investigated by ICP-AES analysis. 500 mg of catalyst material was incinerated in a crucible for 2h at 550 ˚C. The residue was dissolved in 1 mL aqua regia and diluted to 5 mL with distilled water. The average concentration of silver (3 trials) as determined by ICP-AES was found to be 0.0275 mmol/ 500 mg (0.8 mg/ 500 mg).

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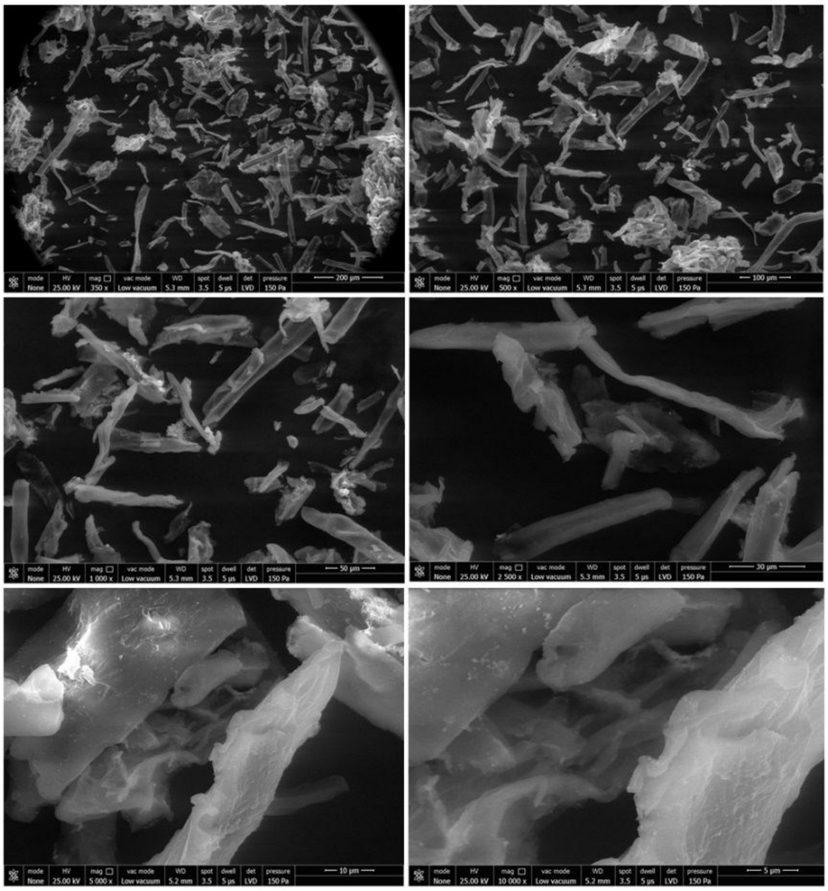

Figure 4. SEM images of Ag NPs/MCC.

