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Graphene oxide immobilized copper phthalocyanine tetrasulphonamide: the first heterogenized homogeneous catalyst for dimethylcarbonate synthesis from CO_2 and methanol†

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The first successful synthesis of DMC directly from methanol and carbon dioxide using a heterogenized homogeneous graphene oxide immobilized copper phthalocyanine tetrasulphonamide catalyst in the presence of *N,N′*-dicyclohexylcarbodiimide (DCC) as a dehydrating agent is described. The presence of a dehydrating agent was found to be vital and in its absence the yield of DMC was found to be decreased significantly. Under the optimized reaction conditions, the maximum yield of DMC reaches up to 13.3%. Although the homogeneous copper phthalocyanine tetrasulphonamide catalyst provided a little higher yield of DMC (14.2%), the facile recovery and recycling ability of the heterogeneous catalyst make the developed method more attractive from environmental and economical viewpoints.

Introduction

Every day, a huge amount of carbon dioxide (CO_2) is emitted as a result of fossil fuel combustion and is accumulated in the atmosphere which in turn is responsible for global warming. Many ways have been proposed to reduce the concentration of CO_2 in the atmosphere. One of the most promising approaches to achieve this target is the utilization of carbon dioxide to value added chemicals which has received considerable interest in recent decades.[1–3] CO_2 can be used as a carbon feedstock for the production of useful chemicals such as dimethyl carbonate (DMC), polycarbonates, carbamates, *etc.* Among these reaction processes, the synthesis of dimethyl carbonate from CO_2 and methanol is of tremendous importance due to its versatile applications such as an electrolytic solution of lithium ion batteries, as a methylating reagent, and as a feedstock for engineering plastics.[4–8] In addition, DMC is considered to be an environmentally friendly oxygenated fuel additive due to its high octane number, low toxicity and biodegradability.[9,10] The conventional method for DMC synthesis involving phosgene and methanol has fallen out of use due to the high toxicity and severe corrosivity of phosgene.[11,12] Subsequently, two processes *i.e.* the ester exchange process and the oxidative carbonylation of methanol have extensively been used for DMC synthesis.[13–22] The more challenging method is the synthesis of DMC directly from carbon dioxide and methanol under mild reaction conditions. Various homogeneous catalysts, such as dialkytin dialkoxides, tin(IV) tetralkoxides, titanium(IV) tetralkoxides, bases and thallium(I) hydroxide have been reported for the synthesis of DMC from CO_2 and methanol.[23–28] However, these methods are associated with certain drawbacks such as difficulty in catalyst recovery, severe reaction conditions and rapid deactivation of the catalyst by process excursions. Subsequently, a number of heterogeneous catalysts such as CeO_2–ZrO_2, Ga_2O_3/$Ce_{0.6}Zr_{0.4}O_2$, H_3PO_4/ZrO_2, $Co_{1.5}PW_{12}O_{40}$, $H_3PW_{12}O_{40}$/$Ce_xTi_{1-x}O_2$, Cu–Ni–diatomite, Cu–Ni–graphite, and Cu–Ni–V_2O_5–SiO_2 have been reported.[29–36] However, rapid deactivation, leaching of metals and poor conversion of methanol to DMC are the major drawbacks associated with these methods.

The above-mentioned drawbacks of homogeneous and heterogeneous catalysts can be solved by heterogenizing the efficient homogeneous catalysts to a suitable solid support matrix. These heterogenized homogeneous catalysts are advantageous as they combine the best qualities of both heterogeneous (easy recovery and recyclability) and homogeneous catalysts (high reactivity and selectivity). Furthermore, these heterogenized homogeneous catalysts hold promise for bridging the gap between industrial catalysts, which carry out simple reactions. In this regard a number of organic and inorganic materials have been used as a support to immobilize the homogeneous catalysts.[37–40]

Recently, graphene oxide (GO) due to the presence of plenty of oxygenic functionalities such as hydroxyl and epoxide groups on both sides of its surface has been acknowledged as one of the

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most promising supports to immobilize various homogeneous materials including transition metal complexes.[41–44]
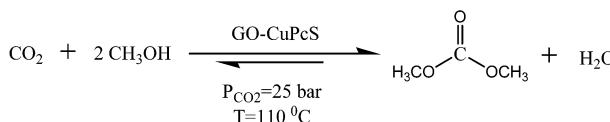
In the present paper we report the first successful synthesis of dimethyl carbonate directly from CO_2 and methanol using graphene oxide immobilized copper phthalocyanine tetrasulphonamide (GO–CuPcS) in the presence of a dehydrating agent (DCC) under mild reaction conditions (Scheme 1). To the best of our knowledge this is the first report on the use of a heterogenized homogeneous catalyst for DMC synthesis.

