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ORIGINAL ARTICLE

Selective cyclodimerization of epichlorohydrin to dioxane derivatives over MOFs

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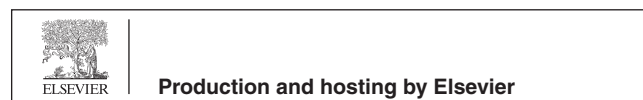
Abstract Glycerol can be converted to valuable products such as epichlorohydrin which is an important intermediate applied in various industries. For example, dioxane derivatives, which are important pharmaceuticals, can be obtained from epichlorohydrin. In the present study, ZIF-8, ZIF-67, MIL-100, and UiO-66 were applied for the direct cyclodimerization of epichlorohydrin. These MOFs were selected because they were already applied as active catalysts in ring opening of epoxides. Among them, ZIF-8 showed the highest activity and selectivity in the absence of any solvent or co-catalyst. Using ZIF-8 as a catalyst, the cyclodimer product (1,4-dioxane 2,5-bis-chloromethyl) was obtained in a yield of about 70% which was significantly superior to previous homo or heterogeneous catalysts for this reaction. Due to ZIF-8 structure and the proposed mechanism, the cyclodimerization reaction catalyzed either by the defects in the structure and/or on the surface. Furthermore, acidic-basic characteristics were also in play. The NH₃ and CO₂ temperature-programmed desorption technique were utilized to identify the active sites and thereby reaction mechanism. Moreover, because of similar properties of ZIF-8 to zeolites, the activity of commercial ZSM-5 for the same reaction was also investigated in this work.

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1. Introduction

Nowadays, biodiesel amounts to almost 10% (w/w) glycerol as coproduct in industrial scale (Pagliaro et al., 2007). Subsequently, glycerol can be converted into other products such as epichlorohydrin which is also an important industrial intermediate. Dioxane and its derivatives are highly in demand as solvents, wetting-dispersing agents, and commercial starting materials (Siskin & Mozeleski, 2004). Currently, there are different methods for the synthesis of dioxane and its derivatives, however direct synthesis from epoxide in a green mode and with high yield, was rarely reported. For example, the cyclodimerization of ethylene oxide (EO) was performed using superacids (Kobayashi et al. 1975). Nevertheless, it turned out that the removal of the acids after the reaction was problematic. In 2004, Siskin and coworkers proposed a synthetic procedure in which the hydroxyl groups of two ethylene glycol molecules were involved in a dehydration reaction to produce dioxane, however, this was not a direct and straightforward method (Siskin & Mozeleski, 2004). Moreover, it was suggested that the cationic polymerization of epoxides, might provide a mixture of polymers and oligomers (Kern, 1868). In some cases, the ring opening reaction produced oligomers as the main product, which because of their usefulness, such catalytic systems proved desirable especially in industry (Kucera et al., 1976; Crabtree et al., 2007; Saegusa & Matsumoto, 1968).

While various catalytic systems have been introduced for ring opening polymerization of epoxides, studies regarding the direct synthesis of oligomers and specifically cyclic oligomers are rare. Hence designing new catalysts that can selectively synthesize oligomers or cyclic-oligomers by new materials with particular structural properties are highly demanded. Metal organic frame works (MOFs) are potential candidates as catalysts and that is because they are crystalline, porous and functional materials which have the advantages of both homo and heterogeneous catalysts. Unambiguously, their significant properties such as high surface area, large pore apertures, high stability and possible organization of active centers make them attractive catalysts for different organic reactions. So far several MOFs have been reported as catalysts for many organic reactions (Chughtai et al., 2015), but there is no account of the use of MOF as catalysts (Lee et al., 2009), in the field of oligomerization or polymerization of epoxides. It has already been reported that epoxides can be oligomerized or polymerized by the cationic or anionic mechanism through Lewis acids and alkoxide base (Crabtree et al., 2007). Besides that, there are some examples of the potential MOFs as catalysts for ring opening of epoxides in other reactions such as fixation of CO₂ into epoxides (Beyzavi et al., 2015). These data, prompted us to utilize some of these active MOFs as catalysts for specific oligomerization of epoxides. Among various MOFs, ZIF-8 (Miralda et al., 2012), ZIF-67 (Mousavi et al., 2016), MIL-100 (Dhakshinamoorthy et al., 2012), and UiO-66 (Kim et al., 2013) were chosen as they demonstrated high catalytic activities for ring-opening of epoxides in other reactions. These MOFs were therefore expected to be potential candidates for the oligomerization or polymerization of epoxides.

