Cu (II) Schiff base complex grafted guar gum: Catalyst for benzophenone derivatives synthesis

Krishna, Shweta Kumari, Deepak Yadav, Sunil K. Sharma



Please cite this article as: Krishna, Kumari S, Yadav D, Sharma SK, Cu (II) Schiff base complex grafted guar gum: Catalyst for benzophenone derivatives synthesis, *Applied Catalysis A, General* (2020), doi: https://doi.org/10.1016/j.apcata.2020.117519

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2020 Published by Elsevier.



Cu (II) Schiff base complex grafted guar gum: Catalyst for benzophenone derivatives synthesis

Krishna,^{a†} Shweta Kumari,^{a†} Deepak Yadav,^{a,b}, Sunil K. Sharma^{a*}

^aDepartment of Chemistry, University of Delhi, Delhi-110007, India ^bDepartment of Chemistry, Central University of Haryana, Mahendergarh-123031, India

Email: sk.sharma90@gmail.com; Phone number: +91-11-2766-6646 yadav.krishna.sep@gmail.com, shwetasingh.ism@gmail.com, deepakrao2510@gmail.com

†Both authors contributed equally to this manuscript

Gr4aphical abstract

Graphical abstract



Highlights

- Cu-Fe catalyst prepared from LDH structure showed a significant promoting effect for one-pot synthesis of aniline N-alkylation without additives.
- In-situ FT-IR results confirmed that the synergistic Cu and Fe accelerated the reaction.
- Cu-Fe catalyst exhibited good recyclability which is potential for industrial application.

Abstract

In this study Guar gum based Cu(II) Schiff's base complex (GG-Cu) has been synthesized and characterized by FT-IR, PXRD, UV-Visible, TGA, XPS, FESEM, TEM, EDAX, solid-state NMR, Elemental mapping, CHNS and AAS analysis. This moiety has been found to be an efficient heterogeneous catalyst for selective oxidation reactions. Fifteen model reactions have been carried to establish the catalytic behavior of GG-Cu, and five of these yield novel products. The ease of separation of catalyst from the reaction mixture simply by filtration is an added advantage; furthermore the catalyst can be reused up to five times without significant loss of catalytic activity. The overall concept of developing newer, efficient and environmental benign catalysts with ease of separation and recycling ability has been successfully demonstrated. All of the isolated products were fully characterized on the basis of their physical and spectral data.

Keywords: Guar gum, Benzophenone derivatives, Cu complex

1. INTRODUCTION

The use of catalysts in organic synthesis is becoming increasingly common to improve the overall conversion, product purity, and save energy. However the catalyst's toxicity, difficulty in separation from the reaction mixture, and lack of reusability are some of the challenges that still need to be addressed. Designing polymer based material for catalytic activity in organic synthesis

has attracted great interest in recent years.^[1-2] The use of naturally occurring polymers over the synthetic one holds promise due to their abundant availability, low cost and non-toxic nature.^[3-5] Guar-gum (GG) is a naturally occurring, edible biodegradable and nonionic galactomannan polymer extracted from the seeds of *Cyamopsis tetragonolobus*.^[6] It has rod like polymeric structure wherein galactose side chains are linked on the mannose backbone with an average molecular ratio of 1:2. The presence of large number of hydroxyl groups not only confers hydrophilicity but also facilitate it to be readily functionalized with various functional groups, surfactants, gelling agents, and dyes, so as to allow the resultant products to be explored for various pharmaceutical/biomedical/industrial applications.^[7-16] GG is insoluble in most of the organic solvents and thus may be used to develop heterogeneous catalysts for organic reactions. Despite being economical, eco-friendly and easily available, GG has not been fully explored for the development of heterogeneous catalysts in organic synthesis beside the huge potential in this area. Some studies have demonstrated that nanocomposites of GG act as efficient catalystin most

of these reports, GG has been described as an excellent supporting and stabilizing material.^[17-22] Our objective is to modify the structure of guar gum using a simple procedure in order to develop new, efficient and environmental benign heterogenous catalysts. Guar-gum based copper nanoparticulates have been used as a catalyst for the Huisgen [3+2] cycloaddition reaction of azides and alkynes.^[23] Palladium nanoparticles decorated on gaur gum based hybrid material are known to be used for electrocatalytic hydrazine determination.^[24] Sivasankar et al. reported

Fe₃O₄-guar-gum nanocomposites for the reduction of p-nitroaniline.^[25]

