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**ARTICLE TYPE** 

# Solvent-free carbonylation of glycerol with urea using metal loaded MCM-41 catalysts

S. E. Kondawar, A. S. Potdar and C. V. Rode\*

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Reacting glycerol with urea is the most attractive option for the production of glycerol carbonate (GC) as it utilizes two inexpensive chemicals readily available in the chemical cycle, the overall result is the chemical fixation of carbon dioxide. Zn/MCM-41(im) catalyst prepared by wet impregnation method exhibited an excellent activity for the reaction of glycerol and urea with 75% glycerol conversion 10 and 98% selectivity to GC. Such an excellent activity of the catalyst is explained based on the presence of both basic and acid sites on the same catalyst which activates the glycerol and urea molecules, respectively.

## Introduction

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- 15 Today, worldwide commercial production of biodiesel via transesterification route has resulted into the glut of glycerol that is available for its downstream processing to a variety of value added products. 1-3 This provides the best choice for excess glycerol utilization as well as the significant economic incentive 20 for biodiesel process economies. On one hand, selective hydrodeoxygenation of glycerol has been studied extensively to obtain the corresponding hydrogenation and/or dehydration products. <sup>4</sup> On the other hand, glycerol to glycerol carbonate (GC) transformation offers a very challenging and interesting 25 example from scientific and industrial point of view. As glycerol carbonate synthesis involves retention of all the three oxygen atoms of glycerol molecule, it represents a typical case of atom economy. In addition, glycerol carbonate is an environmentally benign polar solvent due to its biodegradability, low toxicity and 30 excellent miscibility with water. <sup>5</sup> More importantly, glycerol carbonate thus obtained from biorenewable resource, can become
- carbonate thus obtained from biorenewable resource, can become a substrate for manufacturing still high value glycidol for the new generation polymers. <sup>6</sup> Current market price of the GC is US \$3-4/kg which is much more significant than that of glycerol (US \$ 35 0.75/kg). The conventional method reported for the synthesis of
- GC is from glycerol and CO or phosene in the presence of solid heterogeneous Cu(I), Cu(II) and soluble PdCl<sub>2</sub>(1,10phenanthroline) catalysts. <sup>7-10</sup> More interestingly, Doro et al. proposed Waker-type Pd/Mn catalyst for direct reaction of 1, 2 40 diols with CO and O<sub>2</sub> to form the corresponding cyclic
- carbonates. <sup>11</sup> However both CO and phosgene being highly toxic, make the entire process environmentally prohibitive. Although direct carboxylation of glycerol using CO<sub>2</sub> has been also attempted for GC, CO<sub>2</sub> activation requires severe conditions
- <sup>45</sup> of temperature and pressure. For example, Aresta et al. reported Sn-based catalyst for the reaction of glycerol and CO<sub>2</sub>, at 180 °C and CO<sub>2</sub> pressure of 5MPa giving only 40% conversion with negligible formation of glycerol carbonate rendering the process

unviable for practical purposes. 12, 13 Third route for glycerol 50 carbonate involves transesterification of glycerol with diethyl/methyl carbonate over hydrotalcite catalysts with almost complete conversion and 76% selectivity to GC. Nevertheless, transesterification proceeds with a very high molar ratio of glycerol: diethyl carbonate of 1:17 which becomes a major 55 bottleneck for commercial production. <sup>14</sup> Again, the carbonates employed during transesterification are generally prepared using phosgene or by energy intensive process involving carboxylation of epoxide thus, posing the serious drawback of handling highly toxic materials. Use of dimethyl carbonate (DMC) could 60 overcome these drawbacks to some extent but requirement of organic solvents, longer reaction time (8h) and tedious downstream processing steps still are the major issues to resolve. Hence, attempts are being focused on using urea due to its ready availability at cheaper cost and safe handling, as well as the 65 ammonia generated in the process can be recycled to produce urea again. This aspect in addition to use of bioglycerol, makes urea based GC synthesis completely atom efficient and sustainable process. GC synthesis via urea route is being studied extensively over the past decade, using mainly noble metal as 70 well as basic oxide type of catalysts. Hammond et al. have reported gold (2.5%Au/ZnO) catalyst for carbonylation of glycerol using urea with 88% conversion but with only 56% selectivity to GC, along with side products like 2,3dihydroxylpropyl carbamate, 4-(hydroxymethyl) oxazolidin-2-75 one, (2-oxo-1,3-dioxolan-4-yl) methyl carbamate. <sup>16</sup> Aresta et al. have proposed a new,  $\gamma$ -zirconium phosphate catalyst that showed good activity with 80% conversion of glycerol with almost 100% selectivity to GC. <sup>17</sup> With a homogeneous ZnCl<sub>2</sub> catalyst almost complete selectivity to GC was reported for 80% conversion of 80 glycerol but it again suffers from catalyst reusability for recycling.<sup>18</sup> Noble metal catalysts like gold and Pd supported on MgO were also proved to be good catalysts for glycerol carbonylation with urea.<sup>19</sup> Other catalyst variations included oxides of Co and La among which La showed higher activity of 85 68% conversion due its strongly basic nature, than cobalt catalyst. <sup>20, 21</sup> Acid-base bifunctional catalysts included hydrotalcite based Zn catalyst that gave the highest activity (82% conversion) and

