#### A GENUINELY MULTIDISCIPLINARY JOURNAL

# CHEMPLUSCHEM

#### CENTERING ON CHEMISTRY

## **Accepted Article**

Title: Hexagonal mesoporous silica-supported copper oxide (CuO/ HMS) catalyst - synthesis of primary amides from aldehydes in aqueous medium

Authors: Manoj Bhanudas Gawande, Ravishankar Kadam, Anuj K. Rathi, Klara Cepe, Radek Zboril, Rajender Varma, and Radha Jayaram

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: ChemPlusChem 10.1002/cplu.201600611

Link to VoR: http://dx.doi.org/10.1002/cplu.201600611



WILEY-VCH

www.chempluschem.org

## WILEY-VCH

## Hexagonal mesoporous silica-supported copper oxide (CuO/HMS) catalyst - synthesis of primary amides from aldehydes in aqueous medium

Ravishankar G. Kadam,<sup>a</sup> Anuj K. Rathi,<sup>b</sup> Klara Cepe,<sup>b</sup> Radek Zboril,<sup>b</sup> Rajender S. Varma,<sup>b</sup> Manoj B. Gawande<sup>b\*</sup>and Radha V. Jayaram<sup>a\*</sup>

#### Dedication

**Abstract:** Hexagonal mesoporous silica (HMS) supported copper oxides (CuO/HMS) have been prepared by sol-gel method and well-characterized by XRD, FT-IR, TEM, N<sub>2</sub> sorption, ICP, XPS, H<sub>2</sub>-TPR, NH<sub>3</sub>-TPD, and HRTEM techniques. An analysis of these results revealed a mesoporous material system with a high surface area (974 m<sup>2</sup>/g) and uniform poresize distribution. The catalytic efficacy of CuO on the HMS support with varying Cu loadings (1, 3, 5, 10 and 15 wt%) was investigated for the transformation of aldehydes to primary amides; 3 wt% CuO/HMS exhibited good catalytic performance in good to excellent yields of amides (60-92%) in benign aqueous medium. The intrinsically heterogeneous catalyst could be recovered after the reaction and reused without any noticeable loss in activity.

#### Introduction

Amide functionality is an important building block of peptides linkage<sup>[1-3]</sup> and for several pharmaceutical products.<sup>[4]</sup> This group occupies an essential role in synthetic chemistry for the preparation of agrochemicals, detergents, and polymeric materials.<sup>[5]</sup> Generally, amides are synthesized either by the reaction of activated carboxylic acid derivatives such as acid chlorides, anhydrides, esters with amines or acid base catalyzed hydration of nitriles.<sup>[6,7]</sup> Beckmann rearrangement and Aube–Schmidt rearrangement are some other protocols for amide synthesis.<sup>[8-10]</sup> However, most of these procedures require the use of stoichiometric amounts of hazardous reagents and also lead to formation of various by-products. In the last few years, several metal-catalyzed processes have been described for the conversion of aldoximes to amides using Au,<sup>[11]</sup> Pd,<sup>[12]</sup> Rh,<sup>[13]</sup> and Ru<sup>[14,15]</sup> as catalyst.

<sup>a</sup>Department of Chemistry, Institute of Chemical Technology, Matunga, Mumbai 400019, India

Ravishankar G. Kadam, Prof. Radha V. Jayaram

E-mail address: manoj.gawande@upol.cz; rv.jayaram@ictmumbai.edu.in Supporting information for this article is given via a link at the end of the document.((Please delete this text if not appropriate)) But these catalytic systems are expensive and required equal quantity of organic bases, making cumbersome separation of the final product. Apart from this, some homogeneous copper salts have been reported for the synthesis of primary amides.<sup>[16,17]</sup>

More recently, Cadierno and co-workers published a review on homogeneous as well heterogeneous catalysts for synthesis of amide via aldoxime rearrangement.<sup>[18]</sup> Under such circumstances, due to the high cost of metal complexes and concomitant toxicity issues of the previously reported catalysts system, there is a genuine need to design and develop suitable and eco-friendly heterogeneous catalytic system.[19,20] For a benign synthesis, water is ideal reaction medium and has been well explored for various types of organic transformations, [19,21-23] including a one-pot synthesis of amide from aldehyde using copper ethylene diamine complex based heterogeneous catalyst,<sup>[23]</sup> manganese oxide based molecular sieve (OMS-2) for the formation of amide from benzyl alcohol<sup>[24]</sup> and some other related catalysts also investigated in water.[22,25-28] During the last decade, porous solids have been explored as an imperative class of materials due to their versatile applications in separation purification and catalytic processes.<sup>[29]</sup> Silica-based porous materials have gained prominence in view of their high thermal stability, large surface area and orderly pore size.[30] Mesoporous silica materials with pore diameter of 2-10 nm commonly termed M41S have been investigated in heterogeneous catalysis and material science.<sup>[31]</sup> By fine tuning the synthetic process various types of silica materials with different pore sizes could be obtained such as hexagonal (MCM-41), cubic (MCM-48) and lamellar (MCM-50). Tanev et al. reported a pathway for the sol-gel preparation of mesoporous silica materials using alkyl amines as templates.<sup>[32]</sup> Generally, HMS materials have high surface area (>1000 m<sup>2</sup>/g) and their N<sub>2</sub> sorption isotherms display a small hysteresis loop with added flexibility that their pore size can be changed by adjusting the length of the surfactant chains;<sup>[33]</sup> HMS has been widely used in catalysis as a support for various catalytic transformations.<sup>[34,35]</sup> In continuation of our studies on the applications of nanomaterials and heterogeneous catalysis, [36-41] herein, we