Our focus is on benzophenone motifs as these are of considerable interest to chemists due to their importance as building blocks in the synthesis of natural products and pharmacological compounds.^[26] Furthermore, benzophenone derivatives are known to induce apoptosis in cancerous cells by generating reactive oxygen species and therefore, have immense potential for

the development of new chemotherapeutic agents.^[27] Benzophenone derivatives have been synthesized in numerous ways, one of the most effective and significant method is the oxidation of benzylic methylenes.^[28] A variety of catalysts have been used to accomplish such oxidation reaction e.g. Ag/SiO₂-CeO₂, Cu/ SBA-15 N-doped graphene, Rh, Bi, Au, Re, PdO/SBA-15, CuNi/Co composites.^[29-42] However, most of these methods suffer from drawbacks such as lack of reusability and selectivity, cumbersome synthesis of the catalyst and lower yield of the products. In order to address these issues, the development of new effective, low-cost and reusable catalysts for the oxidation of benzylic methylene is highly desirable and one of the major goals of this study.^[43]

The catalytically active complexes are known to be either immobilized or grafted on a support harvesting advantages of both homogeneous and heterogeneous catalysis, such as high activity and selectivity together with ease of separation and reusability of the catalyst.^[44-47] Polymers are known to have high affinity for complexes. They can bind to metal complexes through covalent bonding due to the presence of highly reactive groups such as hydroxyl, carboxyl, amino etc.^[2,48] Larionov et al. reported the immobilization of an iridium complex on polystyrene as a catalyst for the Friedel-Crafts alkylation.^[49] Chitosan anchored copper(II) Schiff base complexes are reported as heterogeneous catalysts for *N*-arylation of amines.^[50] Chromium(VI) grafted on mesoporous polyaniline is reported as a reusable heterogeneous catalyst for oxidation reactions.^[51]

Herein, we report the guar-gum anchored copper(II) Schiff base complex as heterogeneous catalyst for the synthesis of benzophenone derivatives under mild reaction conditions. To the best of our knowledge, this is the first report of guar-gum linked Schiff base metal complex used as a catalyst.

2. RESULTS AND DISCUSSION

Guar gum in its native form has very high molecular weight and its extremely high viscosity and gel-forming property limits its use. Therefore, it needs to be depolymerized in order to be used further. Also, physiological properties of guar gum can be improved by the controlled partial hydrolysis (PHGG). A partially hydrolyzed GG with average molecular weight of 31,776 g/mol measured by GPC (Figure S1) and G/M value of 1:1.87 calculated by ¹H NMR (Figure S2) was provided by Lucid Colloids Ltd., Mumbai and used as such. GG anchored Cu(II) Schiff base complex (GG-Cu) was synthesized by following Scheme 1. The GG was first treated with (3aminopropyl)trimethoxysilane (APTMS) to incorporate aminopropyl moieties on the GG surface (APTMS-GG). This was followed by the addition of salicylaldehyde so as to allow amino groups of APTMS moiety and salicylaldehyde to form the Schiff base (L-APTMS-GG). The resulting compound, then complexes with Cu(II) acetate to yield GG based Cu(II) Schiff's base complex GG-Cu (more detail of GG-Cu preparation is given in the ESI⁺[†]).



Scheme 1. Schematic representation for the synthesis of GG-Cu.

Synthesis of the GG based copper(II) Schiff base complex and the intermediate steps were examined by FT-IR, XRD, UV-Visible, TGA, XPS, solid-state NMR, FESEM, EDX, Elemental mapping, TEM and AAS analysis. The structural changes during the anchoring of copper(II) Schiff base complex on GG analyzed by FT-IR is shown in Figure 1. The FT-IR spectrum of GG exhibited a broad intense peak at 3413 cm⁻¹, attributed to O-H (Str), accounting for the presence of several hydroxyl groups which are the linking sites for APTMS.^[52] In addition, strong characteristic peaks at 2905, 1076 and 1006 cm⁻¹ were observed due to the stretching vibration of C-H, C-O-C and C-O groups, respectively in GG.^[53] APTMS-GG in turn shows a correspondingly modified FT-IR spectrum. In particular, peaks at 1130 and 1099 cm⁻¹ were attributed to Si-O-Si and Si-O-C linkages respectively.^[54] The bands at 3427 and 1599 cm¹, due to the presence of -NH₂ groups, confirms

the successful functionalization of GG through silyl ether formation. The FT-IR spectrum of L-APTMS-GG depicted a new peak at 1629 cm^{-1} due to v C=N bond, thus indicating the condensation reaction between the carbonyl group of salicylaldehyde (L) and the amino group of GG-APTMS. Figure 1d shows the FT-IR spectrum of GG-Cu, a band at 1604 cm^{-1} was observed, and blue shift in wavenumber compared with LAPTMS-GG confirmed the coordination of copper ion to azomethine nitrogen of Schiff base. Moreover, new peaks at 675 and 560 cm⁻¹ were observed, which accounts for the stretching mode of Cu-N and Cu-O bonds, respectively.^[55] The above data supports the successful formation of copper(II) Schiff base complex on GG by covalent interaction.