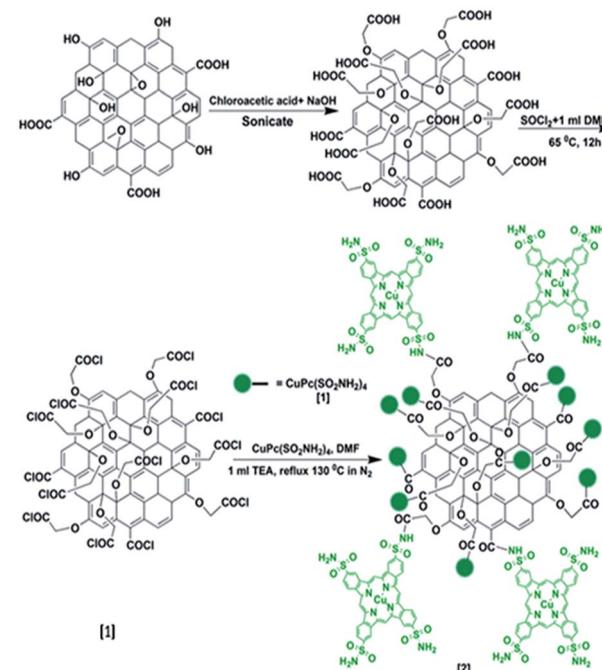## Synthesis and characterization of the catalyst

Graphene oxide, a two dimensional sheet having oxygen functionalities such as –OH, –COOH and epoxide groups on its surface, provided a facile immobilization of copper phthalocyanine tetrasulphonamide (CuPcS) *via* covalent attachment. Graphene oxide sheets were initially modified by the reaction of chloroacetic acid and NaOH under sonication to convert all their oxygen containing functional groups to –COOH. The synthesized material was subsequently treated with sulphonyl chloride ($SOCl_2$) followed by the addition of the CuPcS complex to give heterogeneous GO–CuPcS as shown in Scheme 2.

The synthesized heterogeneous catalyst **2** was characterized by various techniques such as FTIR, TEM, Raman, XRD and TGA analyses. The FTIR spectrum of homogeneous CuPcS (Fig. 1a) reveals its characteristic vibration at 510 cm^{-1}, 715 cm^{-1} and 902 cm^{-1} respectively. The peak at 3170 cm^{-1} is due to the –N–H of sulphonamide and peaks at 1024 cm^{-1}, 1398 cm^{-1}, and 1619 cm^{-1} are related to the C–H, C=N and the pyrrole ring of phthalocyanine. The FTIR spectrum of GO (Fig. 1b) shows the characteristic peaks at 1031 cm^{-1}, 1374 cm^{-1}, 1725 cm^{-1} and 1161.4 cm^{-1} corresponding to the C–OH, alkoxy C–O stretch, C=O– and –C–C– bending vibrations respectively. Changes in the FTIR spectrum after the immobilization of CuPcS on graphene oxide can be clearly seen in Fig. 1c. The shifting of the carbonyl (C=O) peak of GO from 1725 cm^{-1} to 1720 cm^{-1} and the appearance of a new band at 1575 cm^{-1} due to N–H suggest that the CuPcS has been successfully grafted onto the GO support. Furthermore, the appearance of some peaks corresponding to the phthalocyanine ring vibration at 1378 cm^{-1}, 1122 cm^{-1} and 620 cm^{-1} further indicates the covalent attachment of CuPcS to the GO support.

The morphology and structure of as-prepared GO and GO–CuPcS catalysts were investigated *via* transmission electron microscopy (TEM). As presented in Fig. 2a, the TEM image of GO shows transparent stacked sheets having well defined edges. The TEM image of GO–CuPcS (Fig. 2b) shows evenly distributed dark spots, which are probably due to the attachment of the

Scheme 2 Synthesis of GO–CuPcS catalyst **2**.

CuPcS complex on the GO support. Further in Fig. 2b, the folding of sheets appears to be increased because of the π cloud interaction between phthalocyanine and GO sheets. The Selected Area Electron Diffraction (SAED) pattern shows that the synthesized material is amorphous in nature and the number of rings in the SAED pattern indicates that the sheets are probably two to three layers in thickness. Furthermore the EDX analysis clearly indicates the presence of copper in the synthesized heterogeneous material **2** (Fig. 2d).

