



Journal of Nanoscience and Nanotechnology Vol. 14, 4551–4556, 2014 www.aspbs.com/jnn

# Catalytic Performance of Functionalized IRMOF-3 for the Synthesis of Glycerol Carbonate from Glycerol and Urea

Sun-Do Lee, Gyung-Ah Park, Dong-Woo Kim, and Dae-Won Park\*

School of Chemical and Biomolecular Engineering, Pusan National University, Busan 609-735, Republic of Korea

A functionalized isoreticular metal organic framework material, F-IRMOF-3, having a quaternary ammonium group was prepared by fast precipitation and solvothermal method. The synthesized MOFs exhibited good catalytic performance in the synthesis of glycerol carbonate (GC) from glycerol and urea. F-IRMOF-3 having a larger alkyl chain structure and a more nucleophilic counter anion than the synthesized congeners, exhibited better reactivity in the synthesis of GC. The introduction of a ZnO defect into the F-IRMOF-3 structure by fast precipitation was more advantageous for the glycerolysis of urea than the conventional solvothermal method because of the incorporation of acid-base bifunctional active sites by the former method. The effects of reaction parameters such as temperature, reaction time, catalyst loading, and degree of vacuum on the reactivity were also investigated. The F-IRMOF-3 catalyst can be easily recovered and reused without considerable loss of its initial activity.

Keywords: Metal Organic Framework, F-IRMOF-3, Fast Precipitation, Glycerol Carbonate, Glycerol, Urea. 3180.147 On: Wed, 13 Aug 2014 12:31:30 Copyright: American Scientific Publishers

## **1. INTRODUCTION**

Utilization of biomass and biodiesels is now well established as a green alternative to fossil fuels and for reducing carbon dioxide emission.<sup>1–3</sup> An increase in the production of biodiesel has resulted in a surplus of glycerol, owing to a sharp decrease in its price. The utilization of glycerol as a platform chemical represents an opportunity to obtain value-added products from a highly functionalized and cheap raw material, and in recent years, much research has been dedicated to finding new chemical pathways for transforming glycerol to value-added products.<sup>4–6</sup> In particular, selective oxidation,<sup>7,8</sup> reduction to 1,3-propanediol,<sup>9</sup> and etherification to enable the use of glycerol as an additive for fuels have been the subject of extensive research.

Glycerol carbonate (GC), a derivative of glycerol, is a relatively new and interesting material.<sup>10</sup> GC is characterized by low toxicity, good biodegradability, and a high boiling point; consequently, it has been investigated as a novel component of gas-separation membranes, polyurethane foams,<sup>11</sup> surfactants,<sup>12</sup> coatings, paints, and detergents, and as a nonvolatile reactive solvent for several

types of materials. Thus, GC may serve as an inexpensive source of new polymeric materials for the production of polycarbonates and polyurethanes.<sup>13</sup>

GC is conventionally synthesized via typical protocols used for other low-molecular-weight organic carbonates. Transesterification of glycerol can be readily performed using dimethyl carbonate,<sup>14</sup> ethylene carbonate,<sup>15</sup> or propylene carbonate.<sup>16</sup> The carbonates utilized during the transesterification process are typically generated via phosgene utilization or energy-intensive routes employing epoxides. However, the reaction of glycerol with phosgene is limited by the dangerous and environment-unfriendly nature of phosgene as a reactant. Although there are some reports addressing the direct carbonylation of glycerol with carbon dioxide using tin complexes, the applicability of such processes suffers from serious limitations such as unfavorable thermodynamic equilibrium and low yields.<sup>17</sup>

Glycerolysis of urea is an alternative technique that has been recently described in the literature.<sup>18–20</sup> A main advantage of this method is that the reactant, urea, is readily available and inexpensive. In addition, the generated ammonia can be easily converted to urea in the presence of carbon dioxide.