The results revealed that although some of these catalysts could open the ring of epichlorohydrin, only ZIF-8 synthesized

by spray-drying could synthesize 1,4-dioxane-2,5-bis-chloromethyl (cyclodimer) as the main product with high yield. Besides, ZIF-67 could also act as an active catalyst and produced 1,4-dioxane-2,5-bis-chloromethyl, however with a lower yield. Other examined MOFs such as UiO-66 and MIL-100-Fe did not show any catalytic activity for the oligomerization of epichlorohydrin and only partially produced a mixture of dioxane and dioxolane derivatives. Furthermore, the mechanism of this cyclodimerization reaction was proposed based on the evidence obtained by different experiments and temperature programmed desorption (TPD) studies and discussed in this work. Moreover, due to the similarity between ZIFs and zeolites, the catalytic activities of ZIFs were compared to a commercially available zeolite (ZSM-5) with similar particle size. To the best of our knowledge, this is the first report of a heterogeneous catalyst for the direct one-step synthesis of the cyclodimer of epichlorohydrin. Furthermore, this is the first report of MOFs as active and selective catalysts for the oligomerization reaction.

2. Experimental section

2.1. Catalyst preparation and characterization

ZIF-8, ZIF-67, MIL-100, and UiO-66 were synthesized according to the earlier reports. Zeolite ZSM-5 (SiO₂/Al₂O₃ = 25) was purchased from Nankai University Catalyst Co., Ltd. ZIF-8 was prepared by the spray-drying method according to the procedure reported by Carné-Sánchez et al. (2013) and by using an AF-88 labs Spray dryer (S1-1) (AFIND Scientific instrument CO., Ltd.). ZIF-67 (S1-2), UiO-66 (S1-3) and MIL-100 (S1-4) were synthesized according to the previous reports (Banerjee et al., 2008; Wu et al., 2013; Seo et al., 2012). The morphologic properties of all samples are summarized in Table S2-4 and are in good agreement with previously reported results (Chaemchuen et al., 2017; Carné-Sánchez et al., 2013; Banerjee et al., 2008; Wu et al., 2013; Seo et al., 2012).

2.2. Characterization of synthesized MOFs

The X-ray diffraction (XRD) patterns of all MOFs were obtained using a Bruker D8 advanced diffractometer with Cu K α radiation (40 kV, 45 mA with 6°/min scanning rate). The physical properties and gas adsorption-desorption isotherms were applied using the volumetric method on Micrometrics instrument (ASAP 2020 analyzer). The surface morphology was performed through SEM (JSM-IT300/JSM-IT300, from JEOL company). N₂ adsorption-desorption isotherms and pore size distribution of all samples were measured using the volumetric method on Micrometrics instrument ASAP 2020 analyzer. N₂ gas with purity >99.999% was utilized in this study. Firstly, the samples were degassed and evacuated at 200 °C under vacuum for 4 h. The surface area of all samples was measured by the Brunauer-Emmett-Teller (BET) analysis and the Langmuir method. The NMR examination was performed on a Bruker Avance III 500. The acidic and basic properties of MOFs were examined via temperature programmed desorption (TPD) using an AutoChem II 2920 applying NH₃ and CO₂ as probe gases. 0.1 g of catalyst sample (ZIF-8 or ZIF-67) was placed inside the instrument and pretreated at

250 °C for 3 h. Thereafter, the sample was cooled down to room temperature and saturated with dry and pure NH₃ or CO₂ gas. Next, helium gas was sent over the sample (20 mL/min) to remove the physisorbed CO₂ or NH₃ gas. The desorption process was performed from 30 to 270 °C using a heating rate of 10 °C/min. and all the data were obtained by a thermal conductivity detector (TCD). The single-crystal diffraction analysis was obtained using a BRUKER-APEX II at 90 K with X-ray diffractometer. The structure was resolved and refined using a SHELXL-97 program. The GPC tests were performed using PL-GPC 50, Agilent Technologies (column PLgel 5 µm MIXED-C for molecular weight between 200 and 3 million). The reactions were performed under an inert atmosphere using standard Schlenk techniques.

3. Results and discussion

3.1. Catalysts & cyclodimerization of epichlorohydrin

Epichlorohydrin and other chemicals were bought from Sigma-Aldrich and Aladdin chemical Co. and used as received without any further purification unless otherwise noted. The X-ray diffractions of the MOFs are presented in Fig. S2-1. The surface area and other textural properties of all samples were determined by N₂ adsorption-desorption (Table S2-4, Fig. S2-2) analysis. Afterwards, Scanning Electron Microscopy (SEM) was performed for the assessment of the average crystal sizes of all samples (Fig. S2-3).