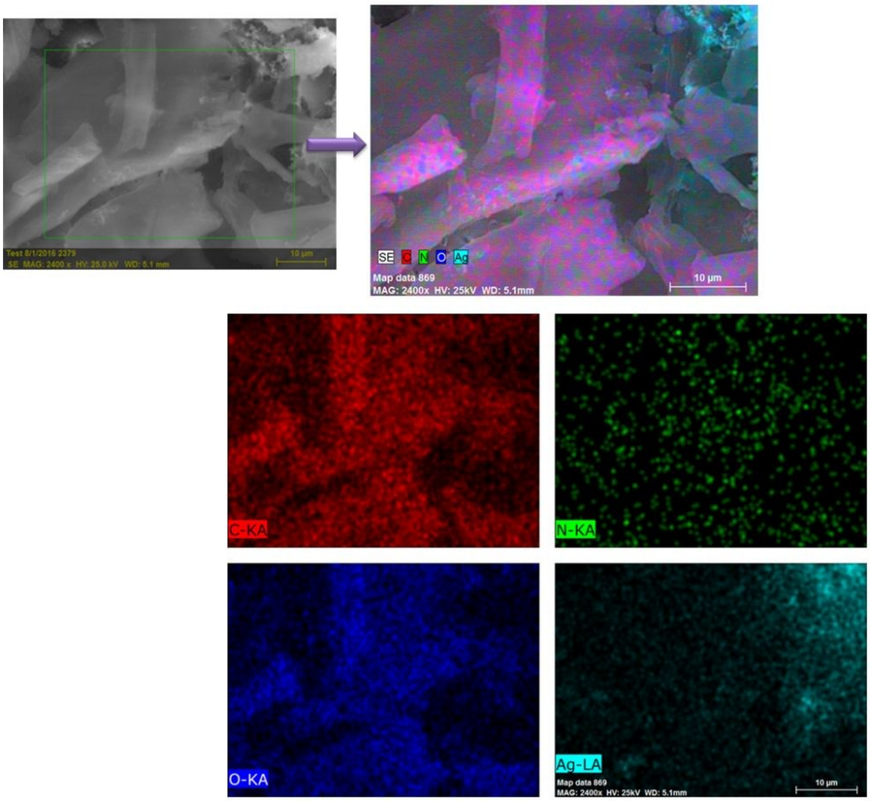

Figure 5. EDS mapping of Ag NPs/MCC.

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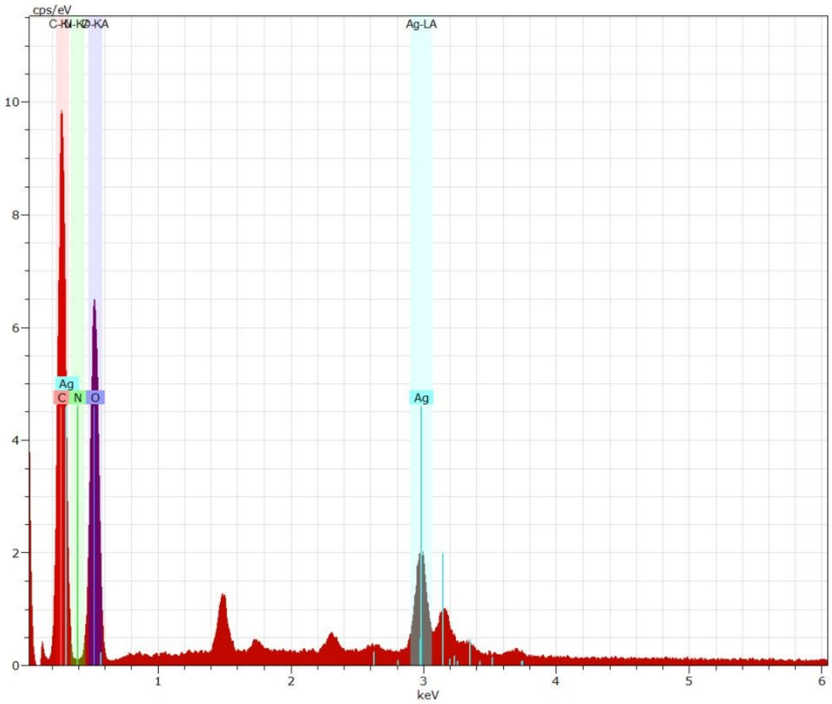

Figure 6. EDX spectrum of Ag NPs/MCC.

Furthermore, the internal morphology and size of Ag NPs were characterized from transmission electronic microscopy (TEM). TEM images of the Ag NPs/MCC catalyst material are represented in **Figure 7**. As shown, all of the Ag NPs were spherical in shape and well dispersed into the support without any aggregation. The particle sizes of Ag NPs were between 2-10 nm as illustrated in histogram. TGA studies for MCC and Ag NPs/MCC were carried out and the graph of the percentage weight loss versus temperature is represented in **Figure S_3** and **Figure S_4**. In case of MCC, slow initial weight loss was attributed to moisture or monomers thereafter, the degradation was rapid between 200 and 380 ˚C which was mainly due to the concurrent cellulose degradation processes including de-polymerization, dehydration and decomposition of glycosyl unit followed by the formation of charred residue. (**Figure S_3**). Final residue at 650 ˚C was 6.910 %. TGA of Ag NPs/MCC showed similar pattern however; in comparison the residue left at 650 ˚C was large (9.684

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%). This large increase in the amount of residue was mainly attributed to Ag NPs (**Figure S_4**).

