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COMMUNICATION

Synthesis of Zeolitic Imidazolate Framework-8 (ZIF-8) Using Glycerol Carbonate as a Green Solvent

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Abstract: In this letter, we show that glycerol carbonate (GlyC), a bio-based derivative of glycerol, can be used as a suitable green solvent for the synthesis of Zeolitic Imidazolate Framework-8 (ZIF-8). Crystallinity, surface area, and porosity of the obtained ZIF-8 crystals were in line with those obtained in dimethylformamide (DMF) and methanol. GlyC was also found to be reusable for several cycles, maintaining the same original quality as solvent for the synthesis.

Introduction

Zeolitic imidazolate framework-8 (ZIF-8) is one of the representative compounds of Metal–Organic Frameworks (MOFs),¹ a class of materials composed of metal cations coordinating organic ligands. Due to their special structure, MOFs have high internal surface area and a large pore size, that render them a good candidate for gas storage, separation, chromatography, electronic applications, and drug delivery.^{2–5} In this respect, many efforts were made to control the ZIF-8 crystal morphology and crystal size distribution. To pursue this goal, the control of crystal size distribution was achieved using different strategies such as the adjustment of the reactant

ratios, the incorporation of additives (e.g., trialkyl amine, cetyltrimethylammonium bromide, formate, etc.), the sources of Zn ions, and the proper selection of the synthetic method (sono-crystallization, micromixer, ionothermal microwave-assisted synthesis, microwave irradiation).⁶ In contrast, the research on new green and bio-based solvents for MOF synthesis is still limited. Indeed, methods using amide-type solvents (e.g., dimethylformamide, DMF) are the most used for the synthesis of ZIF-8⁷ with scant examples based on more environment friendly alternatives, such as methanol⁸ or water.⁹ In fact, DMF is a toxic, fossil-based, polar, and aprotic solvent characterized by a high dielectric constant and a high boiling point, features that favor the progress of the synthetic process,¹⁰ but may pose concerns on the environmental impacts.

To overcome this limitation and with the ambitious idea to substitute DMF with greener alternatives, in this work we report for the first time the preparation of crystalline ZIF-8 in glycerol carbonate (GlyC). GlyC (4-hydroxymethyl-2-oxo-1,3-dioxolane) has attracted increasing interest as one of the most investigated bio-based compounds with many interesting applications in different fields, such as in the synthesis of new chemicals,^{11, 12} the manufacturing of polymers, building blocks for drug preparation, surfactants, cosmetics, and detergent industries.^{12–14} Moreover, the use of GlyC fully respects the 7th principle of Green Chemistry^{15–17} due to its preparation from glycerol

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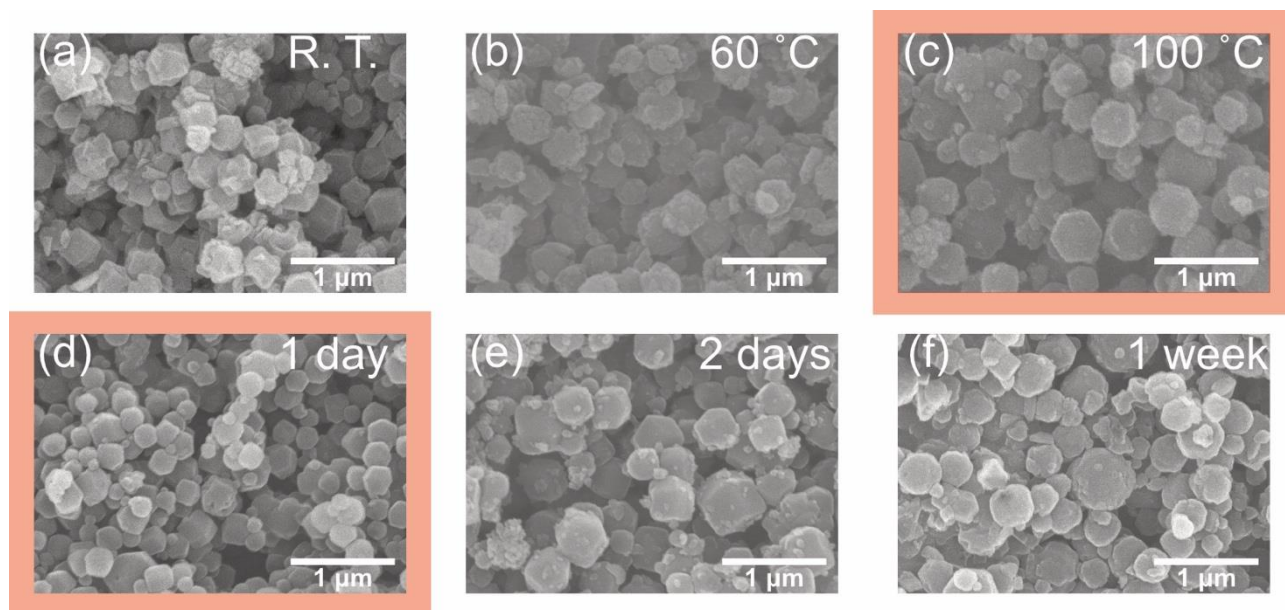


