# **Supporting Information**

## Silver Nanoparticle Embedded Iron Mediated Gel Matrix: Active Catalyst for CO<sub>2</sub> Fixation and A<sup>3</sup> Coupling

Sumit Mondal, Rajesh Patra, Joydeep Ray, Debajit Sarma\*

Department of Chemistry, Indian Institute of Technology Patna, Bihar 801106, India

\*E-mail: <u>debajit@iitp.ac.in</u>

#### Contents

Instrumentation and methods:	S3
Gelation study:	S5
Characterization:	
Table S1: Comparison table for CO2 cycloaddition reactions with Ag@Fe_MG catalyst and reported catalysts.	other 
Substrate scope <sup>1</sup> H-NMR analysis (CO <sub>2</sub> cycloaddition):	S16
Substrate scope <sup>1</sup> H NMR analysis (A <sup>3</sup> multicomponent reactions):	S20
Table S2: Catalytic efficiency comparison for multicomponent A <sup>3</sup> coupling reaction with Ag@Fe_MG catalyst and other reported catalysts.	
Mechanism (multicomponent A <sup>3</sup> coupling reaction):	S27

#### **Instrumentation and methods:**

Characterizations: The rheological characterization were done utilizing a Modular Compact Rheometer by Anton Paar (MCR 102). A PANalytical X'PERT PRO diffractometer was utilized to acquire Powder X-ray diffraction (PXRD) patterns (CuK<sub> $\alpha$ </sub> radiation (k = 1.542 Å; 40 kV, 45 mA)). The infrared spectrum (FTIR) was recorded using a Perkin Elmer FTIR in ATR mode. <sup>1</sup>H and <sup>13</sup>C NMR data were acquired using the Bruker Avance II 400 spectrometer (frequency at 400 MHz). The thermogravimetric analysis of all the samples were carried out from room temperature to 800 °C using Perkin Elmer TGA 8000 instrument programmed at 10 °C per minute heating increment under continuous nitrogen flow (100 mL/min). Diffuse reflectance spectroscopic analysis was performed using a Shimadzu UV2500 spectrophotometer. BaSO<sub>4</sub> was used as reference. The morphophological analysis of xerogel and catalyst were characterized using a Field Emission Scanning Electron Microscope (FESEM; ZEISS GEMINISEM500 assembled with an EDS spectroscopy detector). The microscopic characterization was conducted using a FEI Tecnai G2 F30 S -Twin transmission electron microscope (TEM) operating at 200 kV and a FEI Nova NANOSEM 450. All gas (N<sub>2</sub> and CO<sub>2</sub>) adsorption studies were done using Quantachrome Autosorb iQ2 analyzer. XPS measurements were carried out in an Omicron Nano tech instrument (Al Ka 1486.7 eV). The neutral C 1s peak at 284.8 eV was employed as the reference point for all binding energy calculations. Magnetic behaviour was studied using VSM (Microsense, Model ADE-EV9).

#### Synthesis:

**Linker (TATMB) synthesis procedure.** Cyanuric chloride (2.19 g, 12 mmol) was mixed in a 50 mL beaker with 25 mL of 1,4-dioxane. This mixture was stirred at 0 °C for 40 min. In a 250 mL round bottom (RB) flask, 4-aminobenzoic acid (6.54 g, 48 mmol) was taken and solubilized with water (75 mL). Then, 35 mL of 5 N NaOH and NaHCO<sub>3</sub> (3.3 g, 39.6 mmol) were added to that RB. It was kept at 0 °C for stirring (30 min). After that, the mixture in the beaker was transferred to the RB by dropwise addition. After completion of the addition, the RB was kept for stirring at 0 °C for 45 min. The overall system was refluxed at 100 °C for 24 hours. After cooling the clear solution to ambient temperature, 10% HCL was added to acidify it and keep the pH roughly at 2. Immediately, a white suspension was obtained, which was washed with water/methanol (1:1) mixture and dried in a vacuum oven at 60 °C.