Figure 1. FT-IR spectra of (a) GG, (b) APTMS-GG, (c) L-APTMS-GG and (d) GG-Cu.

Figure 2 demonstrate the XRD patterns of GG, APTMS-GG, L-APTMS-GG, and GG-Cu. In the diffraction pattern of GG, the characteristic peak appeared at $2\Theta = 20.1^{\circ}$.^[56] In the diffraction spectrum of APTMS-GG the characteristic peak of GG is retained, however a new broad peak was observed at 12.67° which corroborate with the existence of an amorphous nature.^[57] No obvious change was observed in XRD pattern of L-APTMS-GG when compared with APTMSGG. Furthermore, the XRD pattern of GG-Cu exhibit a new peak at $2\theta = 26.9^{\circ}$, 32.28° and



38.43° attributing to plane (002), (110) and (111) of CuO, respectively.^[58]

Figure 2. Powder XRD pattern of (a) GG, (b) APTMS-GG, (c) L-APTMS-GG and (d) GG-Cu. UV-vis spectra of GG, APTMS-GG, L-APTMS-GG and GG-Cu are shown in Figure 3. The UVvisible spectrum of GG shows an absorption peak at 262 nm, due to the presence of non-bonding electrons on the hydroxyl group.^[59] However, the UV-Vis spectra of APTMS-GG shows a weak absorption peak at 302 nm, due to the presence of an amine group of APTMS. Figure 3c shows a strong absorption peak at 261, 332 nm due to the n/π^* transition of the imine bond in LAPTMS-GG. The UV-Vis spectrum of the GG-Cu showed a characteristic absorption peak at 328 nm, due to the charge transfer between copper ion and the hydroxyl group of ligand.^[60]



Figure 3. UV-vis spectra of (a) GG, (b) APTMS-GG, (c) L-APTMS-GG and (d) GG-Cu.

The TGA thermogram of GG and GG-Cu are presented in Figure 4. The TGA of GG showed a 10% weight loss in the range of 50-150 °C, due to the loss of adsorbed water molecules. The second weight loss around 63% at 200-420 °C may be due to the polymer decomposition.^[61] However, in GG-Cu, 5% weight loss is observed in the range 30-120 °C, due to the evaporation of water and second loss approximately of 36% was observed at 340 °C, due to the degradation of secondary alcohol in guar gum.^[62] After this it degrades slowly and a total weight loss of 59 % was observed until 600 °C. Thus, it may be concluded that GG-Cu thermally stable up to 600 °C. Quantitative evaluation of grafting of Cu(II) complex on guar gum using TGA data suggest that approx. 25% guar gum is grafted.^[63]



Figure 4. TGA thermogram of (a) GG and (b) GG-Cu.

For the chemical state variation and the surface functionalization in the GG-Cu, X-ray photoelectron (XPS) analysis was carried out Figure 5. Figure 5a shows the presence of Cu, C, O, Si and N species in GG-Cu. The XPS spectrum of the Cu 2p core level spectrum in Figure 5b exhibits two bands located at the binding energies of 951.5 and 931.8 eV which correspond to the binding energy of Cu 2p1/2 and Cu 2p3/2. Meanwhile, a Cu 2p1/2 and Cu 2p3/2 satellite peaks were observed at 959.7 and 941.2 eV, respectively. The deconvoluted C 1s spectrum of the GG-Cu is shown in Figure 5c, it exhibits the typical peaks at 286.4, 284.2, 283.0, 282.3 and 281.6 eV that can be assigned to carbon atoms in C-OH, C=N C–O, C-C and C-H, respectively. Correspondingly, the O 1s peak was observed at energy position 529.4 eV in Figure 5d. The fitted peak values for O 1s were 530.7, 529.5 and 528.0 eV which corresponds to the, O-H, C-O and Cu-O, respectively. The N 1s XPS spectrum (Figure 5e) shows a peak at 397.3 which confirms the presence of N=C.^[64-68] In Figure 5f a band at 100.1 eV attributed to Si-O emerged, which indicate the silylation of the reaction surface. The XPS results further supported the formation of Cu(II) complex grafted on the GG.



Figure 5. X-ray photoelectron (a) survey spectra of GG-Cu, (b) Cu 2p, (c) deconvoluted C 1s, (d) deconvoluted O 1s, (e) N 1s and (f) Si 2p.

A deep understanding of the structure and chemical composition of GG-Cu, was analyzed by solidstate NMR spectroscopy Figure 6. The ¹³C ss nmr spectrum have four set of signals. First region at 171 to 165 ppm due to aromatic carbons attached to hydroxyl group of salicaldehyde, second region at 132 to 103 ppm due to aromatic carbons of salicaldehyde and anomeric carbons for galactose and mannose of guar gum. Third region at 80 to 60 for guar gum and fourth region come at 18 to 10 ppm for APTMS group.^[69-70] The ²⁹Si ss nmr spectrum of GG-Cu also consist a set of signals at -50 to -65 ppm region due to silicon attached with -OMe, -CH₂ and GG environment.^[71] The ss NMR spectra results supported the presence of aromatic as well APTMS and guar gum region in GG-Cu which confirm the formation of Cu(II) complex grafted on the GG.