XRD patterns are used to study the changes in the structure (Fig. 3). The XRD spectrum of GO in Fig. 3a shows a characteristic diffraction peak at 10.8° corresponding to the 001 plane. After immobilization of CuPcS, this peak disappeared and another broad diffraction peak of graphite (002) at 2θ value
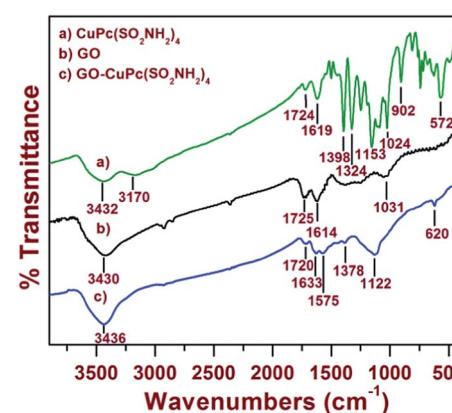

Scheme 1 Synthesis of DMC.

Fig. 1 FTIR of (a) CuPcS; (b) GO; (c) GO–CuPcS.

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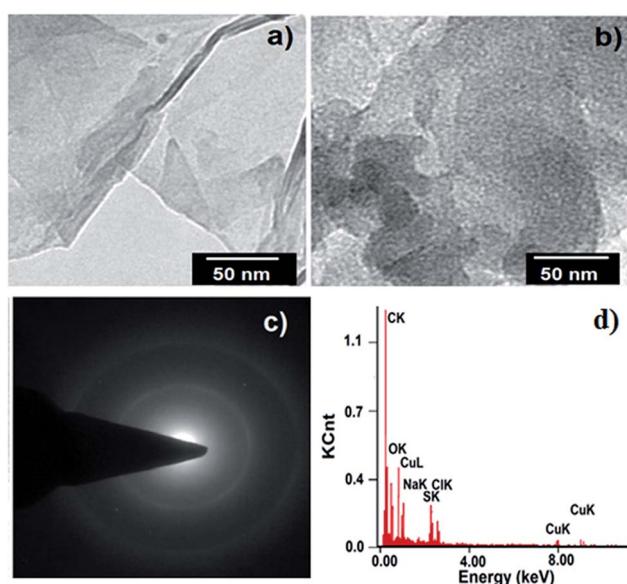This journal is © The Royal Society of Chemistry 2014

Fig. 2 TEM images of (a) GO; (b) GO–CuPcS; and (c) SAED pattern of GO–CuPcS; (d) EDX pattern.

Fig. 3 XRD diffractograms of (a) GO and (b) GO–CuPcS.

Fig. 4 Raman spectra of (a) GO; (b) GO–CuPcS.

number of small graphitic aromatic domains evolved on the surface of graphene oxide, which gives rise to a more conjugated aromatic system than that in graphene oxide (GO). This assumption was further confirmed by the shifting of the G band of GO–CuPcS from 1592 cm^{-1} to 1589 cm^{-1} that was nearly the same as the G band of pure graphite. Further the I_D/I_G value was found to be decreased to 0.75, indicating the successful attachment of CuPcS to the GO support.