**Catalytic conversion propargylic alcohols and CO<sub>2</sub> fixation.** The propargylic alcohol was taken in a 10 ml Schlenk tube for catalytic conversion at room temperature. The catalyst was activated at a temperature of 60 °C for a duration of 12 hours prior to commencing the reactions. For a standard protocol, a mixture of 25 mg of the catalyst, 2 mmol of propargylic alcohol, and 0.2 mmol of DBU was combined with 1 mL of DMF in that Schlenk tube. The carbon dioxide (CO<sub>2</sub>) was introduced into the system using a balloon at a pressure of 1 atmosphere. The mixture was kept for a duration of 24 hours. To maintain a constant supply of CO<sub>2</sub>, the balloons were replaced at regular intervals. Subsequently,

the catalyst was isolated using centrifugation. Following a comprehensive work up process using diethyl ether and cold water, the conversion of propargylic alcohols was assessed using <sup>1</sup>H NMR analysis in CDCl<sub>3</sub> solvent.



**Catalysis for A<sup>3</sup> coupling reaction.** In a 25 mL round bottom flask (RB), benzaldehyde derivative (1 mmol), pyrrolidine (1.2 mmol), and phenylacetylene (1.3 mmol) were mixed with 3 mL of DMF. After adding 25 mg Ag@Fe\_MG catalyst to the mixture, it was heated for 12 hours at 80 ° C in a N<sub>2</sub> environment. After completion of the reaction, centrifugation was carried out to extract the catalyst by diluting the reaction mixture with diethyl ether. The mixture was washed with cold water (at least three times) and dried using sodium sulphate. After that, mixture was concentrated in a rotary evaporator and analysed by <sup>1</sup>H-NMR. The ratio of the unreacted aldehyde product to the propargylamine product was used to examine the conversion.



## **Gelation study:**



Figure S1: Gelation test in presence of Cu salt and linker in variable conditions.



0.1 M in DMSO

No changes were observed during the change in concentration of metal ions also (tried up to 0.3 M).



Figure S2: Gelation test in presence of Ni salt and linker in variable conditions.



Figure S3: Gelation test in presence of Zn salt and linker in variable conditions.



0.3 M in DMF

Figure S4: Gelation test (heat-set) in presence of Fe salt and linker (concentration dependent study).

## **Characterization:**



Figure S5: Frequency sweep rheological study for Fe\_MG gel.



Figure S6: The magnetic hysteresis curve of Fe\_MG xerogel.



Figure S7: FTIR spectra of the linker, Fe\_MG xerogel and nanocatalyst (Ag@Fe\_MG).



Figure S8: UV-vis spectrum for Fe\_MG xerogel.



Figure S9: UV-vis spectrum for Ag@Fe\_MG.



Figure S10: TGA analysis of Fe\_MG xerogel and Ag@Fe\_MG.



**Figure S11a-f:** Elemental mapping of the Ag@Fe\_MG.



Figure S12: EDS SUM spectrum of Ag@Fe\_MG.



Figure S13: PXRD pattern of Fe\_MG xerogel.



Figure S14: XPS broad spectrum for nitrogen (AG@Fe\_MG).



Figure S15: XPS broad spectrum for oxygen (AG@Fe\_MG).



**Figure S16:** PXRD pattern of catalysts prepared from different silver loading (Ag@Fe\_MG1, Ag@Fe\_MG, and Ag@Fe\_MG2) and AgNPs (ICSD 64996), Ag<sub>2</sub>O (ICSD 605623), and Ag<sub>2</sub>O<sub>3</sub> (ICSD 591193).



Figure S17: Bar diagram for catalytic amount based kinetic study for CO<sub>2</sub> cycloaddition reaction.



Figure S18: Kinetic study of the CO<sub>2</sub> conversion through NMR study (time-dependent).

Table S1: Comparison table for  $CO_2$  cycloaddition reactions with Ag@Fe\_MG catalyst and other reported catalysts.