The surface morphology of GG, APTMS-GG, L-APTMS-GG, and GG-Cu are described with the help of FESEM and TEM images. The FESEM images of GG in Figure 7(i)a. show the macromolecule with rough surface topology. FESEM images of APTMS-GG, L-APTMS-GG displays nanostructural features which demonstrated the chemical modification of GG through APTMS and salicylaldehyde in Figure 7(i)b and 7(i)c, respectively. On the other hand, FESEM images of GG-Cu (Figure 7(i)d) exhibits different morphologies having twisted nanostructural irregular-shape and these may serve as an ideal platform for reactant to accomplish the desired product. The TEM image shown in Figure 7(ii) reveals the nanoscopic features of the GG-Cu with a uniform distribution of copper(II) Schiff base complex without aggregation throughout the GG. The EDAX analysis provides detailed chemical analysis on the GG, APTMS-GG, LAPTMS-GG and GG-Cu. The EDAX analysis of GG-Cu in Figure 7(iii)d depicts the change in elemental composition with the introduction of copper, nitrogen and silicon, which are core elements of the complex apart from carbon and oxygen. Further, EDAX elemental mapping was achieved to understand the distribution of the Cu-Schiff base complex on GG. The elemental mapping indicated the uniform distribution of Cu, N and Si over the GG surface 7(iv). Along with the EDAX analysis, the composition of carbon, nitrogen and hydrogen in the GG-Cu complex determined by the CHNS analysis was found to be 26.92 %, 4.16 % and 2.46 %,

195 respectively. Subsequently, the quantitative estimation of the copper content in GG-Cu was done 196 after digestion using AAS and the corresponding copper loading was found to be 1.48 mg L^{-1} .



197





Figure 7. (i) FESEM of (a) GG, (b) APTMS-GG, (c) L-APTMS-GG, and (d) GG-Cu; (ii) TEM images of GG-Cu; (iii) EDAX spectra of (a) GG, (b) APTMS-GG, (c) L-APTMS-GG, and (d) GG-Cu and (iv) elemental mapping of GG-Cu.

The catalytic efficiency of GG-Cu was evaluated in the synthesis of benzophenone derivatives

via an oxidation reaction as shown in Scheme 2 (synthetic details given in the ESI[†][†]).



Scheme 2. Synthesis of benzophenone derivatives via catalytic oxidation.

In order to optimize the reaction conditions for the synthesis of benzophenone derivatives, various parameters such as the catalyst amount, oxidant, reaction time, temperature, and solvent were thoroughly investigated and summarized in the Table 1. Diarylmethane was chosen as a model

reactant for the oxidation reaction, in the control reaction carried out in the absence of a catalyst at reflux, no noticeable reaction was observed (Table 1 entry 1). Even in the presence of

GG in water under reflux for 24 h no product formation was observed (Table1, entry 2). However, in the presence of GG-Cu catalyst and in different solvents, e.g. water, toluene, pyridine, ethanol, DMF and acetonitrile, the product was found to be formed (Table 1 entry 3-8). Acetonitrile was observed to be the solvent of choice for the oxidation reaction. However, oxidant also plays an important role in affecting the reaction to a large extent. In order to study the effect of oxidant, the reaction was carried out in the presence of different oxidants such as TBHP, *m*-CPBA, O₂, H₂O₂ (Table 1, entry 8-11). The optimum yield of 90% was observed while using TBHP as an oxidant. Under these conditions 5 mg of the catalyst was found to be sufficient for the oxidation reaction of diarylmethane. A further decrease in the amount of catalyst (2 mg) was found to significantly hamper the yield (Table 1, entry 13). Therefore, the use of 5 mg of the GG-Cu catalyst at 70 °C in the presence of solvent acetonitrile and TBHP as an oxidant was found to be the optimized reaction condition to afford benzophenone (2a) in excellent yield in a short reaction time (Table 1, entry 14). The generality of the present method was established by using different types of diarylmethane bearing electron withdrawing groups, tosylated group and thiophene moiety to afford the corresponding benzophenone derivatives with excellent yields as shown in Figure 8. A few sulfones were also included in the study as they too constitute an important functional group due to their presence in biologically active compounds, e.g. anticancer, antibacterial, antiglaucoma agents.^[72-73] It may be noted that the benzylic oxidation proceeded exclusively at the methylene group and methyl groups remains unaffected. Amongst the reactions tried, five newer products (2), 2k, 2l, 2m and 2n) were formed. All of the known and new products are characterized by IR, ¹H