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selectivity (88%) to GC.<sup>22</sup> However, similar type of Zn-smectite catalyst showed a lower activity (65% conversion) selectivity (75%) to GC. <sup>23</sup> Recently, a homogeneous ZMG [diamminediisocyanatozinc (II)] complex for the GC synthesis <sup>5</sup> via carbonylation of glycerol with urea showed 71% conversion of glycerol and 92% selectivity to GC. <sup>24</sup> Thus, glycerol carbonylation with urea reported so far, has shown a wide variation in terms of both GC selectivity in the range of 50-70% and glycerol conversion. As this reaction needs an appropriate balance of acidic and basic sites of solid catalyst the scope therefore, still exists to develop a new catalyst system to achieve consistent high activity and selectivity, with an excellent recyclability.

Our results presented here, demonstrate glycerol carbonate <sup>15</sup> synthesis from glycerol carbonylation with urea over a mixed metal oxide catalyst supported on MCM-41 possessing an appropriate balance of acid-base sites under solvent- free conditions and with equimolar glycerol to urea ratio of 1:1. To the best of our knowledge, there is no report to date on the <sup>20</sup> application of MCM-41either as a support or as a catalyst for the synthesis of glycerol carbonate. A series of metals (Cu, Ni and Zn) loaded MCM-41catalysts were prepared by two different methods, such as *in-situ* and impregnation methods, which showed dramatic difference particularly on the GC selectivity due <sup>25</sup> to variation in acid-base sites distribution on the surface.

# Experimental

Glycerol (98%pure) purchased from Merck, India was used after pretreating with molecular sieves at 150 °C to remove moisture.
<sup>30</sup> Urea and H<sub>2</sub>SO<sub>4</sub> were purchased from Thomas Baker, India while, cetyltrimethylammonium bromide (CTAB) and tetraethylorthosilicate (TEOS) were purchased from Aldrich Chemicals, Bangalore, India. All chemicals were used as received without further purification.

#### 35 Characterization of the catalysts

X-ray diffraction (XRD) patterns were recorded on a P Analytical PXRD system (Model X-Pert PRO-1712), using Ni filtered Cu K $\alpha$  radiation ( $\lambda = 0.154$  nm) as an X-ray source (current intensity, 30 mA; voltage, 40 kV) and an X-accelerator <sup>40</sup> detector. The samples were scanned in a 2 $\theta$  range of 0-10° and 10–80° with the step size (2 $\theta$ ) of 0.0080° and scanning rate of 10.944°/s. The species present in the catalysts were identified by their characteristic 2 $\theta$  values of the relevant crystalline phases. The software program X-Pert High Score Plus was employed to

45 subtract the contribution of the Cu Kα 2 line prior to data analysis. The BET surface area, of the catalysts was determined by N<sub>2</sub>

The BET surface area, of the catalysts was determined by  $N_2$ adsorption-desorption technique using Micromeritics-2720(Chemisoft TPx) volumetric instrument. NH<sub>3</sub>-TPD and CO<sub>2</sub>-

- <sup>50</sup> TPD experiments were also carried out on a Micromeritics-2720 (Chemisoft TPx) instrument. In order to evaluate the acidity and basicity of the catalysts, ammonia and carbon dioxide TPD measurements were carried out by: (i) pre-treating the samples from room temperature to 200 °C under helium flow rate of 25
- <sup>55</sup> mL min<sup>-1</sup>, (ii) adsorption of ammonia/carbon dioxide at 40 °C and (iii) desorption of ammonia/carbon dioxide with a heating rate of 10 °C min<sup>-1</sup> starting from the adsorption temperature to 700 °C. Transmission electron microscopy (TEM) analysis was performed on a Jeol Model JEM 1200 electron microscope
- 60 operated at an accelerating voltage of 120 kV. A small amount of specimen was prepared by ultrasonically suspending the powder

sample in ethanol, and drops of the suspension were deposited on a carbon coated copper grid dried at room temperature before analysis.