Much effort has been devoted to search for effective catalysts for the glycerolysis of urea. Homogeneous catalysis

J. Nanosci, Nanotechnol, 2014, Vol. 14, No. 6

\*Author to whom correspondence should be addressed.

employing inorganic salts such as ZnSO<sub>4</sub>,<sup>21</sup> MgSO<sub>4</sub>,<sup>22</sup> and ZnO<sup>23</sup> has been described, and recently, certain heterogeneous systems based on these oxides have been reported.<sup>10, 24</sup> To the best of our knowledge, the use of metal-organic framework (MOF) materials as catalysts for the glycerolysis of urea has not yet been published.

In recent years, MOFs, which are formed by copolymerization of organic molecules with metal ions or metal ion clusters, have received much attention<sup>25-28</sup> owing to their zeolite-like properties such as high internal surface area and microporosity, well-ordered porous structures, and high absorption capacity. Various applications of porous MOFs, including gas storage,<sup>29</sup> separation,<sup>30</sup> magnetism,<sup>31</sup> and catalysis,<sup>32, 33</sup> have been explored. Among these applications, the use of MOFs as catalysts is particularly attractive. Zinc aminoterephthalate metal organic framework, IRMOF-3, has recently been found to be an active heterogeneous catalyst for the Knoevenagel condensation reaction between benzaldehyde and various activated methylene compounds.<sup>32</sup> An adequate combination of a Lewis acid and a Lewis base is reportedly favorable for the synthesis of cyclic carbonates from urea and diols.<sup>18</sup>

In our previous studies, immobilized ionic liquid catalysts were utilized for the synthesis of GC from glycerol and ethylene carbonate<sup>34</sup> or urea.<sup>35</sup> Herein, a functionalized MOF (F-IRMOF-3) possessing an electrophilic center (Zn<sub>4</sub>O) as well as a nucleophilic center (X<sup>-</sup>), was developed as a novel one-component heterogeneous catalyst for the solvent-free synthesis of GC. The developed catalyst exhibits much higher activity than other heterogeneous catalysts reported in prior publications.

### 2. MATERIALS AND METHODS

IRMOF-3 was prepared from triethylamine via fast precipitation by following a synthesis procedure described by Huang et al.<sup>36</sup> In this method, 6.4 g (64 mmol) of triethylamine was gradually added to a N,Ndimethylformamide (DMF) solution (160 mL) containing 4.8 g (16 mmol) of Zn(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O and 1.32 g (8 mmol) of 2-aminoterephthalic acid with stirring at room temperature for 1.5 h. Next, the solid was filtered and thoroughly washed with CH<sub>2</sub>Cl<sub>2</sub>.

A sample of IRMOF-3 (2.4 g) was activated by guest exchange with  $CH_2Cl_2$  (80 mL) for 20 h and was then filtered and dried under vacuum at 130 °C. Next, the activated sample was suspended in dry DMF (80 mL) and treated with three equivalents of methyl iodide (CH<sub>3</sub>I) at room temperature for 4 d. The resulting powder was collected by filtration, which was then thoroughly washed with  $CH_2Cl_2$  and dried under vacuum at 130 °C. This sample was denoted as F-IRMOF-3(MeI). Various alkyl halides such as BuCl, BuBr, EtI, and BuI were also used for the preparation of other F-IRMOF-3 samples of different alkyl chain lengths with various halide anions.



Scheme 1. Activation of urea and glycerol by  $Zn_4O$  and quaternized benzene dicarboxylic acid linker of F-IRMOF-3.

IRMOF-1 was also prepared by the same method as used for IRMOF-3 with the exception that benzene dicarboxylic acid (BDC) was used in place of 2-aminoterephthalic acid. Alternatively, IRMOF-1 [Solvo] with high crystallinity was prepared by the conventional solvothermal crystallization method. For the synthesis of IRMOF-1 [Solvo], zinc nitrate hexahydrate (1.5 mmol) and BDC (0.5 mmol) were dissolved in DMF (50 mL) and placed inside an autoclave. The mixture was heated at 373 K for 24 h; the resulting solid was recovered by filtration, washed twice with DMF, and finally immersed twice in  $CH_2Cl_2$  for 12 h to displace DMF from the pores. Tetrabutylammonium iodide (TBAB) was supplied from Aldrich and used without further treatment.