Entry	Catalyst (mg)	Solvent	Oxidant	Temp (°C)	Time (h)	Yield of 2a ^b (%)	
1		Water	TBHP	Reflux	24		
2	GG (20)	Water	TBHP	Reflux	24		
3	GG-Cu (20)	Water	TBHP	Reflux	24	20	
4	GG-Cu (10)	Toluene	TBHP	Reflux	24	35	
5	GG-Cu (10)	Pyridine	TBHP	Reflux	12	48	
6	GG-Cu (10)	Ethanol	TBHP	Reflux	12	38	
7	GG-Cu (10)	DMF	TBHP	Reflux	12	44	
8	GG-Cu (10)	MeCN	TBHP	Reflux	12	90	
9	GG-Cu (10)	MeCN	m-CPBA	Reflux	12	55	
10	GG-Cu (10)	MeCN	O_2	Reflux	12	37	
11	GG-Cu (10)	MeCN	H2O2	Reflux	12	60	
12	GG-Cu (5)	<u>MeCN</u>	TBHP	70	12	90	
13	GG-Cu (2)	MeCN	TBHP	70	12	65	
14	GG-Cu (5)	MeCN	TBHP	70	08	89	

& ¹³C NMR and Mass spectroscopy. **Table 1.** Optimization of reaction conditions for the oxidation of diarylmethane.^a

^aReaction condition: Diarylmethane (1mmol) TBHP (10 mol %). ^b isolated yield after workup.

Furthermore, comparison of the catalytic efficiency of the GG-Cu with previously reported catalysts, for the preparation of benzophenone derivatives, in terms of the catalyst amount and reaction conditions, is summarized in Table 2.



244

245

Figure 8. Synthesized benzophenone derivatives via catalytic oxidation.

The catalyst was evaluated for its recyclability up to six times. It is apparent from Figure S3 that 246 the GG-Cu catalyst could be reused up to five cycles. However, gradual decline in the catalytic

- 247 activity was noticed after 3rd cycle. The XRD pattern, FTIR and SEM images also showed that
- there was no change in the phase and surface morphology in recycled GG-Cu (Figure S4). AAS

249 of the used catalyst was found to be 1.39 mg/L which was almost similar to the amount of Cu in 250

fresh catalyst. Hence, the catalyst has shown its proficiency for various industrial applications.

251 Table 2. Comparative catalytic performance of the GG-Cu with other previously reported 252 catalysts in oxidation reactions.

253

Entry	Catalyst	Amount of	Oxidant	Time (h)	Solvent/Condition	TON	TOF	Refs.
		catalyst (mg)		yield (%)				
1	CrO ₃	5.9	H ₅ IO ₆	1/99	CH ₃ CN/RT	49.87	49.87	74
2	FeCl ₃ .2H ₂ O	2.7	TBHP	24/91	Pyridine/82 °C	45.55	1.89	75
3	Fe(III)/THA	3.1	H2O2	12/85	CH ₃ CN/60 °C	16.90	1.40	76
4	CuI	9.5	O ₂	24/81	CH ₃ CN /100 °C	7.95	0.33	77
5	Cu(OAc) ₂ .H ₂ O	9.9	TBHP	8/98	H ₂ O/80 °C	19.56	2.44	78
6	[CuI(aas- TPB)]n	30	TBHP	4/99	H ₂ O/RT	19.66	4.91	79
7	GG-Cu	5.0	TBHP	10/90	CH ₃ CN /70 °C	115.77	11.57	This work

254

Based on the literature, a plausible mechanism for the reaction is shown in Scheme 3.^{77,80} It is 255 speculated that first a homolytic cleavage of TBHP occurs in the presence of heat that produce 256 the alkoxy (A) and hydroxyl radicals (equation i) which subsequently reacts with TBHP and 257 form radical B. On the other hand GG-Cu catalyst which binds with the reactant gets activated 258 by the free radical A and removal of acetic acid. In the next step Cu(II) bind with free radical B 259 and produces a highly reactive Cu(III)-peroxide species (2). The peroxide species, then quickly 260 rearranges via a radical pathway with an electron transfer to the catalyst, producing the Cu(II) 262 261 organoperoxides (3). Homolytic dissociation of these organoperoxide by removal of radical 263 hydrogen of the remaining benzylic proton (4) generates the product.



Scheme 3. Plausible mechanism for benzophenone synthesis using the GG-Cu catalyst.3. CONCLUSIONS

We have successfully used a carbohydrate based natural polymer obtained from guar gum (GG) to develop a heterogeneous catalyst for organic reactions. The low cost, nontoxicity, presence of large number of hydroxyl groups, and limited solubility of guar gum in organic solvents are the favourable factors to employ this natural product for the synthesis of heterogenous catalyst.