Fig. 1 SEM micrographs of synthesized ZIF-8 after 2 days of reaction using 10 mM of NaOH at various temperature: (a) room temperatures ($\sim 20^\circ\text{C}$), (b) 60°C , and (c) 100°C . Generated ZIF-8 at 100°C using 10 mM of NaOH for various synthesis times: (d) 1 day, (e) 2 days, and (f) 1 week. All reactions were carried out using $[\text{Zn}(\text{OAc})_2] = 10\text{ mM}$ and $[\text{Hmim}] = 40\text{ mM}$. Panels (c) and (d) are framed in orange to highlight the optimal conditions in terms of temperature and reaction time.

through transcarbonation with dimethyl carbonate. Because of its physico-chemical properties (see Supporting Materials), GlyC is also used as a low-volatile organic solvent, low toxic and biodegradable with a high dielectric constant and dipole moment.¹⁸ Indeed, GlyC shows relevant and promising properties to overcome the limitations related to DMF for ZIF-8 preparation. In this work, to further assess the advantages concerning the use of GlyC for this purpose, solvent recyclability experiments were carried out and both simple E-Factor (SEF) and process mass intensity (PMI) were calculated and discussed.

Results and discussions

Glycerol carbonate was prepared by glycerol transcarbonation with dimethyl carbonate in the presence of Na_2CO_3 as a catalyst (for details see the SI).^{19, 20} In a typical synthetic procedure for ZIF-8, the degassed GlyC solutions of zinc acetate and Hmim containing sodium hydroxide were mixed in glass vials, and then left in a heating block for the reaction to occur. Sodium hydroxide favors the formation of ZIF-8 crystals not only in water but also in less polar solvents.^{21, 22}

First, some preliminary experiments were carried out to obtain the optimal experimental conditions for the synthesis. We investigated the effect of the temperature and of the total reaction time using fixed initial concentrations for the reactants: 10 mM zinc salt and four-fold excess of Hmim ($[\text{Zn}(\text{OAc})_2] = 10\text{ mM}$ and $[\text{Hmim}] = 40\text{ mM}$).²³⁻²⁶ SEM micrographs (details in the SI) in Figure 1 show that crystals having the typical geometry of ZIF-8 form in all experimental conditions when GlyC is used as the reaction medium. In particular, Figures 1 a-c show that the high temperature favors the formation of bigger and more crystalline particles. Concerning the reaction time, we found that one day was the

optimal lapse, as illustrated in Figures 1 d-f. An increased reaction time would lead to the formation of bigger particles on the average, however after 2 days, the bigger crystals were covered by smaller particles (Figure 1 e). After 1 week of reaction, the edges of the crystals became less sharp due to the degradation of the sample.²⁷ Based on these experiments, the optimal experimental conditions for the generation of ZIF-8 in GlyC were found to be the same as those obtained in other solvents, namely high temperature and synthesis time of 1 day.^{1, 28}