For oligomerization of epichlorohydrin, first ZIF-8, synthesized by spray drying, was applied as a model to optimize the reaction conditions. To consider the effect of reaction parameters on the catalytic reactivity of ZIF-8, various reaction conditions were examined and summarized in Table 1. In a typical procedure, 1 g (10.8 mmol) of epichlorohydrin and the requisite amount of ZIF-8 were charged in a Schlenk flask under an inert atmosphere in the absence of any solvent and co-catalyst. The flask was then heated up at different temperatures. The completion of the reaction was monitored by ¹H-NMR and GC. The control tests confirmed that the reaction did not happen in the absence of ZIF-8 catalyst, indicating that the presence of catalyst was crucial for the cyclodimerization of epichlorohydrin. The precursors of ZIF-8 were studied for their individual catalytic performance as well as their combination. As shown in Table 1, individual zinc nitrate or 2-methyl imidazole (entry 1–2, Table 1) as catalysts could not open the epoxide ring. However, the presence of both precursors together as catalysts (entry 3, Table 1) could open the ring of epichlorohydrin. Nonetheless, the results revealed that only negligible cyclic-dimer products were formed and mainly a mixture of dioxolane derivatives was obtained. Afterwards, the influence of the amount of the catalyst was investigated and the results were mentioned in entry 4–6. The results disclosed that at 110 °C and in 18 h of reaction time, the highest yield was obtained when the ratio of substrate to catalyst was 100 (w/w). The effect of reaction temperature on the conversion was summarized in entry 7–9 (Table 1). The results exposed that an optimum conversion (>99%) was obtained at 140 °C which presented the importance of heating for this reaction. A higher temperature did not affect the conversion of epichlorohydrin. The investigation of the reaction time was determined by withdrawing aliquots from the reaction

mixture at various reaction intervals which then were analyzed by GC. (entry 9–11) A 99% conversion was obtained starting from 18 h and 140 °C and further on.

Subsequently, the optimum reaction conditions were applied for the ring opening cyclodimerization of epichlorohydrin using other potential catalysts, such as MIL-100, ZIF-67, UiO-66, and zeolite ZSM-5. The results were summarized in Table 1 (entry 12–15). Apart from ZIF-8, among other catalysts, ZIF-67 showed the highest activity toward producing 1,4-dioxane-2,5-bis-chloromethyl, however, the GC-yield of the desired cyclic dimer (53%) was lower than ZIF-8. UiO-66 and MIL100-Fe could only ring-open epichlorohydrin to a small extent, the yield of the desired cyclodimer product was not that substantial. Although these MOFs are known for their ability to do the CO₂-cycloaddition of epoxides, implying they are able to open the ring of epoxide, the yields from this reaction in our study were just very low. Nonetheless, it should be noted that in all experiments a polar solvent was used (Dhakshinamoorthy et al., 2012; Kim et al., 2013). Therefore, their catalytic activity towards opening the ring of epichlorohydrin might have been decreased drastically in the absence of solvents. In the cases of UiO-66 and MIL-100-Fe as catalysts, after separation of the unreacted epichlorohydrin, the GC-MS analysis of the reaction mixture revealed that mainly a mixture of dioxolane derivatives was produced. Because of the formation of numerous side products, we could not purify and detect these compounds separately.

Moreover, as it is shown in entry 15, ZSM-5 was not an active catalyst for this reaction and even could not open the ring of epichlorohydrin. All these data illustrate that oligomerization of epoxide, or more precisely, the *cyclo*-oligomerization of epoxide may not be as facile as the ring opening of epoxides is (Lee et al., 2009), and therefore it may require a catalyst such as a MOF with a particular structure and properties.

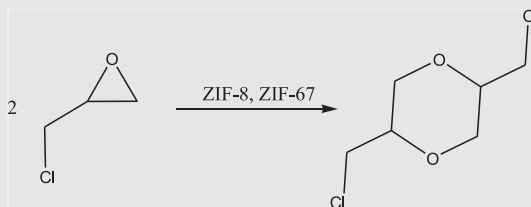
After the completion of the reaction by ZIF-67 and ZIF-8, the crystallization of the reaction mixture occurred. The crystals of 1,4-dioxane 2,5-bis-chloromethyl were collected and analyzed by single crystal X-ray spectroscopy (Fig. 1) (Table S2-5). The result was in excellent agreement with the previous reports (Grinevich et al., 1997). The crystals were also analyzed by ¹H and ¹³C-NMR (Fig. S2-7) and X-ray diffraction (Fig. S2-6).