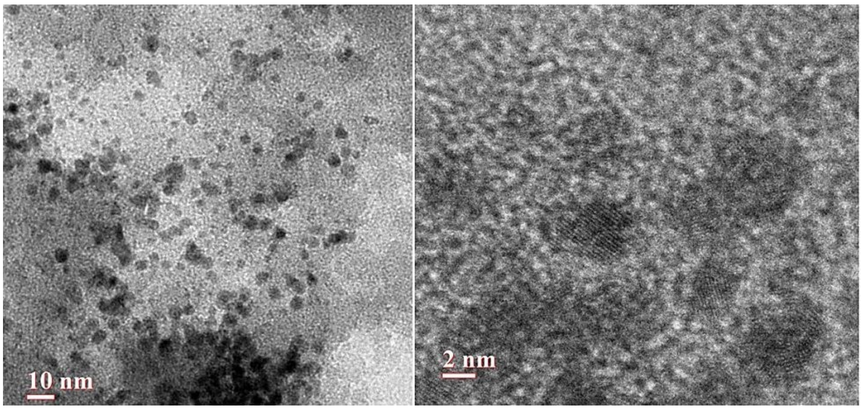


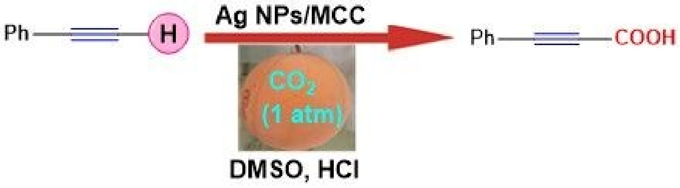
Figure 7. TEM and HR-TEM images of Ag NPs/MCC.

Catalyst potential for Ag NPs/MCC material

Our main objective was to design and develop an active silver based biodegradable, non-toxic and heterogeneous catalyst that can facilitate the carboxylation of phenyl acetylene via C-H bond activation under milder and sustainable reaction conditions. In this regard, microcrystalline cellulose based catalyst would not only render the procedure greener but also applicable in industries and academia in large scale synthesis due to its several promises. Thus, microcrystalline cellulose (MCC) was successfully used as support material for the stabilization of silver nanoparticles (Ag NPs). The silver nitrate ($AgNO_3$) was immobilized over MCC surface via noncovalent interaction with MCC. At initial stage, the comparative catalytic potential of this material (Ag NPs/MCC) were evaluated for the carbonylation of acetylene in to propiolic acid via C-H bond activation reaction. For our initial study, we selected carboxylation of phenyl acetylene as a model reaction (**Scheme 1**). The experimental set up was represented in **Figure S_5**.

The investigation of the effect of various parameters such as catalyst quantity, solvents, reaction time and temperature were also studied on this reaction to achieve the best optimization reaction condition. It has shown that, when the reaction was performed with

$AgNO_3$ or microcrystalline cellulose (MCC) alone as catalyst, trace conversion were observed (**Entries 1, 2, Table 1**). However, the Ag NPs/MCC catalyst shows excellent yield of product (99 %) at 50 ˚C after 16h in DMSO (**Entry 4, Table 1**). In addition, the reaction was also carried out with absence of catalyst and observed no progress of the reaction. (**Entry 3, Table 1**). These results revealed that the catalyst was necessary to proceed the reaction.



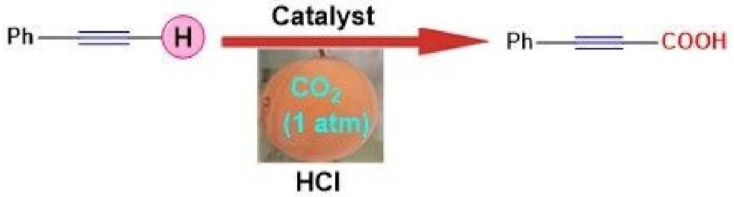
Scheme 1. Carbonylation of Phenyl acetylene via C-H bond activation catalyzed by Ag NPs/MCC.

Importantly, the effect that a solvent exerts on a rate of heterogeneously catalyzed reaction mainly depends on reaction substrates and support material of catalyst. It has shown that the solvents do not merely acts as diluent in which the reactants are dissolved; they can also interact with the catalyst surface and modify the extent to which different kind of substrates are absorbed on the surface of catalyst [40]. The solvents used in the experiments were methanol (MeOH), dimethyl sulphoxide (DMSO), dimethyl formamide (DMF), toluene and acetonitrile. The best yield of phenyl propiolic acid (99 %) was obtained in DMSO (**Entry 4, Table 1**). However, 50 % yield was found in DMF (**Entry 6, Table 1**), 20 % yield in MeOH (**Entry 5, Table 1**) and trace yield of desired product in case toluene and MeCN respectively.