The next step was to explore whether the concentration of the reactants affects the size and the morphology of the ZIF-8 crystals, keeping the same experimental conditions ($\theta = 100^\circ\text{C}$, $t = 1\text{ day}$). Figure 2 summarizes the visual appearance of the colloidal suspension and the morphology of the crystals characterized by SEM measurements. At low concentration of zinc ions (1 mM), no crystallization was observed. Based on the SEM measurements, the best crystallinity was obtained with the ratios $[\text{Zn}(\text{OAc})_2]:[\text{Hmim}] = 10\text{ mM}:20\text{ mM}$, $10\text{ mM}:40\text{ mM}$, and $20\text{ mM}:40\text{ mM}$ (Figure 2 f, g, i). This is an interesting finding because, in most of the studies, the ratio of Hmim to Zn to generate ZIF-8 is greater than the stoichiometric ratio, which is 2:1. So far, the synthesis of ZIF-8 with a stoichiometric ratio of reactants was achieved using either a great amount of base²⁹ or a jet-mixer reactor.³⁰ In contrast, GlyC allowed to synthesize ZIF-8 at the stoichiometric ratio, in mild reaction conditions and using the simple solvothermal set-up. Also, at the ratio $[\text{Zn}(\text{OAc})_2]:[\text{Hmim}] = 10\text{ mM}:20\text{ mM}$, the mass yield of the product was 57.1 %, which is comparable or even higher than that obtained using the common solvothermal set-up with DMF and methanol as solvents.^{28, 31} Further investigations, crystalline phase assignment, specific surface area, pore volume, and recyclability measurements were conducted with a ratio