SI	Material as	Pressure	Temperature	Conversion	Time	References
No.	catalyst	(bar)	(°C)	(%)	(h)	
1.	[Cu <sup>I</sup> ]-Cu-	10	25	91	12	1
	BTC/[Emim][OAc]					
2.	MOFSO <sub>3</sub> Ag	1	25	99	24	2
3.	Ag@UCPP	10	25	98	24	3
4.	Ag@NT-PPN	10	30	98	15	4
5.	Ag-rGO-3	1	30	87	12	5
6.	Cat-M	1	25	91	10	6
7.	Ag/TPP-CTF	1	40	99	12	7
8.	Ag@RB-POP	10	30	94	12	8
9.	[TBA][OPh]/Agl	15	40	81	1	9
10.	AgNO <sub>3</sub> /[Ch][Tri]	1	30	99	24	10
11.	CNT-NHC-Cu	30	80	99	24	11
12.	MTBD	44	100	100	24	12
13.	Ag@Fe_MG	1	25	99	24	This work

## Substrate scope <sup>1</sup>H-NMR analysis (CO<sub>2</sub> cycloaddition):



**Figure S19a**: Conversion of 2-methyl-3-butyn2-ol to corresponding cycloaddition product by Ag@Fe\_MG (<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) spectra).



**Figure S19b**: Conversion of 2-ethyl-3- butyn-2-ol to corresponding cycloaddition product by Ag@Fe\_MG (<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) spectra).



**Figure S19c**: Conversion of 3-ethyl-1- pentyn-3-ol to corresponding cycloaddition product by Ag@Fe\_MG (<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) spectra).



**Figure S19d**: Conversion of 2-isobutyl-3-butyn-3-ol to corresponding cycloaddition product by Ag@Fe\_MG (<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) spectra).



**Figure S19e**: Conversion of 2-phenylbutyn-2-ol to corresponding cycloaddition product by Ag@Fe\_MG (<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) spectra).



Figure S20: (a) PXRD pattern, (b) FTIR spectra of Ag@Fe MG before and after catalysis.



Figure S21: Leaching test by hot filtration method.

Substrate scope <sup>1</sup>H NMR analysis (A<sup>3</sup> multicomponent reactions):



**Figure 22a**: Conversion of 1-(1,3-diphenylprop-2-yn-1-yl)pyrrolidine via multicomponent A<sup>3</sup> coupling reaction (<sup>1</sup>H NMR in CDCl<sub>3</sub> spectrum data).



**Figure 22b**: Conversion of 1-(3-phenyl-1-(p-tolyl)prop-2-yn-1-yl)pyrrolidine via multicomponent A<sup>3</sup> coupling reaction (<sup>1</sup>H NMR in CDCl<sub>3</sub> spectrum data).



**Figure 22c**: Conversion of 1-(1-(4-chlorophenyl)-3-phenylprop-2-yn-1-yl)pyrrolidine via multicomponent A<sup>3</sup> coupling reaction (<sup>1</sup>H NMR in CDCl<sub>3</sub> spectrum data).



**Figure 22d**: Conversion of 1-(1-(4-bromophenyl)-3-phenylprop-2-yn-1-yl)pyrrolidine via multicomponent A<sup>3</sup> coupling reaction (<sup>1</sup>H NMR in CDCl<sub>3</sub> spectrum data).



**Figure 22e**: Conversion of 1-(1-(2-fluorophenyl)-3-phenylprop-2-yn-1-yl)pyrrolidine via multicomponent A<sup>3</sup> coupling reaction (<sup>1</sup>H NMR in CDCl<sub>3</sub> spectrum data).



**Figure 22f**: Conversion of 1-(1-phenyl-3-(p-tolyl)prop-2-yn-1-yl)pyrrolidine via multicomponent A<sup>3</sup> coupling reaction (<sup>1</sup>H NMR in CDCl<sub>3</sub> spectrum data).



**Figure 22g**: Conversion of 1-(1-(4-chlorophenyl)-3-(p-tolyl)prop-2-yn-1-yl)pyrrolidine via multicomponent A<sup>3</sup> coupling reaction (<sup>1</sup>H NMR in CDCl<sub>3</sub> spectrum data).