Further, the effects of various bases such as sodium carbonate (Na_2CO_3), potassium carbonate (K_2CO_3) and trimethyl amine (NEt_3) were screened. It has concluded that the poor yield was noticed in all these bases (**Entries 12-14, Table 1**). Literature reports indicate that the caesium carbonate (Cs_2CO_3) is one of the most commonly used bases to precede the reaction with well product yield. In our studied, the best yield of product was formed in case of Cs_2CO_3. Importantly, it has shown that the combination of Cs_2CO_3 with DMSO plays a crucial role to boost the conversion to the desired product with high yield. In addition, the stronger polar solvent (DMSO) may promote the dissolution of Cs_2CO_3 in the liquid phase, which was responsible for alkynes to free the terminal protons by forming the Ag-C intermediates for further carboxylation. [33, 41]

After successfully optimization of the base and solvent, the effect of temperature on the carbonylation of phenyl acetylene was investigated by changing the reaction temperature from 40 °C to 50°C. In our delight, the yield of phenyl propiolic acid was increased from 67 % to 99 %. In addition, the reaction was also conducted at room temperature and observed that the poor yield of product be formed (**Entry 17, Table 1**). Therefore, 50 °C was selected as an optimal temperature. It was also shown that the yield of phenyl propiolic acid was increased from 42 % to 99 % as increasing the reaction time from 5h to 16 h. The maximum yield of product was achieved after 16 h. After successfully achieved the optimum reaction time, the effect of catalyst dose was examined by changing the amount of catalyst while keeping the other parameters constant. As we increased the catalyst dose from 20 mg to 30mg, the product yield increased from 82.7 to 99.0 %. We found that the best yield of product was obtained with 30 mg of catalyst (2.0 mol % of Ag). Further increasing the catalyst quantity from 30 mg to 50 mg, the yield was drastically decreased from 99 % to 58.7 %.

Table 1. Catalyst Screening and Reaction optimization[a].



Entry	Catalyst	Solvent	Base	Time (h)	T (°C)	Yield (%)[a, b]

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1	$AgNO_3$	DMSO	Cs_2CO_3	24	50	5 %
2	MCC	DMSO	Cs_2CO_3	24	50	Trace
3	No Catalyst	DMSO	Cs_2CO_3	24	50	N.R
4[b]	Ag NPs/MCC	DMSO	Cs_2CO_3	16	50	99
5	Ag NPs/MCC	MeOH	Cs_2CO_3	16	50	20
6	Ag NPs/MCC	DMF	Cs_2CO_3	16	50	50
7	Ag NPs/MCC	CH_3CN	Cs_2CO_3	16	50	Traces
8	Ag NPs/MCC	Toluene	Cs_2CO_3	16	50	Traces
9[c]	Ag NPs/MCC	DMSO	Cs_2CO_3	16	50	82.7
10[d]	Ag NPs/MCC	DMSO	Cs_2CO_3	16	50	55.9
11[e]	Ag NPs/MCC	DMSO	Cs_2CO_3	16	50	58.7
12	Ag NPs/MCC	DMSO	Na_2CO_3	16	50	02 %
13	Ag NPs/MCC	DMSO	K_2CO_3	16	50	Traces
14	Ag NPs/MCC	DMSO	NEt_3	16	50	Traces
15	Ag NPs/MCC	DMSO	Cs_2CO_3	06	50	42
16	Ag NPs/MCC	DMSO	Cs_2CO_3	10	50	65
17	Ag NPs/MCC	DMSO	Cs_2CO_3	16	RT	Traces
18	Ag NPs/MCC	DMSO	Cs_2CO_3	16	40	67

[a] Reaction Conditions: Alkyne (1 mmol), Catalyst (30 mg), Cs_2CO_3 (1.5 mmol), CO_2 (1 atm), DMSO (5 mL), 16 h, [b] = Reaction was performed by Ag NPs/MCC (30 mg). [c] = Reaction was performed by Ag NPs/MCC (20 mg), [d] = Reaction was performed by Ag NPs/MCC (40 mg), [e] = Reaction was performed by Ag NPs/MCC (50 mg)