Grafting of Cu(II) Schiff base complex on GG via covalent interaction afforded a heterogeneous catalyst which was characterized by FT-IR, PXRD, UV-Visible, TGA, XPS, solid-state NMR, FESEM, TEM, EDAX, Elemental mapping, CHNS, AAS and elemental analysis. The catalyst reported is convenient to use due to its ease of separation from the reaction mixture and is stable in ambient conditions. Furthermore it was found to be highly efficient, selective for the oxidation of methylene group using TBHP as an oxidant. The reusability of the catalyst upto five cycles without any significant loss of activity is an added advantage and allows the catalyst to be considered superior to other commonly available catalysts.

CRediT author statement

Wahyu S. Putro: Investigation, Data curation, Writing- Original Draft Preparation

Takayoshi Hara: Formal analysis

Nobuyuki Ichikuni: Formal analysis

Shogo Shimazu: Conceptualization, Supervision, Writing - Review & Editing, Funding acquisition and Project administration

CONFLICT OF INTEREST

There is no conflict of interest to declare.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

ACKNOWLEDGEMENTS

Financial support from the Department of Science and Technology (DST), Government of India is gratefully acknowledged. We are thankful to Lucid Colloids Ltd., Mumbai for providing guar gum and also thankful to the SAIF IIT Kanpur, USIC, University of Delhi for providing assistance in the analysis of the samples. SK acknowledges the receipt of DSK postdoctoral fellowship.

††Electronic supplementary information (ESI) available: Experimental section, reusability and spectral data of GG-Cu after 5th cycle and spectroscopic results of benzophenone derivatives.

REFERENCES

[1] (a) G. Sharma, S. Sharma, A. Kumar, A. H. Al-Muhtaseb, M. Naushad, A. A. Ghfar, G. T. Mola, F. J. Stadler, Carbohydr. Chem. 199 (2018) 534.

- [2] M. Kaushik, A. Moores, Green Chem. 18 (2016) 622.
- [3] K. S. Soppirnath, T. M. Aminabhav, Eur. J. Pharm. Biopharm. 53 (2002) 87.
- [4] R. L. Whistle, The Encyclopedia of Polymer Science and Technology; Wiley: New York,

1969, 416.

[5] E.S. Abdel-Halim, S. S. Al-Deyab, Carbohydr. Chem. 86 (2011) 1306.

[6] V. Singh, A. Tiwari, D. N. Tripathi, R. Sanghi, J. Appl. Polym. Sci. 92 (2004) 1569.

[7] R. A. Praphakar, M. Jeyaraj, S. Mehnath, A. Higuchi, D. Ponnamma, K. K. Sadasivuni, M. Rajan, J. Mater. Chem. B 6 (2018) 1519.

- [8] M. Prabaharan, Int. J. Biol. Macromol. 49 (2011) 117.
- [9] D. S. Seeli, M. Prabaharan, Int. J. Biol. Macromol. 84 (2016) 10.
- [10] Y. Cheng, K.M. Brown, R.K. Prud'homme, Biomacromolecules 3 (2002) 456.
- [11] S. Mahammad, R.K. Prud'homme, G.W. Roberts, S.A. Khan, Biomacromolecules 7(2006) 2583.
- [12] R. S. Soumya, S. Ghosh, E. T. Abraham, Int. J. Biol. Macromol. 46 (2010) 267.
- [13] S. M. Al-Saidan, Y. S. R. Krishnaiah, V. Satyanarayana, P. Bhaskar, R. S. Karthikeyan,
- Eur. J. Pharm. Biopharm. 58 (2004) 697.
- [14] V. R. Sinha, B. R. Mittal, R. Kumria, Int. J. Pharm. 289 (2005) 79.
- [15] L. Yan, P. R. Chang, P. Zheng, X. Mac, Carbohydr. Polym. 87 (2012) 1919.
- [16] E. S. Abdel-Halim, M. H. El-Rafie, S. S. Al-Deyab, Carbohydr. Chem. 85 (2011) 692.
- [17] D. Schmidt, D. Shah, E. Giannelis, CURR OPIN SOLID ST M 6 (2002) 205.
- [18] A. Kumar, G. Sharma, M. Naushad, A. Kumar, S. Kalia, C. Guo, G. T. Mola, J.

Photochem. Photobiol. A: Chem. 337 (2017) 118.

- [19] J. Balachandramohan, T. Sivasankar, Carbohydr. Polym. 99 (2018) 41.
- [20] S. Pal, A. S. Patra, S. Ghorai, A. K. Sarkar, R. Dasa, S. Sarkarb, Environ. Sci.: Water Res. Technol. 1 (2015) 84.
- [21] P. K. Rastogi, V. Ganesan, S. Krishnamoorthi, Electrochim. Acta 125 (2014) 593.
- [22] K. Baranwal, L. M. Dwivedi, Shehala, V. Singh, Int. J. Biol. Macromol. 120 (2018)2431.