**Figure 22h**: Conversion of 1-(1-(4-bromophenyl)-3-(p-tolyl)prop-2-yn-1-yl)pyrrolidine via multicomponent A<sup>3</sup> coupling reaction (<sup>1</sup>H NMR in CDCl<sub>3</sub> spectrum data).



**Figure 22i**: Conversion of 1-(1,3-di-p-tolylprop-2-yn-1-yl)pyrrolidine via multicomponent A<sup>3</sup> coupling reaction (<sup>1</sup>H NMR in CDCl<sub>3</sub> spectrum data).



**Figure 22j**: Conversion of 1-(1-(4-methoxyphenyl)-3-(p-tolyl)prop-2-yn-1-yl)pyrrolidine via multicomponent A<sup>3</sup> coupling reaction (<sup>1</sup>H NMR in CDCl<sub>3</sub> spectrum data).

SI	Material as	Solvent	Temperature	Conversion	Time	References
No.	catalyst		(°C)	(%)	(h)	
1.	Ag@UiO-66-SH	ACN	80	96	6	13
2.	Fe₃O₄ NPs/GO- CuO NPs	EtOH	90	87	24	14
3.	$Fe_3O_4$ @CuSiO_3	-	100	94	16	15
4.	Cu/BNNS	Water	50	95	16	16
5.	Cu-mCSLDH	Toluene	100	97	12	17
6.	Ag@Fe MG	DMF	80	94	12	This work

 Table S2: Catalytic efficiency comparison for multicomponent A<sup>3</sup> coupling reaction with Ag@Fe\_MG catalyst and other reported catalysts.



**Figure S23**: (a) Recyclability test for A<sup>3</sup> coupling reaction (b) catalyst stability before and after catalysis through PXRD pattern.



**Figure S24:** Leaching test by hot filtration method for multicomponent A<sup>3</sup> coupling reaction.

Mechanism (multicomponent A<sup>3</sup> coupling reaction):



**Figure S25:** Mechanism of the A<sup>3</sup> coupling by Ag@Fe\_MG nanocatalyst for multicomponent synthesis of propargylic amines.

### **References:**

1. Li, Y.; Wei, Z.; Hu, J.; Deng, T., Cu (i)-containing MOF as an efficient catalyst for the reactions of carbon dioxide and propargylic alcohols to form carbonates at room temperature. *New J. Chem.* **2023**, *47* (10), 4784-4789.

2. Das, R.; Nagaraja, C., Highly efficient fixation of carbon dioxide at rt and atmospheric pressure conditions: Influence of polar functionality on selective capture and conversion of CO<sub>2</sub>. *Inorg. Chem.* **2020**, *59* (14), 9765-9773.

3. Wang, X.; Li, W.; Wang, J.; Zhu, J.; Li, Y.; Liu, X.; Wang, L.; Li, L., A dual-functional urealinked conjugated porous polymer anchoring silver nanoparticles for highly efficient CO<sub>2</sub> conversion under mild conditions. *Dalton Trans.* **2020**, *49* (37), 13052-13059.

4. Chen, Y.; Lei, L.; Ren, Q.; Li, J.; Gao, J.; Lin, J.; Qiu, Y.; Ji, H., Ag nanoparticles anchored on nanotubular porous porphyrin networks for carboxylative cyclization of propargyl alcohols with CO<sub>2</sub>. *Asian J. Org. Chem.* **2022**, *11* (9), e202200194.

5. Zhang, X.; Chen, K. H.; Zhou, Z. H.; He, L. N., Reduced graphene oxide supported Ag nanoparticles: An efficient catalyst for CO<sub>2</sub> conversion at ambient conditions. *ChemCatChem* **2020**, *12* (19), 4825-4830.

6. Cui, M.; Qian, Q.; He, Z.; Ma, J.; Kang, X.; Hu, J.; Liu, Z.; Han, B., Synthesizing Ag nanoparticles of small size on a hierarchical porosity support for the carboxylative cyclization of propargyl alcohols with CO<sub>2</sub> under ambient conditions. *Chem. Eur. J.* **2015**, *21* (45), 15924-15928.