A wide substrate scope was subjected to C-H activation of terminal alkyne to corresponding to carboxylic acid derivatives catalyzed by Ag NPs/MCC. In our delight, the carboxylation of phenyl acetylene and its derivatives (electron withdrawing and electron donating) were preceded smoothly leading to the formation of corresponding carboxylic derivatives. In case of Cyclopropyl acetylene and 1-hexyne derivatives, gave lower yield of product as compare to phenyl acetylene and its different substituents. Therefore, it is revealed that the Ag NPs/MCC catalyst can be widely and efficiently used for CO_2 fixation by terminal alkynes as carboxylic acids precursor.

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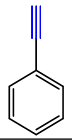
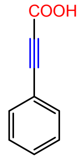
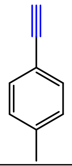
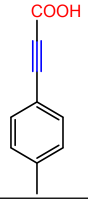
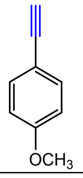
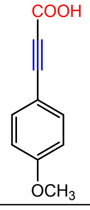
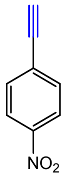
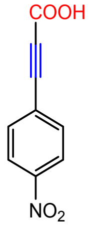
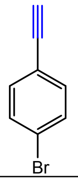
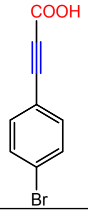
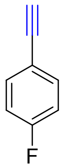
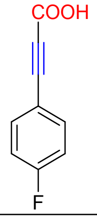
Table 2. Scope of Carbonylation of various terminal alkynes catalyzed by Ag NPs/MCC.

Entry	Reactant	Product	Yield (%)
1			99
2			99
3			98
4			95
5			98
6			99

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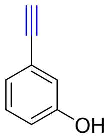
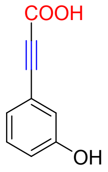
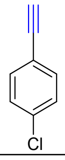
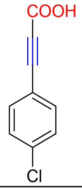
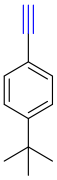
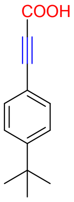
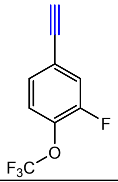
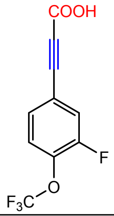
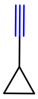
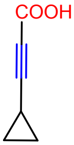
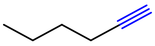
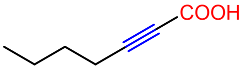
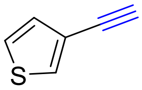
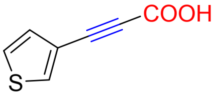
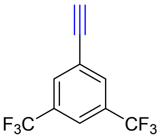
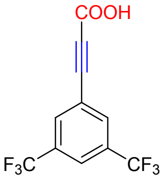
7			98
8			92
9			90
10			99
11			85
12			87
13			92
14			90

[a] Reaction Conditions: Alkyne (1 mmol), Ag NPs/MCC (30 mg), CS_2CO_3 (1.5 mmol), CO_2 (1 atm), 50 ˚C, DMSO (5 mL), 16 h, Isolated yield.

Based on the literature reports, we have proposed the reaction mechanism for the selective C-H carbonylation of terminal acetylene with CO_2 catalyzed by Ag NPs/MCC. At initial stage, the C-H bond (sp hybridization) of terminal alkyne was first coordinated to the

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Ag NPs present on MCC. After that, it was deprotonated by the presence of Cs_2CO_3 to form silver acetylide intermediate (**Figure S_6, 1**). Then the electrophilic attack of carbon dioxide taking place to the silver acetylide complex to demonstrate the transition state (**Figure S_6, 2**). Afterwards, the formation of the silver carboxylate (**Figure S_6, 3**) followed by the transmetallation in presence of Cs_2CO_3 and terminal alkyne molecules to form cesium carboxylate (**Figure S_6**, **4**). Subsequently, the reaction mixture was acidified with concentrated HCl up to pH = 1 to afford the desired product (**Figure S_6, 5**). Importantly, it was noticed that the synergistic effect between silver NPs and Cs_2CO_3 can play a more crucial role to enhance the activity of present catalyst material (Ag NPs/MCC).