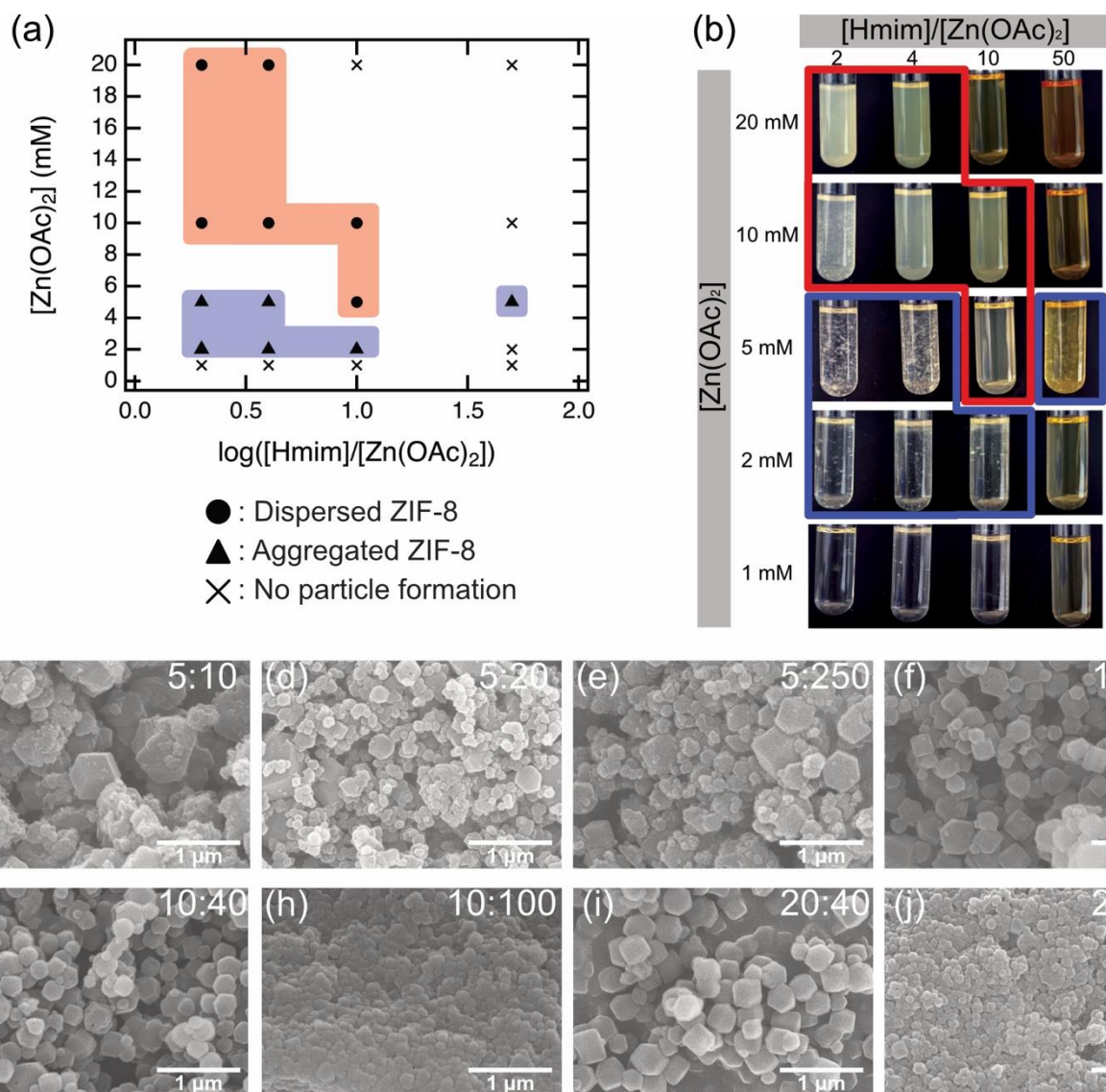


Fig. 2 (a) Effect of the initial concentration of the reactants on the reaction and (b) photographs of the reaction mixture after 1 day at 100 °C. (c) SEM micrographs of ZIF-8 particles at $\theta = 100$ °C, $t = 1$ day, and $[\text{NaOH}] = 0.01$ M using $[\text{Zn}(\text{OAc})_2]:[\text{Hmim}] =$ (c) 5 mM:10 mM, (d) 5 mM:20 mM, (e) 5 mM:250 mM, (f) 10 mM:20 mM, (g) 10 mM:40 mM, (h) 10 mM:100 mM, (i) 20 mM:40 mM, and (j) 20 mM:80 mM, respectively.

$[\text{Zn}(\text{OAc})_2]:[\text{Hmim}]$ of 10 mM:20 mM, i.e. at the lowest concentration of Hmim.

After the synthesis at a high concentration of Hmim (> 100 mM), the solution turned to a yellowish colour, as reported in Figure 2 b. This was likely due to reactions of Hmim with the base and of the GlyC with the Hmim. In detail, the reaction of Hmim with NaOH leads to the formation of sodium 2-methylimidazolate which is the active organic ligand for ZIF-8 synthesis. This molecule shows significant absorption in the UV-vis range, depending on the solvent. Moreover, preliminary experiments carried out using sole Hmim and GlyC reveal the formation of side-products which will be characterized in a future work (more details in the SI). However, in the optimal concentration range for the formation of ZIF-8 crystals, the effect of the side reactions was negligible due to the relatively low concentrations of both cations and linkers.

To characterize the solid products, we performed PXRD and nitrogen adsorption measurements (Figure 3). The recorded

PXRD pattern showed excellent crystallinity and a good match with data reported in the literature (Figure 3 a). The average specific surface area of the ZIF-8 crystals was found to be $660 \text{ m}^2 \text{ g}^{-1}$ which is roughly 50% less than the usual value of the samples synthesized in other organic solvents, e.g., DMF.^{1, 28, 32} The shape of both the type III isotherm and the type H3 hysteresis let us assume that there are several macropores in the structure, and that the pore size distribution is wide. The total pore volume is $0.58 \text{ cm}^3 \text{ g}^{-1}$ (Figure 3b). The most characteristic pore size (radius) falls in the range of ca. 50 Å (Figure 3c), which is representative for mesoporous ZIFs.³³

In passing we recall that GlyC undergoes a yellowing degradation in the presence of bases [F. Sarri, D. Tatini, D. Tanini, M. Simonelli, M. Ambrosi, B.W. Ninham, A. Capperucci, L. Dei and P. Lo Nostro, J. Mol. Liq. 2018, 266, 711–717].