Fig. 5 shows the TGA curves of the as prepared CuPcS, GO and GO–CuPcS, respectively. The TGA of CuPcS (Fig. 5a) shows a small weight loss nearly at 100 °C which is due to the adsorbed water or other solvent molecules. Another small weight loss nearly at 175 °C is attributed to the degradation of sulphonamide functionalities of CuPcS. The subsequent major and sharp weight loss, observed at 375 °C, is attributed to the degradation of the phthalocyanine ring structure. The thermogram of GO (Fig. 5b) shows an initial weight loss nearly at 108 °C, evidently
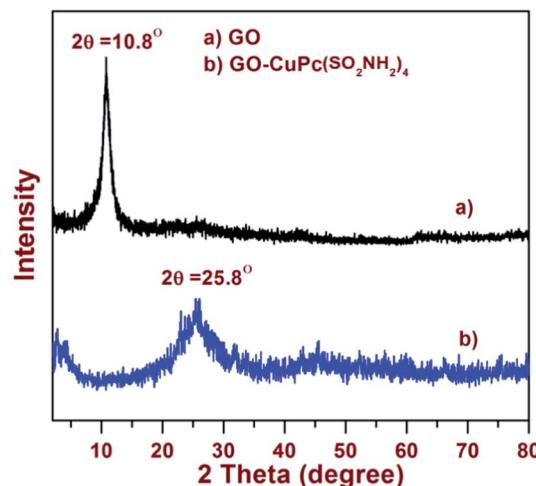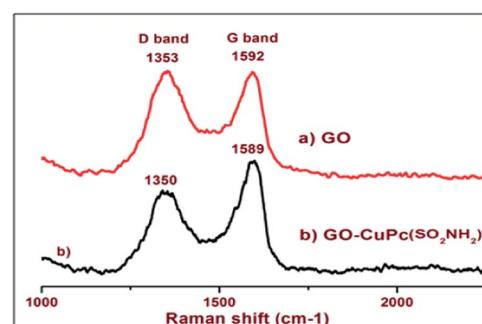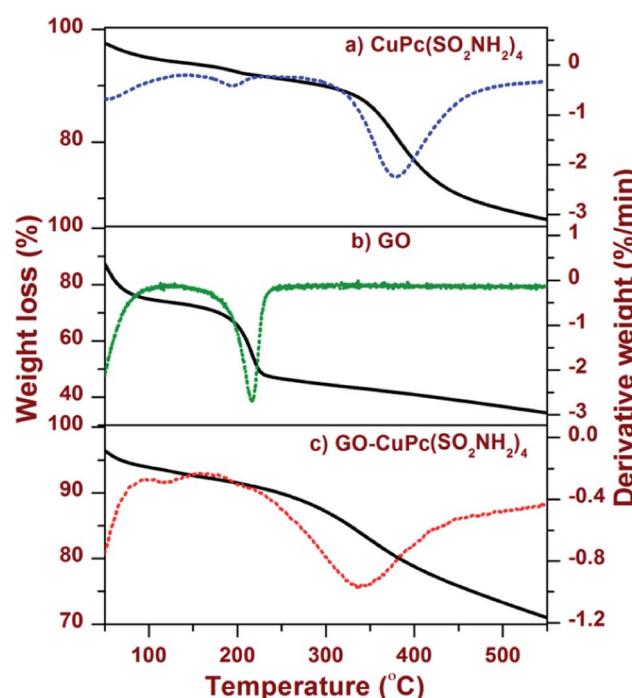

Fig. 5 DT-TGA thermograms of (a) CuPcS; (b) GO; (c) GO–CuPcS.

~26° appeared. This further confirms that the exfoliation of the layered GO–CuPcS is obtained (Fig. 3b).[11]

Fig. 4a and b show the Raman spectra of GO and GO–CuPcS respectively. As shown in Fig. 4a, two characteristics bands *i.e.* the D band (1353 cm^{-1}) and the G band (1592 cm^{-1}) are of nearly equal intensity. The D band is observed due to the large numbers of defects in the form of sp^3 carbons in GO sheets. However the G band is observed due to the sp^2 carbons of aromatic rings and in-plane vibration of sp^2 carbon bonded atoms. The integral intensity ratio of D and G bands (I_D/I_G) was found to be 1.0 which indicates a large number of defects in GO in the form of epoxide and other oxygen containing functionalities. In comparison to GO, in GO–CuPcS a very small shift of D and G bands towards lower frequency was observed. This is most likely due to the attachment of complex molecules a

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owing to the evaporation of water molecules which are held in the material. The second significant weight loss, observed in the range of 180–240 °C, is attributed to the thermal decomposition of oxygen carrying functionalities. The thermogram of GO–CuPcS (Fig. 5c) shows an exothermic major weight loss over a wide range of temperature (300–500 °C) due to the slow decomposition of the phthalocyanine moieties which further indicates that the synthesized heterogeneous catalyst is adequately thermally stable.

The loading of CuPcS onto the GO support was determined by estimating the copper content *via* inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and was found to be 1.2 wt% (0.18 mmol g^{-1}).