<sup>&</sup>lt;sup>b</sup>Regional Centre of Advanced Technologies and Materials, Faculty of Science, Department of Physical Chemistry, Palacky University, Šlechtitelů 11, 783 71, Olomouc, Czech Republic.

Dr. Anuj K. Rathi, Prof. Rajender S. Varma, Prof. Radek Zboril, Dr. Manoj B. Gawande

## **FULL PAPER**

report the synthesis of HMS supported copper oxides (Scheme 1) as low-cost benign catalysts for the conversion of aldehydes to corresponding amides in water.



**Scheme 1.** Graphical representation for the synthesis of HMS supported copper oxides

#### **Results and Discussion**

The synthesized CuO/HMS catalysts were examined for their structural and chemical properties by XRD, X-ray photoelectron spectroscopy (XPS), atomic absorption spectroscopy (AAS), transmission electron microscopy (TEM), PSD, pore volumes, temperature programmed desorption (TPD-NH<sub>3</sub>), temperature-programmed reduction (TPR), Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and high angle annular dark-field scanning transmission electron microscopy (HAADF-STEM).

XRD patterns of HMS and CuO/HMS samples showed typical reflections of the corresponding silica structure (Figure 1). The wide angle powder XRD patterns of calcined HMS material (15CuO/HMS) display two peaks positioned at 35.5° and 38.7° corresponding to (002) and (111) lattice planes of monoclinic CuO species.<sup>[42]</sup> The XRD patterns in (Figure 1) suggest that there are no visible diffraction peaks representing crystalline CuO present in the sample with Cu loading less than 10 wt%. These CuO nanoparticles might be present as smaller crystallites in diameter, which are undetectable by XRD. At higher Cu loadings (15wt% Cu), small XRD reflections are noticed due to crystalline CuO and the intensities of these reflections are found with the increase of Cu loading.<sup>[43]</sup> Broad and diffuse diffraction peak around  $2\theta = 21.7^{\circ}$  indicates amorphous nature of silica. In low angle measurement for fresh catalyst, the presence of only peak at 2 theta position 2.363° (equivalent to d-spacing 3.7348 nm) point that silica does not exhibits neither hexagonal nor cubic ordering. This only line



indicates mesoporous structure of material with random

orientation of silica.

Figure 1. XRD patterns of the CuO/HMS catalysts.

This observation, along with the TEM results (Figure 2a, 2b and Figure S2, see SI) indicate that most of copper oxide is incorporated on the inside walls of HMS and found to be of spherical in shape. 3 wt% CuO/HMS as analyzed by TEM images show a wormhole-like mesopore structure and well dispersion of CuO nanoparticles of nearly 20 nm size (Figure 2a and 2b).



Figure 2. TEM images of 3 wt% CuO/HMS with scale bars of (a) 200 nm; (b) 20 nm.

The FT-IR spectrum of CuO-HMS shows a broad absorption around 3600-3200 cm<sup>-1</sup> ascribed to the overlapping of the O-H stretching of adsorbed water bands and silanols see (Figure S3, supporting Information).<sup>[44]</sup> The band observed near 1640 cm<sup>-1</sup> corresponds to the bending mode of vibration of -OH groups of adsorbed water.<sup>[45]</sup> The differentiation between copper hydroxide at around 938 and 694 cm<sup>-1</sup> and copper hydrosilicate at ca. 670 cm<sup>-1</sup> can be made from the frequencies of the O-H bands.<sup>[46]</sup> Figure S2 indicates that there is no band corresponding to Cu-O-H bond at 690 cm<sup>-1</sup>, suggesting the absence of Cu(OH)<sub>2</sub> after calcination. The shoulder peak at around 600 cm<sup>-1</sup> corresponds to Cu(II)-O species<sup>[47]</sup> and the new band observed at around 964 cm<sup>-1</sup> imply a bond formation (Cu-O-Si)<sup>[48]</sup> during catalyst

## **FULL PAPER**

preparation. The surface textural properties of the catalyst supports and CuO/HMS indicate that with increase in copper loading, the surface area of the mesoporous material decreases (Table 1).