X-ray diffraction patterns were collected on an XPERT PRO X-ray diffractometer using a Cu K $\alpha$  radiation source ( $\lambda = 1.54056$  Å), operating at 40 kV and 45 mA. The continuous mode was used for collecting data at a scanning speed of 0.03 °/S. FT-IR spectra were acquired with a Nicolet 560 instrument using KBr pellets. The morphology of F-IRMOF-3 was identified using SEM. The surface area was calculated from nitrogen adsorption measurements acquired using a BET apparatus (Micromeritics ASAP 2020). The amount of N<sup>+</sup> in F-IRMOF-3 was determined by ion chromatography (Dionex, ICS-5000).

The synthesis of GC from the reaction of glycerol with urea, as shown in Scheme 1, was carried out in a 50-mL autoclave reactor equipped with a magnetic stirrer. For a typical reaction, the F-IRMOF-3 catalyst, glycerol (50 mmol), and urea (50 mmol) were charged into the reactor. When the desired temperature was attained, the reaction was initiated by stirring under vacuum or nitrogen. Analysis of the products and reactants was performed using a gas chromatograph (HP 6890N) equipped with an FID and a capillary column (HP-5, 5% phenyl methyl siloxane). Tetraethylene glycol (TEG) was used as an internal standard. The selectivity toward GC production was calculated using glycerol as a limiting reactant.

## 3. RESULTS AND DISCUSSION

#### **3.1.** Characterization of Catalysts

WXRD results for IRMOF-1, IRMOF-1 [Solvo], IRMOF-3, and F-IRMOF-3 are presented in Figure 1.

J. Nanosci. Nanotechnol. 14, 4551-4556, 2014



Figure 1. XRD analyses of (a) IRMOF-1, (b) IRMOF-3, (C) F-IRMOF-3(BuI).

The results demonstrate the crystalline nature of all of the IRMOF samples; the structure of F-IRMOF-3 was well retained even after functionalization of IRMOF-3 with an alkyl halide for 4 days. The initial BET surface area of IRMOF-3 was 248 m<sup>2</sup>/g, which decreased to 53 m<sup>2</sup>/g after functionalization with CH<sub>3</sub>I.

Figure 2 shows the FT-IR spectra of IRMOF-1, IRMOF-1 [Solvo], IRMOF-3, and F-IRMOF-3. Compared to IRMOF-3, three new peaks were observed at 3010, 1480, and 945 cm<sup>-1</sup> in the case of F-IRMOF-3, which indicate that CH<sub>3</sub>I was successfully introduced into the framework of IRMOF-3 resulting in the conversion of  $-NH_2$ to a quaternary ammonium salt species. The peaks near 1480 cm<sup>-1</sup> in the FT-IR spectrum of F-IRMOF-3 were assigned to C—N stretching vibrations.<sup>37</sup> The FT-IR spectra indicate the presence of a quaternary ammonium salt in F-IRMOF-3.

The thermal stability of the IRMOF-1 catalysts prepared by various methods was evaluated via TGA analysis



Figure 2. FT-IR spectra of (a) IRMOF-1 [Solvo], (b) IRMOF-1, (c) IRMOF-3, (d) F-IRMOF-3(BuI).

J. Nanosci. Nanotechnol. 14, 4551-4556, 2014



Figure 3. TGA curves of (a) IRMOF-1 [Solvo], (b) IRMOF-1.

(Fig. 3). The thermograms of IRMOF-1 and IRMOF-1 [Solvo] show two typical weight losses between 25 and 600 °C. The first weight loss to up to 160-180 °C is attributed to the loss of water (free water molecules within the pores as well as those coordinated to the zinc framework) and DMF solvent in the pores. The second weight loss between 350 and 520 °C corresponds to the combustion of the organic moiety of the IRMOF-1 structure.<sup>38</sup> IRMOF-1, which was prepared by fast precipitation, exhibited significantly higher weight loss than IRMOF-1 [Solvo]. Based on the mathematical analysis of the TGA curves, the ZnO defects were quantified to be 4.7 wt.% for IRMOF-1 and 0.8 wt.% for IRMOF-1 [Solvo]. TGA analyses of F-IRMOF-3(BuI) and F-IRMOF-3(BuI) [Solvo] are also shown in Figure 4, and the ZnO defects were estimated to be 19.8 wt.% and 8.1 wt.%, respectively.