Catalytic activity of GO–CuPcS for DMC synthesis

The catalytic activity of the prepared heterogeneous GO–CuPcS **2** was tested for the synthesis of DMC directly from the reaction of carbon dioxide and methanol in the presence of a dehydrating agent (DCC) at 110 °C and 25 bar pressure of CO_2 for 2.5 h. The experiments were carried out in a stainless steel 15 ml autoclave under stirring. After completion of the reaction, the vessel was cooled to room temperature and the catalyst was separated by filtration. The resulting reaction mixture was analyzed by GC and GC-MS. The maximum yield of DMC under the optimized reaction conditions was found to be 13.3% (Table 1, entry 1). In order to compare the catalytic activity of the heterogeneous catalyst with its homogeneous analogue, we carried out the synthesis of DMC from methanol and CO_2 using homogeneous CuPcS as the catalyst under the described experimental conditions. The reaction was found to be a little faster and afforded 14.2% yield of DMC in 2.5 h (Table 1, entry 5). However, facile recovery and efficient recycling ability of the heterogeneous catalyst make the developed method more promising from industrial viewpoints. We also investigated the catalytic activity of various metal phthalocyanine tetrasulpho-namides (MPcS) such as Fe, Co, Ni, Cu and Zn for the synthesis of DMC from methanol and CO_2 under similar reaction

conditions. The results of these experiments are shown in Table 1. Among the various catalysts studied, copper phthalocyanine tetrasulphonamide was found to be the best and gave the highest yield of DMC (Table 1, entry 5). Iron, cobalt and nickel phthalocyanine tetrasulphonamides showed moderate activity and provided a moderate yield of DMC (Table 1, entry 2–4). However zinc phthalocyanine tetrasulphonamide was found to be less effective and provided a poor yield of DMC (Table 1, entry 6) even after a prolonged reaction time (6 h). The exact reason for the enhanced catalytic activity of the copper based catalyst is not known, however, it has been reported that activation of methanol and CO_2 by basic sites and supply of the methyl species from methanol by acidic sites are important steps in the direct synthesis of DMC from methanol and CO_2.[45,46] The interaction of the methanol O atom with a coordinately unsaturated Lewis acid center of the catalyst results in weakening of the C–O bond and produces a methyl cation (CH_3^+). Finally the activated CH_3^+ reacts with the intermediate CH_3OCOO^- to give the desired DMC. As given by the Irving–Wiliams series, the Lewis acidity of the divalent metal ions is in the order of Mn < Fe < Co < Ni < Cu > Zn.[47] Based on this we can presume that the higher acidity of the copper ions may help in activating the methanol which in turn enhances the activity for DMC synthesis.

The presence of a dehydrating agent was found to be vital and in its absence a lower yield of DMC (5.1%) was obtained (Table 1, entry 7). It is most likely due to the reverse decomposition of DMC in the presence of water. In the case of unsubstituted copper phthalocyanine (CuPc), the yield of DMC was found to be lower (Table 1, entry 8). This is probably due to the non-solubility of CuPc in organic solvents like methanol or the absence of NH_2 moieties which are required to provide basicity to activate methanol to give methoxy ion species. However, in heterogenized homogeneous catalysts, the catalyst in solution behaves like a homogeneous one with the additional benefits of facile recovery and recyclability. No DMC formation occurred when the reaction was performed using GO as the catalyst or in the absence of any catalyst under identical experimental conditions (Table 1, entry 9–10).

Besides these experiments, we also investigated the effect of temperature and pressure on the carboxylation of methanol under identical reaction conditions (Fig. 6). At ambient temperature (25 °C), the reaction rate was found to be slow and depended mainly on the CO_2 pressure applied. The observed conversion of methanol to DMC was found to increase with the pressure of CO_2. Among the various conditions studied, temperature 110 °C and CO_2 pressure 25 bar were found to be optimum for the maximum yield of DMC. Further increase in temperature (120 °C) affects the reaction adversely and affords a poor yield of DMC.

Further, the recycling of the developed heterogeneous catalyst **2** was investigated (Fig. 7). After completion of the reaction, the catalyst was separated by filtration and subjected to the next run under identical reaction conditions. The recovered catalyst was tested for subsequent five runs. During these experiments, the yield of DMC remained almost the same, indicating that the

Table 1 DMC synthesis using different catalysts[a]

Entry	Catalyst	Dehydrating agent	Time (h)	Yield[b] (%)	Select. (%)
1	GO–Cu-PcS	DCC	2.5	13.3[c]	98
	GO–CuPcS	—	2.5	5.5[c]	90
2	Fe-PcS	DCC	4	5.1	90
3	Co-PcS	DCC	4	6.6	95
4	Ni-PcS	DCC	4	7.4	98
5	Cu-PcS	DCC	2.5	14.2	98
6	Zn-PcS	DCC	6	2.3	98
7	Cu-PcS	—	2.5	5.1	91
8	Cu-Pc	DCC	4	2.7	89
9	GO	DCC	4	—	—
10	—	DCC	4	—	—

[a] Reaction conditions: methanol (6 ml), catalyst (0.04 g), at 110 °C, 25 bar pressure of CO_2. [b] Isolated yield of DMC. [c] Catalyst (0.2 g).