<sup>65</sup> X-Ray photoelectron spectroscopy (XPS) data were collected on a VG Scientific ESCA-3000 spectrometer using a non-monochromatised Mg K $\alpha$  radiation (1253.6 eV) at a pressure of about 1× 10-9 Torr (pass energy of 50 eV, electron takeoff angle 55) and overall resolution ~0.7 eV determined from the full 70 width at half maximum of the 4f <sub>7/2</sub> core level of the gold surface. The error in the binding energy values were within 0.1 eV. The binding energy values were charge-corrected to the C1s signal (285.0 eV).

## 75 Catalyst preparation

#### Synthesis of catalyst by in-situ metal loading

MCM-41 support was prepared by a hydrothermal synthesis method as described earlier. <sup>25</sup> In a typical synthesis method 2.46 g of NaOH was dissolved in 146 mL of deionised water and <sup>80</sup> stirred for 5 min. To this solution, 5.96 g of cetyl trimethylammonium bromide (CTAB) was added, *and the mixture was stirred for 15 min. A 14 g portion of* tetraethyl orthosilicate (TEOS) was added drop wise, and the pH of solution was maintained in a range of 9-10 by adding dilute H<sub>2</sub>SO<sub>4</sub>.The

85 resulting reaction mixture was stirred for 5 h at room temperature. Thereafter, the entire reaction mixture along with mother liquor was transferred to teflon lined autoclave and heated under static condition at 373 K for 48 h. The resulting solid product was filtered and washed several time with water, dried at 90 353 K overnight, and calcined at 813 K for 6 h.

In a high temperature *in-situ* preparation method calculated amount of Ni, Cu and Zn solution were added before the addition of dilute H<sub>2</sub>SO<sub>4</sub> for maintaining the pH. The prepared catalysts were nominated as Cu/MCM-41 (in), Ni/MCM-41 (in) and <sup>95</sup> Zn/MCM-41(in) respectively.

**Synthesis of catalyst by wet impregnation method** Ni, Cu and Zn (5 wt %) on MCM-41 catalysts were prepared by wet impregnation method. In a typical procedure, mixture of 0.4 g of each of Cu(NO<sub>3</sub>)<sub>2</sub>, NiCl<sub>2</sub>.6H<sub>2</sub>O and Zn(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O dissolved

<sup>100</sup> in 10 mL of water was stirred for 5 min, followed by the slow addition of MCM-41support to the solution. The solution was kept for stirring for 6 h at room temperature. The solvent was evaporated on a rotavap and then the catalysts were calcined at 813K for 3h. The prepared catalysts were nominated as

105 Cu/MCM-41 (im), Ni/MCM-41 (im) and Zn/MCM-41(im), respectively.

#### Synthesis of ZnO by chemical precipitation method

According to this method, two separate solutions zinc sulfate (1.5 mol/L) and sodium bicarbonate (2.5 mol/L) were <sup>110</sup> simultaneously mixed by drop wise addition with continuous stirring at room temperature. The precipitate formed was filtered and washed with deionised water and ethanol. Then it was dried at 50 °C for 24 h followed by calcination at 500 °C for 1 h. The

prepared catalyst was nominated as ZnO (PPT).

#### **Reaction procedure**

The activity evaluation experiments were performed in a glass batch reactor equipped with a reflux condenser. In a typical reaction, respective catalyst (0.23g), glycerol (50 mmol), and urea <sup>120</sup> (50 mmol) were charged into the reactor. The reaction mixture was heated in a silicon oil bath at 140 °C in absence solvent under nitrogen flow. After completion of the reaction, 10 mL of MeOH was added in the reaction crude followed by filtration to remove the catalyst. Repeated washing with MeOH was given to Published on 23 January 2015. Downloaded by University of Texas Libraries on 26/01/2015 00:20:01

the solid catalyst, in order to dissolve any adhered impurities as the catalyst surface. Liquid samples were withdrawn from the reactor and analyzed by gas chromatography to monitor the progress of the reaction. The gas chromatograph (Shimatzu 2025) 5 was equipped with HPFFAP column (30 m length × 0.53mm ID ×1µm film thickness) and a flame ionization detector.

## **Results and Discussion**

The catalytic carbonylation of glycerol with urea to GC needs the balanced strength of both acidic as well as basic sites in a solid <sup>10</sup> catalyst. In order to develop such a catalyst, we chose high surface area (1050 m<sup>2</sup>/g) MCM-41 having acidic sites, as a matrix for dispersion of Cu, Ni and Zn oxides possessing basic characteristics due to  $M^{2+}O^{2-}$  ion pairs. The extent of their basicity would depend on the individual co-ordination numbers of <sup>15</sup> Cu, Ni and Zn.