23

[23] A. Kumar, S. Aerry, A. Saxena, A. Deb, S. Mozumdar, Green Chem. 14 (2012) 1298.

[24] P. K. Rastogi, V. Ganesan, S. Krishnamoorthi, Electrochim. Acta 125 (2014) 593.

[25] J. Balachandramohan, S. Anandan, T. Sivasankar, Ultrason. Sonochem. 40 (2018) 1.

[26] K. Surana, B. Chaudhary, M. Diwaker, S. Sharma, Med. Chem. Commun. 9 (2018)1803.

[27] K. Matsumoto, Y. Akao, E. Kobayashi, T. Ito, K. Ohguchi, T. Tanaka, M. Iinuma, Y. Nozawa, Bio.Pharm. Bull. 26 (2003) 569.

[28] C. Miao, H. Zhao, Q. Zhao, C. Xiaa, W. Sun, Catal. Sci. Technol. 6 (2016) 1378.

[29] Z. Guo, B. Liu, Q. Zhang, W. Deng, Y. Wang, Y. Yang, Chem. Soc. Rev. 43 (2014)3480.

[30] M. J. Beier, B. Schimmoeller, T. W. Hansen, J. E. T. Andersen, S. E. Pratsinis, J. D.Grunwaldt, J. Mol. Catal. A: Chem. 331 (2010) 40.

[31] B. Akhlaghinia, H. Ebrahimabadi, E. K. Goharshadi, S. Samiee, S. Rezazadeh, J. Mol.Catal. A: Chem. 357 (2012) 67.

[32] C. Krishna, P. Neeli, A. Narani, R. K. Marella, K. Seetha, R. Rao, D. R. Burri, Catal.Commun. 39 (2013) 5.

[33] P. Tang, Y. Gao, J. Yang, W. Li, H. Zhao, D. Ma, Chin. J. Catal. 35 (2014) 922.

[34] M. Ghiaci, F. Molaie, M. E. Sedaghat, N. Dorostkar, Catal. Commun. 11 (2010) 694.

[35] A. Selvamani, M. Selvaraj, P. Santhana Krishnan, M. Gurulakshmi, K. Shanthi, Appl. Catal. A 495 (2015) 92.

[36] R. Jothiramalingam, B. Viswanathan, T. K. Varadarajan, J. Mol. Catal. A: Chem. 252(2006) 49.

[37] A. J. Catino, J. M. Nichols, H. Choi, S. Gottipamula, M. P. Doyle, Org. Lett. 7 (2005)

5167.

[38] Y. Bonvin, E. Callens, I. Larrosa, D. A. Henderson, J. Oldham, A. J. Burton Barrett, J. M. Aj, Org. Lett. 7 (2005) 4549.

[39] H. Li, Z. Li, Z. Shi, Tetrahedron 65 (2009) 1856.

[40] A. V. Biradar, T. Asefa, Appl. Catal. A 435 (2012) 19.

- [41] H. Peng, A. Lin, Y. Zhang, H. Jiang, J. Zhou, Y. Cheng, C. Zhu, H. Hu, ACS Catal. 2(2012) 163.
- [42] A. Mittal, S. Kumari, Parmanand, D. Yadav, S. K. Sharma, Appl. Organomet. Chem.
- (2020) doi.org/10.1002/aoc.5362.
- [43] M. Zarghani, B. Akhlaghinia, RSC Adv. 6 (2016) 38592.

[44] M. Arsalanfar, A. A. Mirzaei, H. R. Bozorgzadeh, A. Samimi, R. Ghobadi, J. Ind. Eng. Chem. 20 (2014) 1313.

- [45] L. Spadaro, F. Arena, M. Granados, M. Ojeda, J. Fierro, F. Frusteri, J. Catal. 234 (2005)451.
- [46] D. B. Bukur, X. Lang, D. Mukesh, W. H. Zimmerman, M. P. Rosynek, C. P. Li, Ind. Eng.Chem. Res. 29 (1990) 1588.
- [47] H. N. Pham, A. Viergutz, R. J. Gormley, A. K. Datye, Powder Technol. 110 (2000) 196.
- [48] B. Altava, M. I. Burguete, E. G. Verdugo, S. V. Luis, Chem. Soc. Rev. 47 (2018) 2722.
- [49] V. A. Larionov, T. Cruchter, T. Mietke, E. Meggers, Organometallics 36 (2017) 1457.
- [50] Anuradha, S. Kumari, D. D. Pathak, Tetrahedron Lett. 56 (2015) 4135.
- [51] U. Mandi, M. Pramanik, A. S. Roy, N. Salam, A. Bhaumik, S. K. M. Islam, RSC Adv. 4 (2014) 15431.