Table 1. Surface properties of HMS and CuO/HMS catalysts.

Catalysts	BET surface area (m <sup>2</sup> g-1)	Cu loading (wt %)	Pore diameter (nm)	Pore volume (cm₃g-1)
HMS	974	0	2.9	0.73
1CuO/HMS	951	0.8	2.8	0.70
3CuO/HMS	894	2.6	3.0	0.68
5CuO/HMS	825	4.3	2.8	0.66
10CuO/HMS	788	8.8	3.5	0.60
15CuO/HMS	754	13.5	3.7	0.56

The N<sub>2</sub> adsorption-desorption isotherms and the pore size distribution curves of the catalysts and the bare support are provided in (see Figure S4 a and b, Supporting Information). The HMS and CuO/HMS materials show type IV isotherms with a sharp inflection due to capillary condensation at P/P<sub>0</sub> = 0.4–0.8 with H<sub>4</sub>-type hysteresis loop<sup>[49]</sup> corresponding to a typical mesoporous material with slit channels. As the synthesis of HMS is based on the hydrogen bonding interaction, the pore size is sensitive to reaction temperature. With an increased temperature, the interaction between inorganic species and surfactants can be weakened, resulting in a large spacing between them and thus a large pore size observed under such conditions.

The pore size can be continuously adjusted with extended reaction durations<sup>[50]</sup> and pore size distribution curves derived from desorption are shown in (Figure S3b). The increase of CuO loading in Cu/HMS catalysts leads to less capillary condensation as indicated by the decrease in surface area and pore volume (Table1), presumably because of the pore filling by CuO species. The surface composition and chemical state of 3 wt% CuO/HMS was further examined through XPS analysis which shows that the nature of copper in the form of CuO by the presence of peaks at 933.83 eV (assigned to Cu2p3/2 in (Figure 3).<sup>[51, 52]</sup> Further, elemental mapping of copper, silica and oxygen was accomplished by HRTEM analysis. The high resolution (HR) TEM image clearly revealed that the silica nanoshere are of spherical shape, (200-250 nm) which was also discerned by

high-angle annular dark-field imaging scanning TEM (HAADF-STEM) (Figure 4). In TEM and HRTEM images, we tried to locate the CuO nanoparticles but they are not clearly visible because of their small size; the average particle size was observed between 13-18 nm (Figure 2, Figure 4, and Figure S5). From elemental mapping images, it clearly shows that the Cu species are homogeneously dispersed among Si and O elements, indicating the possible immobilization outer surface of the silica matrix (Figure 4 c-f).

#### Catalysts performance:

Catalytic activity of the prepared CuO/HMS materials was investigated for the amidation reaction using benzaldehyde as a model substrate. To optimize the reaction conditions, a series of experiments with varying amounts of CuO/HMS (1 to 15 wt% CuO/HMS) were conducted (Table 2). The results revealed that







**Figure 4.** (a) HRTEM image (b) HAADF-STEM image, (c-f) EDS elemental mapping showing the spatial distributions of Cu (c), O (d), Si (e) and Cu, O, and Si together (f).

## WILEY-VCH

3 wt% CuO/HMS catalyst was optimum for getting 100% conversion and 92% selectivity of benzamide within 10 h (Table 2, entry 8), while 5 wt% CuO/HMS, 10 wt% CuO/HMS and 15 wt% CuO/HMS provided less catalytic activity for the amidation reaction using benzaldehyde as a model substrate. To optimize the reaction conditions, a series of experiments with varying amounts of CuO/HMS (1 to 15 wt% CuO/HMS) were conducted (Table 2). The results revealed that 3 wt% CuO/HMS catalyst was optimum for getting 100% conversion and 92% selectivity of benzamide within 10 h (Table 2, entry 8), while 5 wt% CuO/HMS, 10wt% CuO/HMS and 15 wt% CuO/HMS provided less amounts of products (Table 2, entries 9-12). Furthermore to elucidate the catalyst role we have performed the control experiment, in which we have carried out reaction without catalyst in the presence of hydroxylamine hydrochloride (NH<sub>2</sub>OH.HCl) to check whether the reaction can be catalyzed by the small amount of HCl content in hydroxylamine. We found without catalysts even after increasing the loading of NH<sub>4</sub>OH.HCI (1-3 equivalent) no amide formation observed (Table 2, entries 1-2). All experiment later on carried out by using base treated NH<sub>2</sub>OH.HCl as per mentioned in procedure.