Table 1 Crystallite size and surface area of prepared catalysts.						
Sr. No.	Catalysts	Crystallite size by XRD (nm)	BET Surface Area (m <sup>2</sup> /g)			
1	Cu/MCM-41(in)	43	788			
2	Cu/MCM-41(im)	45	798			
3	Ni/MCM-41(in)	51	968			
4	Ni/MCM-41(im)	44	736			
5	Zn/MCM-41(in)	-	753			
6	Zn/MCM-41(im)	-	692			
7	MCM-41cal	-	1050			
	550°C					

The surface areas of the parent MCM-41 along with the <sup>20</sup> catalysts prepared by *in-situ* and impregnation method are presented in Table 1. Cu, Ni and Zn loaded MCM-41 catalysts irrespective of their method of preparation, showed substantially lower surface area than that of the parent MCM-41, confirming the loading of the respective metal into the matrix. <sup>26</sup> The surface <sup>25</sup> area of Ni impregnated on the MCM-41, was lower than that of the Ni/MCM-41 prepared by the *in-situ* protocol. This could be explained as the impregnation protocol would allow the surface of MCM-41 also covered by NiO while, *in-situ* preparation preferably involves NiO occupying pores of the matrix. Whereas <sup>30</sup> in case of CuO loaded MCM-41, both impregnated and *in-situ* 

- catalysts showed 798 m<sup>2</sup>/g and 788 m<sup>2</sup>/g surface area, respectively. The specific surface area of the MCM-41 samples was found to decrease on loading the ZnO which indicates the insertion of ZnO inside the mesopores.
- <sup>35</sup> XRD patterns of various (Cu, Ni and Zn)/MCM-41 are shown in Fig. 1. All the catalysts, showed a strong reflection at  $2\theta$ value of 2.3° due to (1 0 0) plane and two weak peaks at  $2\theta = 4.1^{\circ}$ and 4.9° due to (1 1 0) and (2 0 0) planes, respectively which is consistent with the characteristic diffraction patterns of
- <sup>40</sup> mesoporous MCM-41 confirming the retention of typical hexagonal structure of MCM-41 in all the samples. The intensity of the diffraction peak (1 0 0) of the Cu/MCM-41(im) was strong as compared with that of all the other samples, suggesting that the mesoporous ordering of Cu/MCM-41(im) was higher than that of <sup>45</sup> the other samples.



Fig.1.XRD patterns of the (a) MCM-41 cal 550°C, (b) Cu/MCM-41 (in), (c) Cu/MCM-41 (im), (d) Ni/MCM-41(im), (e) Ni/MCM-<sup>50</sup> 41(in), (f) Zn/MCM-41(in).



Fig.2 (A) Wide angle XRD patterns of the (a) MCM-41 cal 550°C, (b) Cu/MCM-41 (in), (c) Cu/MCM-41 (im),(d) Ni/MCM-41(in), (e) Ni/MCM-41(in), (f) Zn/MCM-41(in), (g) Zn/MCM-55 41(im)

Wide angle XRD pattern of various M/MCM-41 catalysts are shown in Fig.2 A. In all the samples, a broad peak at  $2\theta = 23.3^{\circ}$ (4 1 1) was assigned to SiO<sub>2</sub> (orthorhombic) [JCPDF File No. 82-1395]. In case of Cu/MCM-41 sample, peaks at  $2\theta = 35.2^{\circ}$  (1 1 60 1), 38.6°(1 1 1) and 48.7° (2 0 2) were assigned to CuO phase [JCPDF File No.80-1917] but this was of weak intensity. In Ni/MCM-41(im) sample, three peaks at  $2\theta = 37.2^{\circ}$  (1 1 1), 43.2° (2 0 0) and 75.4°(3 1 1) were assigned to NiO phase [JCPDF FILE No.86-0681]. However, these peaks were not observed in 65 case of Ni/MCM-41 sample prepared by in-situ method. The reason might be uniform distribution of NiO within the sheets of MCM-41matrix and XRD being surface technique, peaks corresponding to NiO phase could not be visible. In case of both impregnated and in-situ prepared samples of Zn-MCM-41, no 70 any reflections corresponding to ZnO phases were observed which clearly indicated that ZnO nanoparticles were uniformly distributed inside the silica framework which is in accordance with the earlier reports on similar systems. <sup>27</sup> The formation of CuO, NiO and ZnO basic phases in the respective catalysts were responsible for their basicity required in glycerol carbonylation <sup>5</sup> with urea. On the other hand, wide angle XRD pattern of bare ZnO prepared by precipitation method in Fig 2 B showed strong peaks at  $2\theta = 31.7^{\circ}$  (1 0 0),  $34.4^{\circ}$  (0 0 2),  $36.2^{\circ}$  (1 0 1),  $47.6^{\circ}$  (1 0 2),  $56.7^{\circ}$  (1 1 0),  $66.4^{\circ}$  (2 0 0) and  $72.6^{\circ}$  (0 0 4) which were assigned to ZnO phases [JCPDF No.800075].