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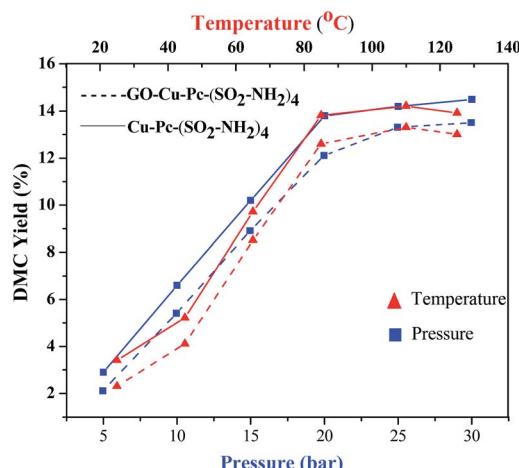This journal is © The Royal Society of Chemistry 2014

Fig. 6 Effect of temperature and pressure on the yield of DMC by using (a) CuPcS; (b) GO–CuPcS.
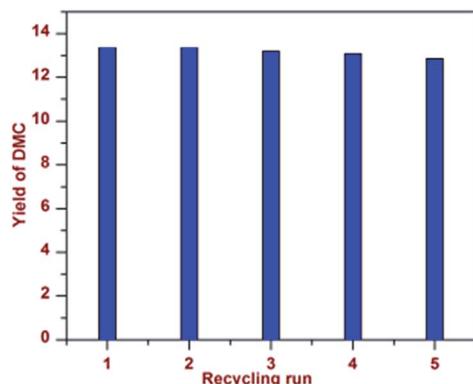

Fig. 7 Recycling of the GO–CuPcS for DMC synthesis.

developed catalyst can be recycled for several runs without a significant loss in catalytic activity.

To check the leaching of the metal during the reaction, the recovered catalyst as obtained after five runs was subjected to ICP-AES analysis. The copper content in the recovered catalyst was found to be (2.38%), which is almost similar to the fresh one (2.4%). These studies suggested that the catalyst had no

Table 2 Comparison of catalytic activity of GO–CuPcS for DMC synthesis with the literature known methods[a]

Entry	Catalyst	DMC yield (%)	Ref.
1	Organotin compound	14	48
2	$Co_{1.5}PW_{12}O_{40}$ heteropolyanion	6.5	33
3	Cu–Ni bimetallic nanocatalyst	4	34
4	CeO_2	9	49
5	K_2CO_3	12	25
6	Mg–Al hydrotalcite–silica lyogels	15.9	50
	Basic ionic liquid (CH/CH_3I)	2.7	51
7	GO–CuPcS	13.3	—

[a] CH = Choline hydrochloride.

leaching during the reaction and was truly heterogeneous in nature.

Last but not least, we have compared the catalytic activity of the developed catalyst with the literature known methods (Table 2). As shown, the developed catalyst provided comparable or a higher yield of DMC with the added benefits of easy accessibility, high stability and efficient recycling of the catalyst.

Conclusions

We have demonstrated the first successful synthesis of DMC directly from methanol and carbon dioxide using a heterogenized homogeneous graphene oxide immobilized copper phthalocyanine tetrasulphonamide catalyst in the presence of a dehydrating agent. Under the optimized reaction conditions *i.e.* 110 °C temperature and 25 bar CO_2 pressure the maximum yield of DMC was obtained as 13.3% in 2.5 h. The developed heterogeneous catalyst exhibited slightly lower activity than its homogeneous analogue; however the facile recovery and efficient recycling of the heterogeneous catalyst make the developed methodology superior and advantageous from industrial viewpoints. The developed catalyst did not exhibit any leaching as determined by ICP-AES analysis. The copper content in the recovered catalyst after five runs was found to be 2.38% which was almost similar to the fresh one (2.4%). To the best of our knowledge this is the first example of a heterogenized homogeneous catalyst for DMC synthesis from methanol and CO_2. We believe that our finding will be useful to the scientific community for real life application of this catalyst for controlling the ever increasing CO_2 concentration in the atmosphere.

Acknowledgements

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