After separation of the crystals, a yellow liquid remained which was analyzed by GC-MS (Fig. S2-8) and GPC to identify whether any polymers existed. The GC-MS results clarified that the side products were a mixture of dioxolane derivatives, while the GPC analysis confirmed that no polymer was formed under these reaction conditions.

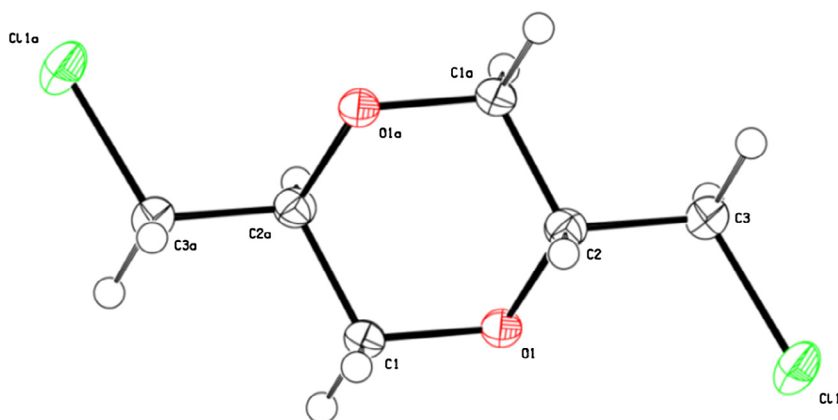
Remarkable other epoxides such as styrene oxide and propylene oxide could not generate cyclic compounds and only mixtures of linear oligomers were obtained. This demonstrated that using ZIF-8, only epichlorohydrin could form the cyclodimer product with a high yield and for other epoxides, the optimum reaction conditions still need to be investigated.

3.1.1. Reusability study

Another important issue that should be considered is the reusability of the catalyst. Therefore, after the completion of the reaction by ZIF-8 and ZIF-67, both catalysts were separated by centrifugation and washed with dichloromethane three times and dried under vacuum at 100 °C. Unfortunately,

Table 1 Different reaction conditions for the cyclodimerization of epichlorohydrin using various catalysts.

Entry	Sample	Catalyst (mg)	Substrate (g)	Temperature (°C)	Time (h)	Epichlorohydrin conversion	Cyclodimer GC yield (%)
1)	Zn(NO ₃) ₂ ·4H ₂ O	10	5	110	24	0	0
2)	2-methyl Imidazole	10	2	110	24	0	0
3)	Entry (1) + (2)	10	2	110	24	> 99%	~5
4)	ZIF-8	10	2	110	16	51%	29
5)	ZIF-8	10	1	110	16	71%	45
6)	ZIF-8	10	0.7	110	16	79%	45
7)	ZIF-8	10	1	120	18	82%	49
8)	ZIF-8	10	1	140	18	> 96%	64
9)	ZIF-8	10	1	150	18	> 99%	63
10)	ZIF-8	10	1	140	20	> 99%	70
11)	ZIF-8	10	1	140	22	> 99%	70
12)	ZIF-67	10	1	140	20	90%	53
13)	MIL-100-Fe	10	1	140	20	12%	~0
14)	UiO-66	10	1	140	20	15%	~0
15)	ZSM-5	10	1	140	20	0	0

**Fig. 1** The crystal structure of compound 1,4 dioxane-2,5-bis-chloromethyl.

ZIF-67 decomposed after the first use and lost its crystalline structure. The XRD pattern of ZIF-67 was changed totally and showed that its crystalline structure almost completely decomposed during the catalytic reaction (Fig. S2-9).

ZIF-8 was reused for ring-opening cyclodimerization of epichlorohydrin. The catalytic activity of ZIF-8 decreased to 19% which was much lower than the catalytic activity of the fresh sample. The XRD pattern of the reused ZIF-8 was illustrated in Fig. S2-9 proposing that the crystalline structure of ZIF-8 partially collapsed. The crystallinity value of ZIF-8 after the first use was calculated and reported in supporting information (55%) (Fig. S2-10) based on the previous reports by R. Surendar et al. The results confirmed that ZIF-8 lost

approximately 45% of its crystallinity when the crystallinity value of ZIF-8 before the reaction was taken as 100% (similar to previous reports of Surendar and Chaemchuen (Surendar et al., 2010; Chaemchuen et al., 2017)). Consequently, this decline in crystallinity might result in a lower catalytic activity of ZIF-8 for the next cycle. Although, another reason for the lower catalytic performance of ZIF-8 might be the blockage of the pores of the MOF by products, which was reported previously for ZIF-8 as a catalyst for the CO₂-cycloaddition reaction with epoxide as substrates (Miralda et al., 2012).