Here, the key transition state (**Figure S_6, 2**) in the solvent was investigated by density functional theory (DFT) calculations. In this following step, the complex of deprotonated phenyl acetylene is considered as the reactant molecule. The following **Figure S_7** displays the relative free energy profiles for the Ag NPs catalyzed carbonylation of phenyl acetylene with CO_2 via C-H bond activation in different solvents such as DMSO, DMF, MeOH, Toluene and acetonitrile solvent. In case of DMSO, deprotonated phenylacetylene coordinates with CO_2 with the alkynyl C≡C triple bond by a moderate energy barrier of 13.75 kcalmol^{-1} (E_{DMSO}). The desired product was formed by the coordination of PhC≡C-COO to the Ag NPs with decreasing energy (-4.74 Kcalmol^{-1}) in comparison to the complex of deprotonated phenylacetylene (**Figure S_7, Table S_1**). Therefore, the result obtain from DFT calculation indicates that the Ag NPs could be an effective catalyst for the carbonylation of phenyl acetylene via C-H bond activation. In addition, based on the literature and our finding indicates that the higher polar solvent (DMSO) may be more beneficial and efficient for the synthesis of propiolic acid.[32]

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Further, to investigate the scalability of our optimized reaction conditions, a gram-scale reaction was conducted by using 0.348 g of phenyl acetylene. In our delight, the scale-up reaction afforded the phenyl propiolic acid with 85 % yield after 16 h (**Scheme 2**).

Scheme 2. Gram-Scale Synthesis of Phenyl propiolic acid catalyzed by Ag NPs/MCC.

Phenyl propiolic acid was further derivatized into useful heterocyclic compounds and organo sulfone such as aminoindolines, pyrrolo[1,2a] quinoline and arylacetylenic sulfones (**Scheme 3**). Aminoindolizine and pyrrolo[1,2-a] quinolines are the most significant structural frameworks found in various natural products as well as in various drugs.[42] In further, the present catalyst material Ag NPs/MCC was successfully applied for the synthesis of aminoindolizine and pyrrolo [1,2a] quinoline via A^3 coupling reaction with decarboxylative pathway. The desired products such as aminoindolines and pyrrolo [1,2a] quinoline were obtained with excellent yield (96-98 %) in ethylene glycol as recyclable and biodegradable solvent. Furthermore, the arylacetylenic sulfone was synthesized by the treatment of phenyl propiolic acid with iodine and tert-butyl hydroperoxide (TBHP) to form the desired product with 92 % yield.[43]

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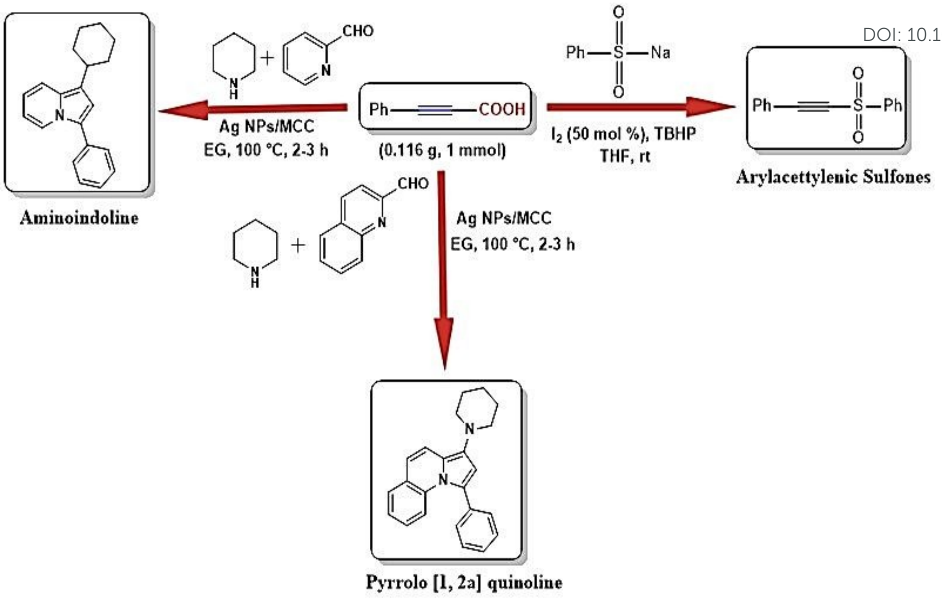

Scheme 3. Synthetic Application of the Phenyl propiolic acid.