Fig 2 (B) Wide angle XRD pattern of Bare ZnO cal 500 °C

The acidity of the catalyst is also necessary in glycerol carbonylation reaction for the activation of carbonyl group of urea molecule to facilitate its interaction with glycerol.<sup>22</sup> Hence, 15 the strength and nature of acid sites of our catalysts were determined by NH<sub>3</sub>-TPD and the results are shown in Table 2. Although NH<sub>3</sub>- TPD gave the total acid strength without distinguishing Lewis and Brønsted acidity, the distribution of acid sites was observed in low (50-200°C), medium (200-400°C) 20 and high (400-700°C) temperature regions. MCM-41 support without loading of any metal, showed the lowest total concentration of acidic sites in terms of 0.01628 mmole g<sup>-1</sup>NH<sub>3</sub> desorbed (Fig 3). All the catalysts prepared by wet impregnation method invariably showed higher acid strength than those 25 prepared by in-situ hydrothermal method. Cu-MCM-41 catalyst prepared by *in-situ* protocol showed 0.02281 mmole g<sup>-1</sup> total acidity which was lower as compared to the impregnated catalyst (0.02883 mmole/gm NH<sub>3</sub>) whereas Ni-MCM-41 catalyst showed total acidity in the lower temperature region (50-200 °C) with <sup>30</sup> 0.02432 mmole g<sup>-1</sup> of NH<sub>3</sub> desorbed. Both impregnated and *in*situ prepared Zn-MCM-41 catalyst samples showed total acid strength of 0.0285 mmole g<sup>-1</sup> and 0.0205 mmole g<sup>-1</sup>, respectively,

with the highest concentration in the range of 100-200 °C relevant

(g) (f) (e) (d) (c) (b) (a) 100 200 300 400 500 600 700

**Temperature(°C) Fig.3 (A)** NH<sub>3</sub> –TPD plots of various catalysts.







to the reaction temperature. Where as in

35

Sr. No.	Catalysts	Total NH <sub>3</sub> desorbed (mmole g <sup>-1</sup> )	Temperature range -wise desorption of NH <sub>3</sub> (mmole g <sup>-1</sup> )			
			40-200°C	200-400°C	400-800°C	
1 2	MCM-41 cal 500°C Cu/MCM-41(in)	0.01628 0.02281	0.01174 0.00915	0.0083	0.00454 0.00536	
3	Cu/MCM-41(im)	0.02883	0.02608	0.00275	-	
4	Ni/MCM-41(in)	0.02432	0.02432	-	-	
5	Ni/MCM-41(im)	0.02724	0.02724	-	-	
6	Zn/MCM-41(in)	0.02851	0.01045	0.00666	0.0114	
7	Zn/MCM-41(im)	0.02054	0.01572	-	0.00473	
8	Bare ZnO cal 500°C	0.04778	0.01787	0.017	0.01291	

case of bare ZnO prepared by precipitation method showed the highest total acidity of 0.0477 mmole g<sup>-1</sup> of NH<sub>3</sub> desorbed.



Fig.4 (B) CO<sub>2</sub>- TPD of Bare ZnO cal 500 °C.

- <sup>5</sup> glycerol carbonylation with urea is also mediated by basic sites for activation of glycerol molecule which then becomes prone to attack the carbonyl carbon of urea molecule as illustrated in Scheme 2b. Hence, the basic strength of the catalyst was determined by CO<sub>2</sub>-TPD and the results are presented in Table 3.
- <sup>10</sup> A small peak below 100 °C was observed in all the samples due to the physically adsorbed CO<sub>2</sub>. Among all the catalysts, the highest amount of CO<sub>2</sub> desorbed, 5.298 mmole g<sup>-1</sup> was observed in case of Cu/MCM-41 (im) sample with a peak located at 357 °C. While in case of Ni/MCM-41(im) catalyst, a broad peak at
- <sup>15</sup> 350 °C was observed with 3.218 mmole g<sup>-1</sup> of CO<sub>2</sub> desorption. Total amount of desorbed CO<sub>2</sub> in case of Zn/MCM-41(in) and Zn/MCM-41(im) was 0.385 mmole g<sup>-1</sup> and 1.617 mmole g<sup>-1</sup> at 189 °C and 334 °C, respectively, which is quiet lower as compared to all other catalysts. The bare ZnO showed basicity of <sup>20</sup> 1.793 mmole g<sup>-1</sup> in terms of CO<sub>2</sub> desorbed with a sharp peak at 286 °C.