#### Effect of reactant concentration:

To evaluate the effect of reactant concentration, reactions were carried out with different concentrations of hydroxyl amine and aldehyde 0.5, 1, 2, 3 and up to 4 equivalents by keeping one reactant constant, we found that 1:1 equivalent concentration of aldehyde to hydroxylamine hydrochloride is adequate to provide excellent yield (Table S1, entries 1-7).

#### Effect of Catalyst Loading:

The effect of catalyst loading was studied in the range of 20 mg to 60 mg for catalyst 3%CuO/HMS to check the selectivity towards the product (Table S1, entries 8-11). The conversion was linear for all catalyst loading. However the selectivity toward benzamide increases from 65%-92%. This is may be increase in the number of active sites of CuO species in the catalyst. However, beyond a catalyst loading of 50 mg there was no significant increase in product yield. Hence further experiments were carried out using 50 mg catalyst.

To clarify and understand the influence of different supports with CuO, we have prepared three catalysts with 3wt% loading of CuO/SiO<sub>2</sub>, CuO/Al<sub>2</sub>O<sub>3</sub> and CuO/MCM-41 and tested the catalytic reactions; 72%, 55% and 81% selectivities were obtained, respectively (Table 2, entries 14-16). Even with 1 g scale of benzaldehyde the corresponding product was obtained in good yield (88%,Table 2, entry 17). Further, we learnt that by

controlling the loading of CuO would attain the smaller crystalline size and it shows more pronounced effect. Consequently, we found that that the smaller crystalline nature of 3wt% of CuO/HMS shows efficient activity than other catalysts. Furthermore to explore the role of HMS support, we have carried out experiments with individual catalysts namely HMS and CuO; the benzamine (2a) product was obtained with less selectivity (20% and 50% respectively; Table 2, entries 4 and 5). Even the physical mixture of HMS and CuO powder (Table 2, entry 13) provided comparatively less yield, which is less than intact 3wt%CuO/HMS.

#### **Effect of Temperature:**

Effect of temperature on the conversion of aldehyde to amide was studied from 40 to 100 °C (Figure S6 a). It was observed that as the temperature increases, the conversion of aldehyde increased and formation product amide also increased simultaneously. However, in between the 80 to 100 °C, the selectivity toward benzamine increases. Initial rates of reaction were calculated and used to make the Arrhenius plot from which apparent activation energy of 11 kcal/mol obtained (Figure S6 b).

The significance of immobilizing CuO on HMS has clearly demonstrated the synergism between the silica support and copper nanoparticles. HMS is mesoporous material in present catalysts that provides the high surface area, and thermal stability to the supported metal oxide species. It also assists to minimize the leaching problem of metal species in the reaction medium to avoid the contamination of the metal oxide species with reaction products; sintering and agglomeration of metal species support play key role to keep the all supported species finely dispersed in small crystalline size. Supported catalyst can easily be separated out during the final purification of the product. The acidic properties of catalyst CuO/HMS are mainly ascribed to the very high dispersion of the oxidic phase. High dispersion of metal oxide onto an inorganic HMS matrix offers improved active sites and also allows enhances electronic and catalytic properties.[53]

With the comparatively low loading of CuO on silica support, we did observe the smaller crystalline nature of oxide species which display good performance than other catalysts.<sup>[54]</sup> The acidic nature of the CuO/HMS catalyst was measured by TPD, NH<sub>3</sub>; we found the moderate acidic sites 871.47 µmol/g.

Herein, we also performed the TPR experiment with 3wt%CuO/HMS and 15wt% CuO/HMS to evaluate the dispersion of CuO on the support and found the catalyst 3wt%CuO/HMS reduced at low temperature with sharp peak than 15wt% CuO/HMS (Figure 5). In the literature it is also

reported that lower metal loading display higher dispersion, and larger reactive surface area.<sup>[55]</sup> Further increase in metal loading up to 15 wt %, the comparative influence dispersed CuO crystallites decreases whereas that of the poorly dispersed species becomes much more visible.<sup>[56]</sup>



Figure 5. TPR analysis of 3wt% CuO/HMS and 15wt%.

In CuO/HMS catalysts copper with (+2) oxidation state would form possible coordinate bond with nucleophiles like oxime and nitrile in reaction and assist the formation of primary amide throug dehydration via rearrangement mechanism. In case of reduced copper (0) HMS we found the low yield of the corresponding product (Table 2, entry 9) and can be associated with the less Lewis acidic nature of Cu(0) as compared to Cu(+2), which presumably did not allow better coordination with oxime/nitrile and only helped to anchor the nanoparticles on the HMS support.