Table I shows the quantification of the immobilized quaternary ammonium salt in the various F-IRMOF-3 species evaluated based on ion chromatography. These catalysts contained 1.0-4.3 mg of N<sup>+</sup>/g-cat.



**Figure 4.** TGA curves of (a) F-IRMOF-3(BuI) [Solvo], (b) F-IRMOF-3(BuI).

Catalytic Performance of Functionalized IRMOF-3	for the Synthesis	of Glycerol Carbonate	e from Glycerol and Urea	Lee et al.
	2	5	2	

Table I. Amount C	or in the F-IRM		
Catalyst	F-IRMOF-3 (BuCl)	F-IRMOF-3 (BuBr)	F-IRMOF-3 (BuI)
N <sup>+</sup> concentration (mg N <sup>+</sup> /g cat.)	4.26	1.93	1.04

**3.2. Evaluation of Reactivity of F-IRMOF-3 Catalysts** 

Table II shows the selectivity, yield, and conversion of glycerol to GC using the IRMOF-1 and F-IRMOF-3 catalysts having various alkyl chain linkers and counteranions under a vacuum pressure of 14.7 kPa after 3 h of reaction at 140 °C. A glycerol conversion of 62.9% was achieved using ZnO only. Compared to IRMOF-1 that does not possess a functional group in the BDC linker, all of the F-IRMOF-3 catalysts having a quaternary ammonium group exhibited higher catalytic activity for the glycerolysis of urea. The quaternary ammonium salt is a typical ionic liquid, and 51.2% glycerol conversion was achieved with TBAB itself.

The F-IRMOF-1 catalyst prepared by fast precipitation exhibited higher GC yield than IRMOF-1 [Solvo] prepared by the solvothermal method. The difference in the catalytic activity of the two F-IRMOF-3(BuI) catalysts prepared via different methods can be related to the difference in the concentration of defects in both the catalysts. The amount of excess ZnO residue in the F-IRMOF-3(BuI) catalysts prepared by fast precipitation is consistent with more defects (19.8 wt.%) than those present in the sample prepared by the solvothermal method (8.1 wt.%). Note that the fast precipitation process should lead to less crystalline samples containing more defects. As shown in Table II, the ZnO nanoparticles alone showed a GC yield of 43.5%. The F-IRMOF-3(BuI) catalyst prepared by fast precipitation produced 71.0% glycerol conversion and 67.8% yield of GC, which is also higher than that achieved with F-IRMOF-3(BuI) [Solvo].

 Table II.
 Reactivity of different catalysts for the synthesis of GC from glycerol and urea.

Catalyst	$X_G$ (%)	$S_{GC}$ (%)	$Y_{GC}$ (%)
ZnO	62.9	69.2	43.5
IRMOF-1	64.4	64.8	41.7
$TBABr^{a}$	51.0	60.4	30.8
$\mathrm{TBAI}^{b}$	51.2	64.4	33.0
IRMOF-1 [Solvo] <sup>c</sup>	58.8	64.2	37.7
F-IRMOF-3(MeI)	63.7	78.1	49.7
F-IRMOF-3(EtI)	69.7	84.8	59.1
F-IRMOF-3(Bul)	71.0	95.5	67.8
F-IRMOF-3(BuBr)	66.6	95.3	63.5
F-IRMOF-3(BuCl)	65.8	94.8	62.4
F-IRMOF-3(BuI) [Solvo] <sup>c</sup>	65.2	85.9	56.1

*Notes*: Reaction conditions: Urea = 50 mmol, Glycerol = 50 mmol, Cat. = 0.23 g (5 wt.%), Temp. = 140 °C, Degree of vacuum = 14.7 kPa, Reaction time = 3 h; <sup>a</sup>Tetrabutyl ammonium bromide (1 mol% was used); <sup>b</sup>Tetrabutyl ammonium iodide (0.5 mol% was used); <sup>c</sup>Catalysts were prepared by the solvothermal method. All the other IRMOF catalysts were prepared by the fast precipitation method. Very recently, Xamena et al.<sup>33</sup> also reported similar phenomena with IRMOF-3 samples prepared by various methods in relation to Knoevenagel condensation reactions. They concluded that in the case of IRMOF-3, and more specifically IRMOF-3 prepared by fast precipitation, the presence of Zn–OH and/or ZnO in conjunction with amino groups may contribute to the final observed activity. This contribution may occur through an independent catalytic route and/or a synergistic effect in which the amino groups act as basic sites, while the Zn–OH or ZnO defects function as acid sites.