[52] K. Dutta, B. Das, D. Mondal, A. Adhikari, D. Rana, A. K. Chattopadhyay, R. Banerjee, R. Mishra, D. Chattopadhyay, New J. Chem. 41 (2017) 9461.

- [53] S.-N. Yuen, S.-M. Choi, D. L. Phillips, C.-Y. Ma, Food Chem. 114 (2009) 1091.
- [54] H. P. Mungse, S. Verma, N. Kumar, B. Sain, O. P. Khatri, J. Mater. Chem. 22 (2012)5427.
- [55] S. Kumari, A. Shekhar, D. D. Pathak, RSC Adv. 6 (2016) 15340.
- [56] A. Tiwari, S. P. Singh, J. Appl. Polym. Sci. 108 (2008) 1169.
- [57] A. Kumar, A. Dey, S. Mozumdar Bull. Mater. Sci. 38 (2015) 1025.
- [58] S. Khan, A. A. Ansari, A. A. Khan, M. Abdulla, O. Al-Obaidd, R. Ahmadd, Colloid
- Surface B. 153 (2017) 320.
- [59] U. S. Dharsana, M. K. N. S. Varsha, A. A. K. Behlol, A. Veerappan, R. Thiagarajan,
- RSC. Adv. 5 (2015) 30248.
- [60] C. E. Jones, S. R. Abdelraheim, D. R. Brown, J. H. Viles, J. Biol. Chem. 279 (2004)32018.
- [61] R. Sharma, B. S. Kaith, S. Kalia, D. Pathania, A. Kumar, N. Sharma, R. M. Street, C. Schauer, J. Environ. Manage. 162 (2015) 37.
- [62] M. Hussain, T. Zahoor, S. Akhtar, A. Ismail, A. Hameed, J. Food Sci. Technol. 55 (2018) 1047.
- [63] O. Zabihi, M. Ahmadi, T. Abdollahi, S. Nikafshar, M. Naebe, Sci. Rep. 3560 (2017) 1.
- [64] Q. Zhao, C. Bai, W. Zhang, Y. Li, G. Zhang, F. Zhang, X. Fan, Ind. Eng. Chem. Res. 53 (2014) 4232.
- [65] N. Kannari, J.-i. Ozaki, Carbon 50 (2012) 2941.
- [66] Z.-P. Zhao, M. S. Li, J.Y. Zhang, H. N. Li, P. P. Zhu, W. F. Liu, Chem. Res. 51 (2012) 9531.
- [67] Z. Zude, Z. Xiong, Z. Tao, Y. Huaming, L. Qingliang, J. Mol. Struct. 478 (1999) 23.
- [68] D. R. Dreyer, A. D. Todd, C.W. Bielawski, Chem Soc Rev. 43 (2014) 5288.

[69] X. Cao, F. Xiao, P. Duan, J. J. Pignatello, J. Mao, K. Schmidt-Rohr, Carbon 153 (2019) 173.

[70] S. Haslingera, S. Hietalab, M. Hummela, S. L. Maunub, H. Sixtaa, Carbohydr. Polym.

207 (2019) 11.

[71] C.-J. Lu, H. Chen, D.-K. Chen, H. Wang, Z.-P. Yang, J. Gao, H. Jin, Org. Biomol. Chem. 14 (2016) 10833.

[72] K. A. Smith, R. J. Kirkpatruck, E. Oldfield, D. M. Henderson, American Mineralogist 68 (1983) 1206-1215.

[73] D. Yadav, S. K. Sharma, R. S. Menon, Org. Biomol. Chem. 17 (2019) 4073.

[74] S. Yamazaki, Org. Lett. 1 (1999) 2129.

[75] M. Nakanishi, C. Bolm, Adv. Synth. Catal. 349 (2007) 861.

[76] A. Al-hunaiti, M. Ra⁻⁻isa⁻⁻nen, T. Repo, Chem. Commun. 52 (2016) 2043.

[77] H. Sterckx, J. D. Houwer, C. Mensch, I. Caretti, K. A. Tehrani, W. A. Herrebout, S. V. Doorslaer, B. U. W. Maes, Chem. Sci. 7 (2016) 346.

[78] J. Wu, Y. Liu, X. Ma, P. Liu, C. Gu, B. Dai, Chin. J. Chem. 35 (2017) 1391.

[79] X. Wang, M. Liu, Y. Wang, H. Fan, J. Wu, C. Huang, H. Hou, Inorg. Chem. 56 (2017) 13329.

414 [80] C. Walling, L. Heaton, J. Am. Chem. Soc. 87 (1965) 38.