After optimizing the reaction conditions, the versatility of catalysts was established using an array of substituted and heteroaryl aldehydes; corresponding products were obtained in good to excellent yields (Table 3, entries 1-13, 60-92%). As expected, electron donating and withdrawing groups affected the rate of reaction and the yield of product formation; reaction with benzaldehyde and ortho- and para- substituted methoxy benzaldehydes gave excellent yields (Table 3, entries 1, 4, and 5) whereas ortho- and para-substituted chloro- and nitro aryl aldehydes gave good yields (Table 3, entries 2, 3, 12, and 13). In contrast, 4-cyanobenzaldehyde gave only moderate 60% yield (Table 3, entry 10).

 Table 3. CuO/HMS catalyzed conversion of various aldehydes to primary amides.<sup>a</sup>



<sup>b</sup>Isolated yields. <sup>c</sup>Yields were determined by using GC using biphenyl as an internal standard.

### WILEY-VCH

Table 2. Comparison of various catalysts for the conversion of							
alder	nyde to benzamide	ə.ª Q		Ņ	NOH (	CN	
$\sim$	L. Catalyst		2 (				
	H Water, 100 °C	→ 💭	- + [		+		
1	- NH <sub>4</sub> OH	2a		2b	2	2c	
	Conversio Yie		ield (	%)	TON		
No	Catalyst		0-	0h	0-		
	Catalyst	n (%)	2a	20	20		
1	NH <sub>4</sub> OH.HCl <sup>b</sup>	95	-	95	5	NA	
2	NH <sub>4</sub> OH.HCl <sup>c</sup>	100	-	98	2	NA	
3	NH₄OH	100	-	98	2	NA	
4	HMS	100	20	70	10	NA	
5	CuO powder	100	50	40	10	59	
6	Cu powder	100	25	60	15	29	
7	1CuO/HMS	100	45	40	15	5874	
8	3CuO/HMS	100	92	8	-	3655	
9	5CuO/HMS	100	85	10	<5	1991	
10	10CuO/HMS	100	60	36	<4	694	
11	15CuO/HMS	100	37	60	3	281	
12	3Cu(0)/HMS	100	30	64	6	1370	
13	HMS and CuO <sup>d</sup>	100	52	36	12	148	
14	3CuO/SiO <sub>2</sub>	100	72	19	9	2860	
15	3CuO/MCM41	100	81	14	5	3218	
16	3CuO/Al <sub>2</sub> O <sub>3</sub>	80	55	34	16	2185	
17	3CuO/HMS <sup>e</sup>	100	88	13	-	3456	

<sup>a</sup>Reaction conditions: aldehyde (1 mmol), hydroxylamine (1 mmol), CuO/HMS (3 wt%, 50 mg), water (3 mL) 100 °C, 10 h. Yields were determined by GC analysis using biphenyl as an internal standard; <sup>b</sup>NH<sub>4</sub>OH.HCl(3mmol),<sup>c</sup>NH<sub>4</sub>OH.HCl(3 mmol)10h; 24 h; Cu powder, 24 h.<sup>d</sup>Physical mixture of HMS and CuO powder. <sup>e</sup>1 gm scale reaction.

Incorporation of CuO species, more than 3 wt%, might increase the particle size of CuO *via* agglomeration, which may block the active site of the catalysts thus lowering the activity.

The reaction profile for the conversion of benzaldehyde to benzamide 2a (Figure 6) showed that benzaldoxime 2b, was initially formed with high selectively as a major product with high reaction rate as well benzonitrile 2c also with minimum selectivity. As the reaction proceeded further, we found the gradually increase in the formation of benzamide 2a and in the meanwhile selectivity of benzaldoxime 2b and benzonitrile 2c slowly decreased. Finally at the 10<sup>th</sup> hour of reaction 92% selectively benzamide 2a was observed and benzaldoxime 2b remained with only 8%. The reaction pathway goes through a maximum indicating a consecutive reaction. The previously reported protocols are quite comparable and reaction gets completed within 10 h (Table S2, Supporting Information).



Figure 6. Conversion of benzaldehyde to benzamide.

On the basis of literature accepted mechanism pathway has been proposed through various metal catalysed rearrangement.<sup>[11-13,15]</sup> In our case for this reaction, we used supported copper CuO/HMS species copper is present of Cu (II) state. The mechanism of reaction mostly proceeds via the formation benzaldoxime 2b from the reaction of aldehyde 1 and hydroxylamine hydrochloride. Subsequently, benzaldoxime 2b forms coordination bond with acidic sites of CuO to produce benzonitrile 2c via dehydration. In the next step, the benzonitrile 2c and benzaldoxime 2b will form the coordination bond with active acidic CuO sites and nucleophilic centre will be formed at nitrile carbon, followed by generation of metal containing five member ring culminating in attack of oxime as a nuleophilile (Figure 7). Further benzamide 2a will be generated via decomposition of five member ring. In aqueous reaction medium water acts as a nucleophile, as suggested by Williams et.al by performing the experiment with oxygen labelled water.<sup>[57]</sup> (Figure 6) shows the mechanistic pathway wherein consumption of initially formed nitrile species progressed with the reaction to generate the final amide product.