In the present case of F-IRMOF-3(BuI), a similar synergistic process may also occur, accounting for the good catalytic activity of this catalyst. The acid sites in F-IRMOF-3(BuI) may arise because of a defective origin by the inclusion of ZnO particles during the synthesis.

Changing the alkyl chain linker from methyl in F-IRMOF-3(MeI) to butyl in F-IRMOF-3(BuI) resulted in an increase in the conversion of glycerol, primarily because the electron-donating ability of the butyl group is stronger than that of the methyl group, and hence, the electron density is concentrated around the center of the active site in the butyl group. Increasing the bulkiness of the alkyl chain forces the I<sup>-</sup> ion away from the cation to a greater extent, thereby resulting in less electrostatic interaction between the anion and the cation.<sup>35, 36</sup> These results are in good agreement with previous parallel reports on the effects of the alkyl chain length.<sup>39–42</sup>

<sup>Cl</sup> Comparison of the catalytic activities of the MOFs based on the counter anions revealed that the conversion of glycerol in the presence of F-IRMOF-3 containing I<sup>-</sup> was higher than when Cl<sup>-</sup> and Br<sup>-</sup> were present. The effect of the counteranion on the reactivity is attributed to the nucleophilicity of the anion, where the I<sup>-</sup> counterion has the highest nucleophilicity among the three halide anions.<sup>43, 44</sup>

The effect of reaction time on the synthesis of GC was studied at 140 °C under a reduced pressure of 14.7 kPa. As



Figure 5. Effect of reaction time on the reactivity of F-IRMOF-3(BuI). Reaction conditions: Urea = 50 mmol, Glycerol = 50 mmol, Cat. = 0.23 g (5 wt.%), Temp. = 140 °C, Degree of vacuum = 14.7 kPa.

J. Nanosci. Nanotechnol. 14, 4551-4556, 2014

Lee et al. Catalytic Performance of Functionalized IRMOF-3 for the Synthesis of Glycerol Carbonate from Glycerol and Urea

Table III. Effects of reaction temperature on the synthesis of GC from glycerol and urea

8-) · · · · · · · · · · · · · · · · · · ·			
Temp. (°C)	$X_G (\%)$	$S_{ m GC}~(\%)$	Y <sub>GC</sub> (%)
100	7.2	20.2	1.5
110	10.4	39.3	4.1
120	31.8	47.3	15.1
130	45.8	66.0	30.2
140	71.0	94.5	67.1
150	84.2	79.2	66.7
160	87.0	27.7	24.1

Notes: Reaction conditions: Urea = 50 mmol, Glycerol = 50 mmol, Cat. = 0.23 g (5 wt.%) F-IRMOF-3(BuI). Degree of vacuum = 14.7 kPa. Reaction time = 3 h.

revealed in Figure 5, the conversion of glycerol increased as the reaction progressed. At the early stage of the reaction at 0.5 h, the GC selectivity was <65%, implying that substantial amounts of the reaction intermediate, HPC (2,3-dihydroxypropyl carbamate), remained in the reaction mixture. As the reaction progressed, HPC was further converted to GC and the selectivity toward GC production continuously increased up to 91%. The main by-product (other than HPC) was (2-oxo-1,3-dioxolan-4yl)methyl carbamate (ODMC).