A more detailed structural characterization and metal particle size of freshly prepared catalysts were studied by HR-TEM. The honeycomb feature, typical of MCM-41 is clearly seen 25 for all the samples (Fig 5(A). a - d), which suggests that hexagonal pore channels were retained even after the addition of various metal components. HR-TEM image of Zn/MCM-41(in) sample taken with beam direction perpendicular to the pores indicates well aligned hexagonal pores. One cannot observe the <sup>30</sup> particles of ZnO in the channels of MCM-41 by TEM method, probably due to the fact that the weak contrast exists between the silica framework of MCM-41 and ZnO particles.<sup>28</sup> In line with this observation, absence of ZnO phases in XRD clearly indicates

- that ZnO was well dispersed in the framework of MCM-41. <sup>35</sup> Nonetheless, strong zinc signals could be clearly observed in the EDX spectrum of Zn/MCM-41 as depicted in Fig.5 (B), confirming the presence of ZnO in MCM-41. On the other hand, Fig. 5(d) shows the HR-TEM of Ni/MCM-41(im) sample with well dispersed NiO particles having cube shape morphology and
- <sup>40</sup> d-spacing of 0.22 nm, matching with the value obtained by XRD. This sample possessed a larger particle size of 44 nm and a wider size distribution (40-60 nm) than both Ni/MCM-41 and Cu/MCM-41samples prepared by *in-situ* method. These features were due to an excellent dispersion of the metal oxide particles
- <sup>45</sup> within MCM-41 framework for the samples prepared by *in-situ* method. The peaks for Cu, Ni and Zn were clearly detected in EDX, confirming the presence of Cu, Ni and Zn atoms in the respective catalysts.
- The presence of ZnO was confirmed by X-ray 50 photoelectron spectroscopy. The total scan of Zn/MCM-41 (im) catalyst suggest that only Si, Zn, O and C elements were present and no other impurity except carbon was present in the sample. All the binding energies were corrected with reference to the carbon 1s binding energy position at 284.4 eV. The detail scans 55 of O1S, Zn  $2P_{1/2}$  and Zn $2P_{3/2}$  are illustrated in Fig 6. Deconvolution of O1s spectra resulted into three peaks with binding energies of 532.9, 531.5 and 530.6 eV (Fig.6 (b)). The peaks at 531.5 eV and 530.6 eV were due to O1s for ZnO in accordance with the values reported by Lihitkar et al. 60 Additional peak observed at BE = 532.9 eV was due to oxygen of adsorbed -OH over the surface of the catalyst. The binding energies for Zn2p3/2 and 2p1/2 were observed at 1022.2eV and 1045.3eV, respectively, with spin orbital splitting of ~23.1eVwhich was quite different from those for metallic Zn
- 65 (24.6 eV) and bare ZnO (~ 22.2eV).<sup>30</sup> This clearly suggests that in our Zn/MCM-41 (im) catalyst, ZnO was not pure instead, it was bound to silica surface of MCM-41 support.

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<b>Table 3.</b> $CO_2$ -TPD results of prepared catalysts.						
Sr. No.	Catalysts	Total CO <sub>2</sub> desorbed	Temperature range -wise desorption of $CO_2$ (mmole g <sup>-1</sup> )			
		(mmole g <sup>-1</sup> )	40-200 °C	200-400 °C	400-800 °C	
1	Cu/MCM-41(in)	4.64432	0.32698	0.866080	3.45126	
2	Cu/MCM-41(im)	5.29841	1.37886	1.28595	2.6336	
3	Ni/MCM-41(in)	4.49588	0.2874	-	4.20848	
4	Ni/MCM-41(im)	3.21815	0.3791	1.2494	1.58965	
5	Zn/MCM-41(in)	1.38550	0.03540	1.3468	0.0033	
6	Zn/MCM-41(im)	1.61776	0.33142	0.49061	0.79573	
7	Bare ZnO cal 500°C	1.79352	1.0684	0.72512	-	



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**Fig.5** (A)TEM images at different resolution of various catalysts (a) Cu/MCM-41(in), (b) Cu/MCM-41(in), (c) Ni/MCM-41(in), (d) Ni/MCM-41(in), (e) Zn/MCM-41(in), (f) Zn/MCM-41(in).







<sup>15</sup> Fig. 6 XPS spectra of (a) Zn2p of Zn/MCM-41(im), (b) O1s of Zn/MCM-41(im).