Reusability of a catalyst is an important factor from economic point of view. The activity of CuO/HMS catalyst was investigated by repeating experimental cycles under optimized conditions using benzaldehyde as the substrate (Figure 8). After completion of the reaction, the catalyst was recovered (by filtration or centrifugation), washed with water and methanol and dried at 80 °C and reused for next cycle. The concentration of Cu species leached into the reaction mixture was determined by ICP analysis and found be 0.002 mmol of the total Cu content in 3 wt% CuO/HMS catalyst even after seven cycles. This clearly indicates the stability and reusability of the chosen catalyst system.



Catalysts: Cu<sup>2+</sup>=CuO/HMS

Figure 7. Proposed mechanism for formation of primary amide.



Figure 8. Reusability test for the catalyst.

#### Conclusion

We have established an effective mesoporous silica coppercatalysed amide synthesis from aldehydes with superb functional group tolerance in aqueous medium under mild reaction conditions. The copper loading has profound effect on the structure and textural properties and the catalytic activity. The oxidation state of copper in the catalysts was confirmed to be Cu (II) (CuO) and an interaction with the HMS support was established. Notably, 3 wt% catalysts delivered excellent results comparative to other catalysts containing lower and higher copper content. This protocol facilitates an easy access to amides from reaction of aldehydes with hydroxylamine. Activity of the catalysts enhances as the CuO loads on the HMS support up to some extent in which 3wt%CuO/HMS and 5wt%CuO/HMS showed the highest catalytic performance. Kinetic studies reveal the enhancement of active sites with catalyst loading. The catalysts were stable and reusable without any considerable loss in activity for several cycles making them economically and environmentally viable.

#### Experimental

#### **Catalyst Preparation**

In a typical synthesis, 6.4 g dodecyl amine (DDA) was dissolved in a mixture of 50 mL of ethanol and 70 mL of deionized water under vigorous stirring. A dilute aqueous solution of 0.7 g of Cu (NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O was then added followed by the drop wise addition of stoichiometric amount of tetraethylorthosilicate (TEOS) in ethanol and isopropyl alcohol (IPA); molar composition of this solution being 1:7:1 (TEOS: EtOH: IPA). The stoichiometric amount of Si is relative to the amount of copper. The solution was then stirred at 323 K for 4 h and the gel was aged for 24 h at 313 K. The gel was then collected by centrifugation, washed thoroughly with deionized water and absolute ethanol, and dried in air for 24 h at 373 K, followed by calcination in air for 4 h at 723 K. Various loadings of copper metal on HMS have been obtained by this one-pot synthesis (OPS) method.

## General procedure for CuO/HMS catalyzed synthesis of amides

A mixture of aldehyde (1 mmol), solution of hydroxylamine hydrochloride (1 mmol) and sodium bicarbonate (2 mmol or excess) in 3 mL water were prepared and filtered the aqueous solution used as hydrochloride salt free hydroxyl amine, 3 wt% CuO/HMS (50 mg) was taken in a reaction vessel and stirred at 100 °C for appropriate time (Table 3). Progress of the reaction was monitored by GC analysis. After completion of the reaction, the catalyst was separated by centrifugation and the reaction mass was extracted with ethyl acetate. The organic phase was chromatography (silica 230–400; n-hexane/ethyl acetate mixture) to afford the desired product

#### Acknowledgement

The author Ravishankar Kadam is thankful to the UGC-UPE Green Technology centre, New Delhi, India for awarding the fellowship. The authors also thank Ms. J. Stránská for TEM, j. Josef Kašlík for small angle XRD analysis and Martin Petr for XPS and acknowledge support from the Ministry of Education, Youth and Sports of the Czech Republic (LO1305). The authors

further acknowledge the assistance provided by the Research Infrastructure NanoEnviCz, supported by the Ministry of Education, Youth and Sports of the Czech Republic under Project No. LM2015073.

<sup>†</sup>Electronic supplementary information (ESI) available. General information, TEM images, FT-IR, BET surface area, catalyst comparison activity.