Table III shows the effects of reaction temperature on the synthesis of GC in the presence of F-IRMOF-3(BuI). The conversion of glycerol continuously increased as the temperature increased from 100 to 160 °C. The selectivity toward GC production increased with temperature, reaching a maximum of 94.5% at 140 °C; however, the selectivity decreased when the temperature became >150 °C, plausibly because of the transformation of GC to ODMC or the polymerization of GC and/or glycerol. The formation of polymers from GC or glycerol is reported as one of the main factors responsible for the low selectivity toward GC.15

Table IV shows the effects of the degree of vacuum on the reactivity of the F-IRMOF-3 catalyst. The conversion of glycerol increased as the degree of vacuum increased from 101.3 to 11.3 kPa. Application of a high degree of vacuum could enhance the removal of the generated ammonia gas, thereby accelerating the forward reaction of glycerol and urea. The selectivity to GC continuously increased as the degree of vacuum applied increased from

Table IV. Effects of degree of vacuum on the synthesis of GC from glycerol and urea.

Pressure (kPa) <sup>a</sup>	$X_G$ (%)	S <sub>GC</sub> (%)	Y <sub>GC</sub> (%)
11.3	73.2	94.6	69.2
14.7	71.0	94.5	67.1
28.0	68.7	86.1	59.2
54.6	43.2	61.2	26.4
101.3	35.5	58.4	20.7
N <sub>2</sub> purge <sup>b</sup>	81.3	87.8	71.4

Notes: Reaction conditions: Urea = 50 mmol, Glycerol = 50 mmol, Cat. = 0.23 g (5 wt.%) F-IRMOF-3(BuI), Temp. = 140 °C, Reaction time = 3 h; <sup>a</sup>Absolute pressure; <sup>b</sup> N<sub>2</sub> purge with a flow rate of 150 mL/min.

J. Nanosci. Nanotechnol. 14, 4551–4556, 2014

Table V. Recycle test of F-IRMOF-3(Bul)

Run	$X_G (\%)$	S <sub>GC</sub> (%)	Y <sub>GC</sub> (%)
Fresh	71.0	94.5	67.1
lst	70.0	91.0	63.7
2nd	68.2	87.6	59.7
3rd	66.1	83.7	55.3

Notes: Reaction conditions: Urea = 50 mmol, Glycerol = 50 mmol Cat. = 0.23 g (5 wt.%), Temp. = 140 °C, Degree of vacuum = 14.7 kPa, Reaction time = 3 h.

101.3 to 11.3 kPa, given that a high degree of vacuum may inhibit the reverse reaction whereby GC converts to glycerol and the polymerization of GC and/or glycerol occurs. Interestingly, removal of ammonia by nitrogen purging at a flow rate of 150 mL/min was as effective as operation under a high degree of vacuum.

Previous studies<sup>45</sup> in conjunction with the above findings suggest that the catalysts should possess both Lewis acidity and basicity to be active for the reaction between glycerol and urea, and there is a subtle balance between the acidity and basicity: the Lewis acid group is required for the activation of the carbonyl group of urea and the Lewis base functions for the activation of the hydroxyl groups of glycerol.<sup>15, 18, 46</sup> In this regard, for the reaction of glycerol and urea in the presence of the catalytic system F-IRMOF-3(AX), ZnO and the quaternized functional group could respectively be considered as a Lewis acid and a Lewis base, as shown in Scheme 1.

The role of the quaternized functional group as a Lewis base in the activation of glycerol was substantiated by Park et al.45 in which, based on FT-IR and <sup>1</sup>H NMR analysis, strong hydrogen bonding interactions between the hydroxyl group of glycerol and the chloride anion of NH<sub>4</sub>Cl were reported. Fujita et al.<sup>23</sup> also suggested the interaction of ZnO and urea. They reported homogeneous catalysis of ZnO by forming a complex with urea through the dissolution of zinc oxide into the mixture of glycerol and urea.

The stability of the immobilized IL catalyst was evaluated using recycling experiments. In each cycle, the used catalyst was separated by filtration, washed with methanol to remove the products adhering to its surface, dried at room temperature, and then directly reused for the next run without regeneration. Table V shows the activity of the reused F-IRMOF-3 catalyst. Upon reusing the conversion of glycerol and the selectivity toward GC decreased slightly indicating that the catalyst can be reused for up to three consecutive cycles without significant loss of activity.