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#### Activity measurement

- <sup>5</sup> A comparison of activity of various catalysts, expressed in terms of conversion, TOF and selectivity is presented in Table 4. Both Cu catalysts prepared by impregnation and *in-situ* hydrothermal methods, showed almost same performance (65-66% conversion) but GC selectivity was significantly higher (83%) for the <sup>10</sup> impregnated Cu catalyst. In both the cases, glycidol formation up to 5% was observed however, the major difference was the formation of (2-oxo-1, 3-dioxolan-4-yl) methyl carbamate to the extent of 27%, sacrificing the GC selectivity, in case of *in-situ* prepared sample. Although glycidol formation is via GC,
- <sup>15</sup> however being a 3-membered ring its formation and stability is more difficult energetically than that of a 5-membered GC.<sup>31</sup> Due to this, probably in the reported literature so far, glycidol has not been observed, while our Cu-catalyst system showed appreciable amount of glycidol. Between the two Ni catalysts, the
- <sup>20</sup> impregnated Ni/MCM-41, showed the highest conversion of 68% as well as GC selectivity of 98% in 3h time. In both the Ni catalysts glycidol formation was minimum, in a range of 0.8-1.2%. Where as, Zn catalyst showed highest conversion of 65 and 69% respectively, with almost 98% selectivity towards the
- <sup>25</sup> glycerol carbonate without further dehydration to form glycidol. Due to excellent performance shown by Zn catalyst, the reaction was studied for extended hours and both *in-situ* and impregnated Zn catalysts gave 73 and 75% conversion within 5 hr. The promising performance of this Zn catalyst could be due to the <sup>30</sup> appropriate balance of both acidic and basic sites.<sup>32</sup> The presence
- <sup>30</sup> appropriate balance of both actific and basic sites.<sup>44</sup> The presence of ZnO as evidenced in XPS (Fig.6) was responsible for the basic sites required for the activation of glycerol molecule by abstracting its acidic proton (Scheme 2a). The RO<sup>-</sup> thus formed subsequently attacks the carbonyl of urea (carbo-cation)
   <sup>35</sup> generated by the Brǿnsted acidic sites formed on MCM-41.<sup>22</sup> The extent of basicity desirable for optimal performance of Zn/MCM-41(im) catalyst is highlighted by the

Table 4 Activity results of prepared catalysts for glycerol carbonylation.

observation of lower activity of Cu and Ni containing catalysts as CuO and NiO was more basic than ZnO shown by CO<sub>2</sub>-TPD <sup>40</sup> results discussed previously (Fig. 4).<sup>33</sup> In addition, the amphoteric ZnO possesses appropriate balance of acid- base sites is also responsible for the highest selectivity to GC whereas, Cu and Ni catalyst due to their higher basicity catalyze the further dehydration step to form glycidol. The critical role of amphoteric <sup>45</sup> ZnO sites could be also understood by few control experiments. The activity and selectivity of only MCM-41 was lower 51% and 92% respectively, than that of Zn/MCM-41(im) as MCM-41 possessed only acidic sites. Similarly, the performance of basic ZnO alone prepared by precipitation also showed lower activity, <sup>50</sup> however selectivity to GC was comparable to that of Zn/MCM-41(im) catalyst.

In order to investigate the mechanistic pathway, instead of urea, carbonylimidazole was reacted with glycerol to form glycerol carbonate. As shown in Scheme 2, intermediate is <sup>55</sup> formed with the elimination of one mole of imidazole, which further undergoes attack of a secondary –OH group on to the carbonyl carbon to form GC with elimination of a second molecule of imidazole.

Catalyst stability was proved by its recycle experiment in 60 which Zn/MCM-41 catalyst was separated by filtration after its use, washed with methanol followed by calcination at 813 K for 5h. Fig. 7 clearly reveals that after the third recycle also, 73% conversion of glycerol with 98% selectivity to GC was achieved. Catalyst stability was also confirmed by performing the standard 65 leaching test, in which the catalyst was removed from the reaction by filtration after 60 min, and the reaction was continued with the filtrate devoid of catalyst. The conversion was 58% at the end of 60 min. and no any appreciable increase in the conversion (57%) was observed even after 3 h, (Fig. 8) which 70 confirmed that there is no leaching of the catalyst ruling out possibility of any homogeneous complex formation with zinc. Quantitative elemental analysis of the reaction crude after separation of the catalyst by filtration, was done by inductively coupled plasma optical emission spectroscopy (ICP-OES) on a