#### **Keywords**

Mesoporous silica, Copper Oxide, Heterogeneous catalysis,

#### References

- [1] G. S. Singh, Tetrahedron, 2003, 59, 7631-7649.
- [2] F. Albericio, Curr. Opin. Chem. Biol., 2004, 8, 211-221.
- [3] B.Shen, D. M. Makley, J. N. Johnston, Nature, 2010, 465, 1027-1032.
- [4] S. H. Cho, E. J. Yoo, I. Bae, S. Chang, J. Am. Chem. Soc., 2005, 127, 16046-16047.
   [5] J. O. Conv. D. Leffer, O. Thermore, M. T. Williams, Com. Diamod.
- [5] J. S. Carey, D. Laffan, C. Thomson, M. T.Williams, Org. Biomol. Chem., 2006, 4, 2337-2347.
- [6] J. March. M. B. Smith, Advanced Organic Chemistry: Reactions, Mechanisms, and Structure, Wiley, Hoboken, NJ, 6<sup>th</sup> ed., 2007.
- [7] E. Valeur, M. Bradley, Chem. Soc. Rev., 2009, 38, 606-631.
- [8] E. Beckmann, Ber. Dtsch. Chem. Ges. 1886, 19, 988–993.
- [9] M. T. Nguyen, G.Raspoet, L. G.Vanquickenborne, J. Am. Chem. Soc., 1997, 119,2552-2562.
- [10] R. E. Gawly, Org. React. 1988, 35, 1.
- [11] R. S. Ramón, J.Bosson, S.Díez-González, N.Marion, S. P.Nolan, J. Org. Chem. 2010, 75, 1197-1202.
- [12] M. A. Ali, T. Punniyamurthy, Adv. Synth. Catal., 2010, 352, 288-292.
- [13] H. Fujiwara, Y. Ogasawara, K. Yamaguchi, N. Mizuno, Angew. Chem., Int. Ed., 2007, 46, 5202-5205.
- [14] D. Gnanamgari, R. H.Crabtree, Organometallics, 2009, 28, 922-924.
- [15] N. A.Owston, A. J. Parker, J. M. J. Williams, Org. Lett., 2007, 9, 3599-3601.
- [16] N. C. Ganguly, S. Roy, P. Mondal, *Tetrahedron Lett.*, 2012, 53, 1413-1416.
- [17] S. K. Sharma, S. D.Bishopp, C.L. Allen, R Lawrence, M. J Bamford, A. A Lapkin, P.Plucinski, R. J. Watson, J. M. J.Williams, *Tetrahedron Lett.*, 2011, 52, 4252-4255.
- [18] P. Crochet, V.Cadierno, Chem. Commun., 2015, 51, 2495-2505.
- [19] M. B. Gawande, P. S. Branco, R. S. Varma, Chem. Soc. Rev., 2013, 42, 3371-3393.
- [20] R. K. Sharma, S. Sharma, S. Dutta, R.Zboril, M. B. Gawande, Green Chem., 2015, 17, 3207-3230.
- [21] M. B. Gawande, V. D. B. Bonifacio, R. Luque, P. S. Branco, R. S. Varma, *Chem. Soc. Rev.*, **2013**, 42, 5522-5551.
- [22] S. Rostamnia, N. Nouruzi, H. Xin, R. Luque, Catal. Sci. Technol., 2015, 5, 199-205.
- [23] C. J. Li, L. Chen, Chem. Soc. Rev., 2006, 35, 68-82.
- [24] K. Yamaguchi, H. Kobayashi, Y. Wang, T. Oishi, Y. Ogasawara, N. Mizuno, Catal. Sci. Technol., 2013, 3, 318-327.
- [25] A. Martínez-Asencio, M. Yus, D. J. Ramón, *Tetrahedron*, **2012**, 68, 3948- 3951.
- [26] B. K. Allam, K. N. Singh, *Tetrahedron Lett.*, 2011, 52, 5851-5854.
- [27] R. Garcia-Alvarez, M. Zablocka, P. Crochet, C. Duhayon, J. P. Majoral, V. Cadierno, *Green Chem.*, **2013**, 15, 2447-2456.
- [28] R. R. Gowda, D. Chakraborty, Eur. J. Org. Chem., 2011, 2011, 2226-2229.
- [29] M. E.Davis, Nature, 2002, 417, 813-821.