#### 4. CONCLUSIONS

Glycerolysis of urea using IRMOF-1 and functionalized F-IRMOF-3 was evaluated herein, illustrating the importance of the structure and preparation method of the MOF catalysts on their efficacy. The incorporation of ZnO defects into the F-IRMOF-3 structure by fast precipitation is advantageous for the glycerolysis of urea because of the introduction of acid-base bifunctional active sites. F-IRMOF-3 exhibited good catalytic activity even in the absence of a solvent. ILs with longer alkyl chains and more nucleophilic counteranions exhibited better reactivity for the synthesis of GC. High temperature, long reaction time, and a high degree of vacuum were favorable for the high conversion of glycerol. The F-IRMOF-3 catalyst can be easily recovered and reused without considerable loss of its initial activity.

**Acknowledgments:** This study was supported by the Korean Ministry of Education through National Research Foundation (2012-001507) and LINC program.

#### **References and Notes**

- G. Knothe, J. V. Gerpen, and J. Krahl (eds.), The Biodiesel Handbook, AOCS Press, Champaign, IL (2005).
- S. T. Bagley, L. D. Gratz, J. Johnson, and J. McDonald, *Environ. Sci. Tech.* 32, 1183 (1998).
- 3. M. Mittelbach and C. Remschmidt, Biodiesel-the Comprehensive Handbook, Graz, Austria (2004), Vol. 87.
- T. Werpy and G. Petersen, Top value added chemicals from biomass, US Department of Energy (USDOE) (2004), Vol. 1. No.: DOE/GO-102004-1992
- 5. C. Toro, P. Hidalgo, and R. Navia, J. Biobased Mater. Bioenergy 5, 55 (2011).
- 6. V. Sricharoenchaikul and D. Atong, J. Biobased Mater. Bioenergy 6, 643 (2012). Delivered by Publishing Te
- N. Dimitratos, J. A. Lopez-Sanchez, and G. J. Hutchings, *Topics* Catal. 52, 258 (2009).
- 8. C. L. Bianchi, P. Canton, N. Dimitratos, F. Porta, and L. Prati, *Catal. Today* 102, 203 (2005).
- 9. M. A. Dasari, P. P. Kiatsimkul, W. R. Sutterlin, and G. J. Suppes, *App. Catal. A: Gen.* 281, 225 (2005).
- M. Aresta, A. Dibenedetto, F. Nocito, and C. Ferragina, J. Catal. 268, 106 (2009).
- D. Randall and R. D. Vos, Novel chemical blowing agent, EP 419,114, April (1991).
- M. Weuthen and U. Hees, A process for the preparing alkyl and/or alkenyloligoglykosidglycerinethern, Ger. Patent DE 4335947, April (1995).
- 13. V. Plasman, T. Caulier, and N. Boulos, *Plast. Addit. Compd.* 7, 30 (2005).
- Y. Fukuda and Y. Yamamoto, Method for producing glycerol derivative, JP 023930, February (2009).
- M. J. Climent, A. Corma, P. D. Frutos, S. Iborra, M. Noy, A. Velty, and P. Concepcion, *J. Catal.* 269, 140 (2010).
- 16. Z. Mouloungui, J. W. Yoo, C. A. Gachen, and A. Gaset, Process for the preparation of glycerol carbonate from glycerol and a cyclic organic carbonate, especially ethylene or propylene or propylene carbonate. EP 0739888, October 30 (1996).
- 17. M. Aresta, A. Dibenedetto, F. Nocito, and C. Pastore, J. Mol. Catal. A: Chem. 257, 149 (2006).