Further, to investigate the stability and reusability of the present catalyst from the viewpoint of industrial application, a set of experiments was performed at 1 mmol scale of phenyl acetylene using the model reaction and optimization reaction conditions. After the completion of reaction, the catalyst was recovered using a filtration, washed with hot acetone to remove the sorbed product, and further reused for the next cycle. The results indicated that the Ag NPs/MCC catalyst could be recycled and reused up to five cycles with slightly decrease its activity (**Figure 8**). In addition, the absence of metal leaching was further confirmed by using ICP-AES analysis of the catalyst before and after completion of the reaction. The concentration of silver present in fresh catalyst was found to be 2.5 mol %. It was observed that the concentration of elemental silver was found to be almost constant up to the three runs (2.41 mol %). However, its concentration was decreased after fifth run (2.2 mol %). This is mainly due to the loss of catalyst mass during the mechanically operation; separation, filtration and drying process.

To evaluate the effect of particle size and morphology of the silver nanoparticles, TEM analysis was carried out for the recovered catalyst after five cycles. The results

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indicated that the most of the particles were found between 5-12 nm. Slightly agglomeration was found that results some bigger size particles mainly due to the migration and coalescence of silver nanoparticle that were usually possible at the exposed surface of the MCC (**Figure S_8**). The IR and XRD spectrum of the recycled catalyst was also performed and it has found that no other peaks were recorded (**Figure S_9, Figure S_{10}**). These results illustrate that the Ag NPs/MCC catalyst behaves as a heterogeneous catalyst for the carbonylation of terminal acetylene via C-H bond activation reaction. The catalytic activity of Ag NPs/MCC for the synthesis of phenyl propiolic acid was compared with that of previous work related to silver based catalysts with different supports material (**Table S_2**). The Ag NPs/MCC shows higher yield of desired product with good substrate scope. Further, the catalyst was also more effective for the scalable synthesis of propiolic acid (3 mmol), easier to synthesized, cost-effective, biodegradable, non-toxic and recyclable.

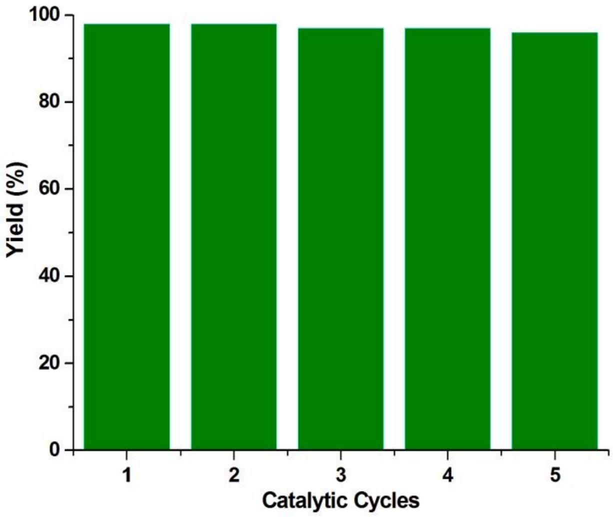

Figure 8. Reusability of Ag NPs/g-C_3N_4 towards the Carboxylation of phenyl acetylene.

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CONCLUSIONS

In conclusion, we have developed a greener and sustainable protocol for the carboxylation of terminal alkynes with CO_2 corresponding to propiolic acid via C-H bond activation of the terminal alkyne catalyzed by Ag NPs/MCC catalyst. The silver nanoparticles can be introduced homogeneously into the micro crystalline cellulose (MCC) material. Importantly, the synergy between the Ag NPs and the MCC shows higher activity for the carboxylation of terminal alkynes. Moreover, the present catalyst material shows higher thermal stability, non-toxicity, inexpensiveness, excellent dispersion, easily synthesize and provide researcher a sustainable catalyst material for the development of higher yield of propiolic acid under mild reaction condition. In addition, the following catalyst material also shows higher recyclability and stability and can further reused up to five cycles without significant loss of its activity under the optimization reaction conditions.

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GRAPHICAL ABSTRACT