- [30] R. Luque, A. Mariana Balu, J.Manuel Campelo, M. Dolores Gracia, E. Losada, A. Pineda, A. Angel Romero, J. Carlos Serrano-Ruiz, *Catalysis* 2012,24, 253-280.
- [31] C. T. Kresge, M. E. Leonowicz, Roth, W. J. Vartuli, J. C. Beck, J. S. *Nature*, **1992**, **359**, 710-712.
- [32] P. T. Tanev, T. J. Pinnavaia, Science, 1995, 267, 865-867.
- [33] J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T. W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B.Higgins, J. L.Schlenker, J. Am. Chem. Soc., **1992**, 114, 10834-10843.
- [34] S. H. Wu, C. Y. Mou, H. P. Lin, Chem. Soc. Rev., 2013, 42, 3862-3875.
- [35] X. Fang, X. Zhao, W. Fang, C. Chen, N. Zheng, *Nanoscale*, **2013**, 5, 2205-2218.
- [36] M. B. Gawande, A. Goswami, F.-X. Felpin, T. Asefa, X. Huang, R. Silva, X. Zou, R. Zboril, R.S. Varma, *Chem. Rev.*, **2016**, 116, 3722–3811
- [37] M. B. Gawande, A. Goswami, T. Asefa, H. Guo, A. V. Biradar, D.L. Peng, R. Zboril, R. S. Varma, *Chem. Soc. Rev.*, **2015**, 44, 7540-7590.
- [38] M. B. Gawande, A. K.Rathi, J.Tucek, K. Safarova, N. Bundaleski, N. D. Teodoro, L. Kvitek, R. S. Varma, R.Zboril, *Green Chem.*, 2014, 16, 4137-4143.
- [39] M. B. Gawande, R. Zboril, V. Malgras, Y. Yamauchi, J. Mater. Chem. A.,2015, 3, 8241-8245.
- [40] A. K. Rathi, M. B. Gawande, J. Pechousek, J. Tucek, C. Aparicio, M.Petr, O. Tomanec, R. Krikavova, Z. Travnicek, R. S. Varma, R. Zboril, *Green Chem.*, 2016, 18, 2363-2373
- [41] A. K.Rathi, M. B. Gawande, V. Ranc, J. Pechousek, M. Petr, K. Cepe, R. S. Varma, R.Zboril, Catal. Sci. Technol., 2016, 6, 152-160.
- [42] B. Zhao, P. Liu, H.Zhuang, Z. Jiao, T. Fang, W. Xu, B. Lu, Y. Jiang, J. Mater. Chem. A., 2013, 1, 367-373.
- [43] G. V. Sagar, P. V. R. Rao, C. S. Srikanth, K. V. R. Chary, J. Phys. Chem. B. 2006, 110, 13881-13888.
- [44] L. R. Azizova, T. V. Kulik, B. B. Palianytsia, Zemlyakov, V. N. Tsikalova, V. Y. Chirva, *Nanoscale Res. Lett.*, **2014**, 9.
- [45] C.Henrist, K. Traina, Hubert, G. Toussaint, A. Rulmont, R. Cloots, J. Cryst. Growth., 2003, 254, 176-187.
- [46] T. Toupance, M. Kermarec, J. F. Lambert, C. Louis, J. Phys. Chem. B., 2002, 106, 2277-2286.
- [47] G. Cordoba, R. Arroyo, J. L. G.Fierro, M.Viniegra, J. Solid State Chem., 1996, 123, 93-99.
- [48] L. Chen, T. Horiuchi, T. Osaki, T. Mori, App. Catal. B., 1999, 23, 259-269.
- [49] R. Schmidt, E. W.Hansen, M. Stoecker, D. Akporiaye, O. H. Ellestad, J. Am. Chem. Soc., 1995, 117, 4049-4056.
- [50] A. Vinu, M. Miyahara, K. Ariga, J. Phys. Chem. B, 2005, 109, 6436-6441.
- [51] F. Vila, M. López Granados, M. Ojeda, J. L. G.Fierro, R. Mariscal, *Catal. Today*, **2012**, 187, 122-128.
- [52] S. Murcia-Mascarós, R. M. Navarro, L.Gómez-Sainero, U.Costantino, M. Nocchetti, J. L. G.Fierro, J. Catal., 2001, 198, 338-347.
- [53] F. Zaccheria, N. Scotti, M. Marelli, R. Psaro, N.Ravasio, *Dalton Trans.* 2013, 42, 1319-1328.
- 54] G. Busca, Phys. Chem. Chem. Phys., **1999**, 1, 723-736.
- [55] C. J. G. Van Der Grift, A. F. H. Wielers, A. Mulder, J. W. T. Geus,
- Thermochimica Acta. **1990**, 171, 95-113.
- [56] R.-X. Zhou, T.-M. Yu, X.-Y. Jiang, F. Chen, X.-M. Zheng, *Appl. Surface Sci.*, **1999**, 148, 263-270.
- [57] C. L. Allen, R. Lawrence, L.Emmett, J. M. J.Williams, Adv. Synth. Catal. 2011, 353, 3262-3268.

## WILEY-VCH

## Hexagonal Mesoporous Silica-Supported Copper Oxide (CuO/HMS) Catalyst– Synthesis of Primary Amides from Aldehydes in Aqueous Medium

Ravishankar G. Kadam,<sup>a</sup> Anuj K. Rathi,<sup>b</sup> Klara Cepe,<sup>b</sup> Radek Zboril,<sup>b</sup> Rajender S. Varma,<sup>b</sup> Manoj B. Gawande<sup>b\*</sup> and Radha V. Jayaram<sup>a\*</sup>





Accepted Manuscrip