- 18. Q. Li, W. Zhang, N. Zhao, W. Wei, and Y. Sun, *Catal. Today* 115, 111 (2006).
- M. Okutsu and T. Kitsuki, Method for producing glycerol carbonate, JP 039347, February (2007).
- 20. M. Aresta, J. L. Dubois, A. Dibenedetto, F. Nocito, and C. Ferragina, Synthesis process of polyol carbonate from polyols, conducted in using a solvent selective for polyols carbonates. EP 08305653.1, April (2008).
- 21. T. Sasa, M. Okutsu, and M. Uno, Method for producing glycerol carbonate, JP 067689, April (2009).
- 22. M. Okutsu and T. Kitsuki, Drive equipment of hybrid electric automobile, JP 050415, February (2000).
- 23. S. Fujita, Y. Yamanishi, and M. Arai, J. Catal. 297, 137 (2013).
- 24. C. Hammond, J. A. L. Sanchez, M. H. A. Rahim, N. Dimitratos, R. L. Jenkins, A. F. Carley, Q. He, C. J. Kiely, D. W. Knight, and G. J. Hutchings, *Dalton Trans.* 40, 3927 (2011).
- 25. Z. Wang and S. M. Cohen, J. Am. Chem. Soc. 129, 12368 (2007).
- 26. S. Natarajan and S. Mandal, Angew. Chem., Int. Ed. 47, 4798 (2008).
- 27. A. C. Kathalikkattil and D. W. Park, J. Nanosci. Nanotechnol.
- 13, 2307 (**2013**).
- 28. X. Gu and H. Su, Mater. Focus 1, 97 (2012).
- R. E. Morris and P. S. Wheatley, Angew. Chem., Int. Ed. 47, 4966 (2008).
- B. Chen, C. Liang, J. Yang, D. S. Contreras, Y. L. Clancy, E. B. Lobkovsky, O. M. Yagi, and S. Dai, *Angew. Chem., Int. Ed.* 45, 1390 (2006).
- 31. O. Kahn, Acc. Chem. Res. 33, 647 (2000).
- 32. J. Gascon, U. Aktay, M. D. H. Alonso, G. P. M. V. Klink, and F. Kapteijin, J. Catal. 261, 75 (2009).
- 33. F. X. L. Xamena, F. G. Cirujano, and A. Corma, *Micro. Meso. Mat.* 157, 112 (2012).
- **34.** H. J. Cho, H. M. Kwon, J. Tharun, and D. W. Park, *J. Ind. Eng. Chem.* 16, 679 (**2010**).
- **35.** D. W. Kim, M. S. Park, G. A. Park, S. D. Lee, M. Selvaraj, and D. W. Park, *Res. Chem. Interm.* 37, 1305 (**2011**).
- 36. L. M. Huang, H. T. Wang, J. X. Chen, Z. B. Wang, J. Y. Sun, D. Y. Zhao, and Y. S. Yan, *Micro. Meso. Mat.* 58, 105 (2003).
- 37. N. H. Kim, S. V. Malhotra, and M. Xanthos, *Micro. Meso. Mat.* 96, 29 (2006).
- A. Lieb, H. Leclerc, T. Devic, C. Serre, I. Margiolake, F. Mahjoubi, J. S. Lee, A. Vimont, M. Daturi, and J. S. Chang, *Micro. Meso. Mat.* 157, 18 (2012).
- **39.** L. Han, S. W. Park, and D. W. Park, *Energy Environ. Sci.* 2, 1286 (2009).
- 40. H. L. Shim, S. Udayakumar, J. I. Yu, I. Kim, and D. W. Park, *Catal. Today* 148, 350 (2009).
- 41. H. Kawanami, A. Sasaki, K. Matsui, and Y. Ikushima, *Chem. Commun.* 7, 896 (2003).
- 42. S. S. Wu, X. W. Zhang, W. L. Dai, S. F. Yin, W. S. Li, and Y. Q. Ren, *Appl. Catal. A Gen.* 341, 106 (2008).
- 43. J. Sun, S. Fujita, F. Zhao, and M. Arai, Green Chem. 6, 613 (2004).
- 44. J. I. Yu, H. Y. Ju, K. H. Kim, and D. W. Park, *Korean J. Chem. Eng.* 27, 446 (2010).
- 45. J. H. Park, J. S. Choi, S. K. Woo, S. D. Lee, M. Cheong, H. S. Kim, and H. Lee, *Appl. Catal. A: Gen.* 433, 35 (2012).
- 46. P. Ball, H. Fullmann, and W. Heitz, Angew. Chem., Int. Ed. 19, 718 (1980).

Received: 22 March 2013. Accepted: 10 June 2013.