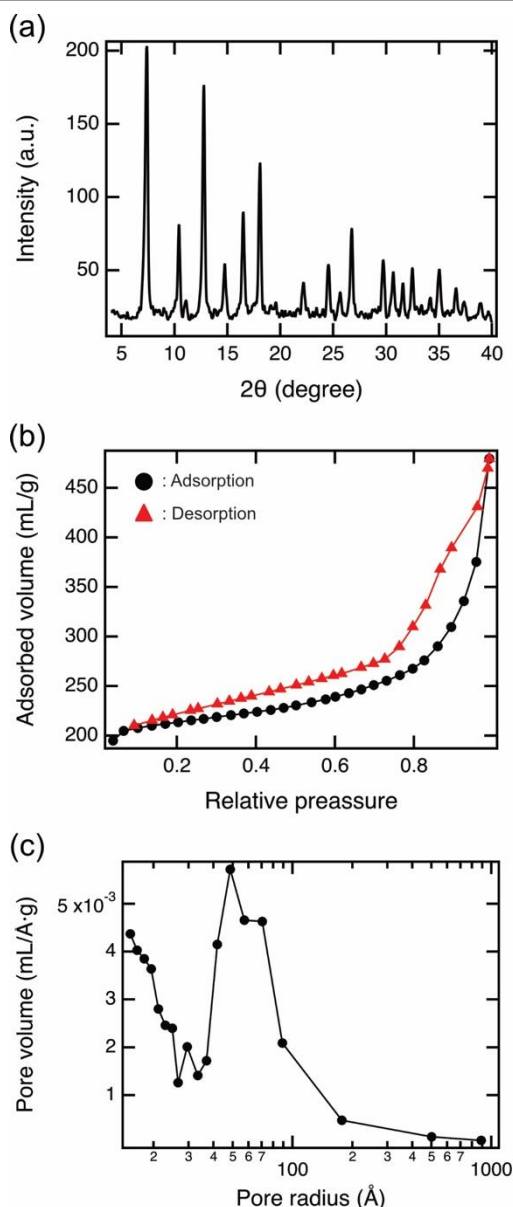


Fig. 3 (a) Powder X-Ray Diffraction (PXRD) pattern, (b) Brunauer–Emmett–Teller (BET) isotherm, and (c) Barrett–Joyner–Halenda (BJH) pore size distribution of ZIF-8 synthesized at 100 °C for 1 day with $[\text{Zn}(\text{OAc})_2] = 10 \text{ mM}$, $[\text{Hmim}] = 20 \text{ mM}$, and $[\text{NaOH}] = 10 \text{ mM}$.

According to the circular economy approach, the recyclability of the solvent is one of the crucial issues that must be considered.^{22, 34–36} We performed the sequential synthesis of ZIF-8 by reusing the same sample of GlyC as solvent for several cycles. SEM measurements and yield calculations revealed the formation of crystals with different yields varied from 1st to 4th cycle: 52.8 % (1st), 58.8 % (2nd), 62.8 % (3rd), and 74.1 % (4th cycle), respectively (Figure 4). Increasing yield could be due to remaining and accumulating unreacted species (Zn^{2+} and Hmim) in the system after each cycle.

Process mass intensity (PMI) has been proposed as a key mass-based metric.³⁷ In the last years, several works concerning the adoption of PMI have been published to analyze the process's efficiency in terms of mass.³⁸ We used both sEF and