7. Yang, Y.; Li, Y.; Zhang, Z.; Chen, K.; Luo, R., In Situ Anchoring of Small-Sized Silver Nanoparticles on Porphyrinic Triazine-Based Frameworks for the Conversion of  $CO_2$  into  $\alpha$ -Alkylidene Cyclic Carbonates with Outstanding Catalytic Activities under Ambient Conditions. *ACS Appl. Mater. Interfaces.* **2023**, *16* (1), 411-424.

8. Yu, X.; Yang, Z.; Zhang, F.; Liu, Z.; Yang, P.; Zhang, H.; Yu, B.; Zhao, Y.; Liu, Z., A rose bengal-functionalized porous organic polymer for carboxylative cyclization of propargyl alcohols with CO<sub>2</sub>. *Chem. Commun.* **2019**, *55* (83), 12475-12478.

9. Ngassam Tounzoua, C.; Grignard, B.; Brege, A.; Jerome, C.; Tassaing, T.; Mereau, R.; Detrembleur, C., A catalytic domino approach toward oxo-alkyl carbonates and polycarbonates from CO<sub>2</sub>, propargylic alcohols, and (mono-and di-) alcohols. *ACS Sustain. Chem. Eng.* **2020**, *8* (26), 9698-9710.

10. Shi, G.; Zhai, R.; Li, H.; Wang, C., Highly efficient synthesis of alkylidene cyclic carbonates from low concentration CO<sub>2</sub> using hydroxyl and azolate dual functionalized ionic liquids. *Green Chem.* **2021**, *23* (1), 592-596.

11. Zhang, Z.; Gao, H.; Wu, H.; Qian, Y.; Chen, L.; Chen, J., Chemical fixation of CO<sub>2</sub> by using carbon material-grafted N-heterocyclic carbone silver and copper complexes. *ACS Appl. Nano Mater.* **2018**, *1* (11), 6463-6476.

12. Ca', N. D.; Gabriele, B.; Ruffolo, G.; Veltri, L.; Zanetta, T.; Costa, M., Effective guanidine-catalyzed synthesis of carbonate and carbamate derivatives from propargyl alcohols in supercritical carbon dioxide. *Adv. Synth. Catal.* **2011**, *353* (1), 133-146.

13. Aparna, R. K.; Mukherjee, S.; Rose, S. S.; Mandal, S., Silver Nanoparticle-Incorporated Defect-Engineered Zr-based Metal–Organic Framework for Efficient Multicomponent Catalytic Reactions. *Inorg. Chem.* **2022**, *61* (41), 16441-16447.

14. Mirabedini, M.; Motamedi, E.; Kassaee, M. Z., Magnetic CuO nanoparticles supported on graphene oxide as an efficient catalyst for A<sup>3</sup>-coupling synthesis of propargylamines. *Chin. Chem. Lett.* **2015,** *26* (9), 1085-1090.

15. Wang, F.; Feng, H.; Li, H.; Miao, T.; Cao, T.; Zhang, M., 1D Fe<sub>3</sub>O<sub>4</sub>@CuSiO<sub>3</sub> composites catalyzed decarboxylative A<sup>3</sup>-coupling for propargylamine synthesis. *Chin. Chem. Lett.* **2020**, *31* (6), 1558-1563.

16. Piranloo, F. G.; Abharian, M. K.; Kavousi, F.; Luque, R., Copper nanoparticles decorated on boron nitride nanoflakes as an efficient catalyst for the synthesis of propargylamines under green conditions. *J. Mol. Catal.* **2022**, *533*, 112687.

17. Nikkhoo, M.; Amini, M.; Farnia, S. M. F.; Mahdavinia, G. R.; Gautam, S.; Chae, K. H., Preparation and characterization of magnetic chitosan/Cu–Mg–Al layered double hydroxide

nanocomposite for the one-pot three-component (A<sup>3</sup>) coupling of aldehydes, amines and alkynes. *J. Inorg. Organomet. Polym. Mater.* **2018**, *28*, 2028-2035.