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Sr. No.	Catalysts	Conversion (%)	Glycerol carbonate	Glycidol	Other	- (/h)	% Yield GC	Acid/Base Ratio
1	Cu/MCM-41(in) <sup>a</sup>	66	68	4.6	27.4	311	45	0.0049
2	Cu/MCM-41(im) <sup>a</sup>	65	83	4.1	12.4	306	54	0.005
3	Ni/MCM-41(in) <sup>a</sup>	60	89	1.2	9.8	340	53	0.0054
4	Ni/MCM-41(im) <sup>a</sup>	68	98	0.8	1.2	385	67	0.0084
5	MCM-41(cal 550°C) <sup>a</sup>	51	92	1.7	6.3	2.28	47	-
6	Zn/MCM-41(in) <sup>a</sup>	65	98	-	2	368	64	0.0205
7	Zn/MCM-41(im) <sup>a</sup>	69	98	-	2	391	68	0.0126
8	Zn/MCM-41(in) <sup>b</sup>	73	98	-	2	248	71	-
9	Zn/MCM-41(im) <sup>b</sup>	75	98	-	2	255	73	-
10	ZnO cal 500°C	68	99	-	1	231	67	0.0266

**Reaction conditions:** glycerol (4.6g), urea (3.06g), catalyst 0.23g, temperature 145 °C, N<sub>2</sub> flow to remove NH<sub>3</sub> formed during reaction, reaction time (a) 3h, (b) 5h.

Spectro Arcos FHS-12 instrument equipped with winlab software and which did not show any presence of Zn. This confirmed that no catalyst dissolution occurred in the glycerol phase under the reaction conditions. This confirmed that no catalyst dissolution 5 occurs in the glycerol phase under the reaction conditions.

#### Influence of the reaction time

The graphical representation of time online analysis is shown in Fig.9. After 3 h, 68% conversion of glycerol was observed with <sup>10</sup> almost 98% selectivity towards the glycerol carbonate. Extended reaction time up to 7 h gave much higher conversion of 92% with 99% selectivity to GC. Further increase in reaction time up to 12 h reaction time led to a marginal increase in conversion to ~ 94%. This is because of the fact that the reaction is carried out in

<sup>15</sup> pure glycerol which is the limiting reactant hence, as the reaction progresses, the decreasing concentration of glycerol affects the kinetics of the reaction.



**Fig.7** Recycle experiments for the synthesis of glycerol <sup>20</sup> carbonate. Reaction conditions: Glycerol (4.6g), Urea (3.06g), catalyst Zn/MCM-41 (im) 0.23g, Atmospheric pressure with nitrogen as passing gas, 140°C, time 5h.



Fig. 8 Leaching test.



**Fig. 9** Time online analysis for in carbonylation of glycerol over Zn/MCM-41 (im) catalyst. Reaction conditions: glycerol (4.6g), urea (3.06g), catalyst 0.23g, temperature 145  $^{\circ}$ C, N<sub>2</sub> flow to remove NH<sub>3</sub> formed during reaction, reaction time 12 h.



**Scheme 1** Synthesis of glycerol carbonate by carbonylation of glycerol with urea.



Scheme 2 (a) Proposed of mechanism of acidic site of MCM-41 and basic site of metal-oxide catalyzed carbonylation of glycerol.



(b) Proposed mechanism of Lewis acid-base sites of metal-oxide 40 catalysed carbonylation of glycerol.

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**Scheme 3** Carbonylation of glycerol using carbonylimidazole to form glycerol carbonate.

## Conclusions

- A series of transition metal loaded (Cu, Ni and Zn) mesoporous MCM-41 catalyst were prepared by two different protocol *viz insitu* and wet impregnation method to investigate the effect of preparation method and aicd-base sites on to the activity and selectivity of glycerol carbonylation reaction.. Among these catalysts, Zn/MCM-41 (im) prepared by wet impregnation method proved to be the most active catalyst for glycerol carbonate synthesis with 75% conversion of glycerol and 98% 15 selectivity to GC. The higher activity of the catalyst can be
- explain with high surface area of about 692 m<sup>2</sup>/g and well dispersion of ZnO phase over the mesoporous framework of MCM-41 support. Well balanced acid (0.020 mmole/g) and basic site (1.61 mmole/g) present in the catalyst responsible for the
- <sup>20</sup> good catalytic performance. HRTEM images clearly showed presence of amphoteric ZnO phase, which is important for the activation of glycerol molecule. The catalyst was thoroughly characterized by XRD, BET, NH<sub>3</sub>- TPD, TEM and XPS.
- Easy separation, excellent activity and recyclability of the <sup>25</sup> catalyst make it candidate for the application in industrial synthesis of GC.

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## Abbreviations

GC Glycerol carbonate

MeOH Methanol

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# Solvent-free carbonylation of glycerol with urea using metal loaded MCM-41 catalysts

Graphical abstract