PMI to critically address the impacts of the GlyC utilization and recycling but also to compare the ZIF-8 preparation in the presence of different solvents (GlyC, water and DMF). However, it was recognized that these metrics did not address concerns regarding the toxicity and safety of the feedstock materials or wastes.³⁹ The preparation of ZIF-8 in GlyC is performed with a simple E-Factor (sEF) value of 1.5 after four consecutive reaction cycles. Indeed, the possibility to fully recycle the reaction mixture during four consecutive cycles gives an E-factor, for each of these cycles, equal to 0 in agreement with the requirements of the circular approach.³⁴ Results obtained in DMF and water gave an E-factor of 12.2 and 14.6, respectively. These outcomes can be related to the lower ZIF-8 yields in DMF (30.5% w/w) using an Hmim/ Zn^{2+} mole ratio of 8³¹ and to a high excess of Hmim (Hmim/ Zn^{2+} mole ratio of 40) in water (ZIF-8 yield = 97.5% w/w)⁴⁰ The simplified E-factor did not address the impact of water and solvent as, instead, PMI does. Therefore, PMI values are higher than sEFs. PMI values, calculated on the first reaction cycle to compare the three different scenarios, are 206 for GlyC, 70 for DMF, and 312 for water. Furthermore, considering the GlyC recyclability, the PMI⁴¹ reaches the value of 2.8. The obtained results clearly indicated the excellent impact of GlyC on the ZIF-8 synthesis by reducing the production of waste and through its recycling along four consecutive syntheses.

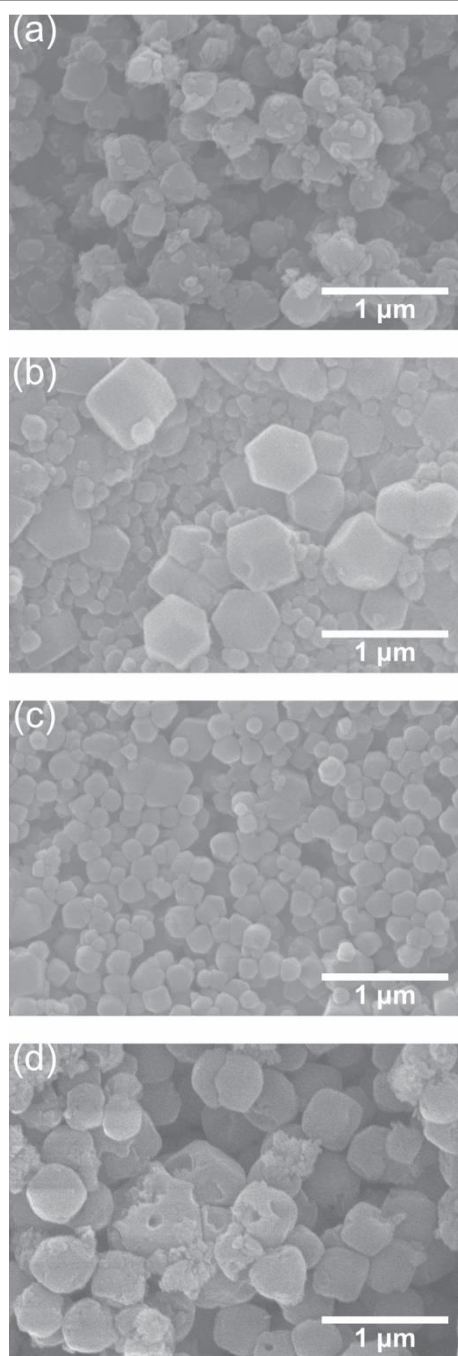


Fig. 4 SEM micrographs of ZIF-8 synthesized in each recycle step: (a) 1st, (b) 2nd, (c) 3rd, and (d) 4th recycles. ZIF-8 was synthesized for every recycling experiment at 100 °C for 1 day with $[\text{Zn}(\text{OAc})_2] = 10 \text{ mM}$, $[\text{Hmim}] = 20 \text{ mM}$, and $[\text{NaOH}] = 10 \text{ mM}$.

Conclusions

In conclusion, in this letter we showed how an effective synthesis of technologically relevant materials, such as MOFs, can be successfully obtained in the bio-based solvent glycerol carbonate. In terms of yield and quality of the products, GlyC proved to be in line with the performances of other solvents, such as DMF and water, but having a milder environmental impact, as calculated by the E-factor and the PMI. From a circularity point of view, the use of a derivative of glycerol for

industrial applications can boost the use of bio-based chemicals and help the transition toward a more sustainable society.

Conflicts of interest

There are no conflicts to declare.

Acknowledgment

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