Although both active catalysts, ZIF-8 and ZIF-67, did not show a good reusability, their many advantages such as cost-effectiveness, easy handling, and preparation, one-step

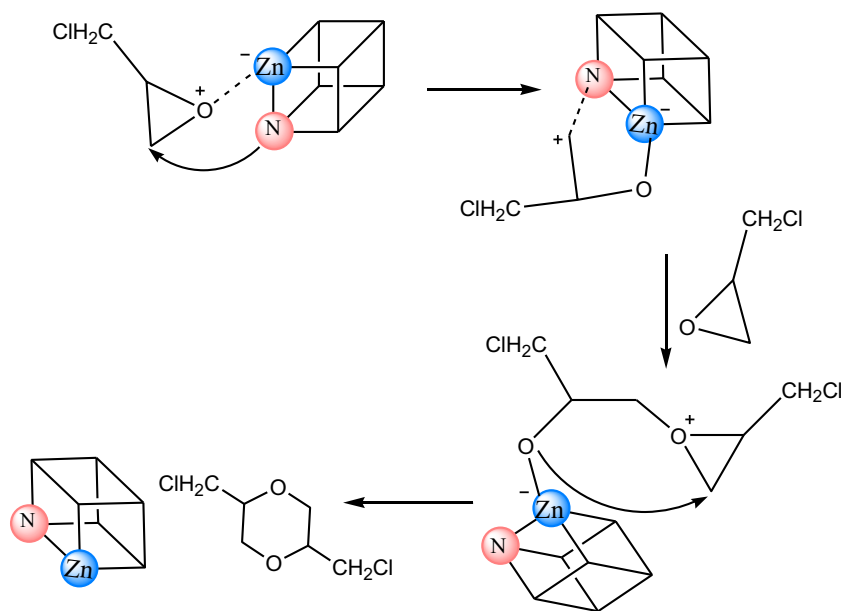


Fig. 2 The proposed mechanism for the ring opening cyclodimerization of epichlorohydrin. (N represents the basic nitrogen of 2-methyl imidazole).

cyclodimerization reaction, simple separation from solution mixture and high conversion to the desired product, make them still worthwhile even for industrial applications.

3.1.2. Reaction mechanism

Although ZIFs are known as “saturated” frameworks (Mueller et al., 2006; Horcajada et al., 2007; Kwak et al., 2009) and thus all linkers are coordinated and the metal cores are coordinately saturated (Chizallet, 2010) and therefore ZIFs are not expected to show catalytic activity. Nevertheless, there are several reports of ZIFs as active catalysts for various reactions such as Knoevenagel condensation reaction, Friedel–Crafts acylation, synthesis of monoglyceride, etc. In most of the cases, the mechanism is linked to the defects inside their structure and/or on the surface (Beyzavi et al., 2015; Lee et al., 2009). Moreover, DFT studies on ZIF-8 by Chizallet (2010) shed light on the active sites of ZIF-8, showing that there were both acidic and basic sites on the defects. It was illustrated that these active sites might contain low-coordinated metal atoms, and free N-moieties belonging to the imidazole linkers.

On the other hand, it has already been reported (Crabtree et al., 2007; Ivanchev et al., 1980) that the ring opening oligomerization of epoxides happens in the presence of Lewis acids and/or metal alkoxide. The main step is the capability of the catalysts to open the ring of epoxide by acting as Lewis acids to form an oxonium ion (Colclough et al., 1959) (Fig. 2). Subsequently, the activated epoxide carbon reacts with another epoxide molecule to produce polymers or oligomers.

It was discussed earlier that ZIF-8 contains Zn(II) acting as strong Lewis acids on its defects or on its surface. However, as shown in Table 1 (entry 1) zinc nitrate (consisting of Zn(II)) could not open the ring of epoxide. This observation proved that for the ring opening of epoxide, both of Lewis acid (Zn (II)) and the basic nitrogen of 2-methyl imidazole linkers cooperatively were able to open the ring of epoxide (Table 1-entry3) (illustrated in Fig. 2).

Regarding this mechanism and in order to evaluate the different catalytic activity observed for ZIF-8 and ZIF-67, the acidic and basic active sites of both catalysts were analyzed by NH_3 and CO_2 TPD measurements. Temperature program desorption (TPD) was reported previously as a suitable method for direct and precise measurement of the amount of acid or base sites in the cases of ZIFs and MOFs (Kuruppathparambil et al., 2016; Zhu et al., 2013; Tian et al., 2015). The results were summarized in Table S-3, in which the amount of acid and base sites of ZIF-8 and ZIF-67 were given. Clearly, the ZIF-8 synthesized by spray drying technique contains more active sites than ZIF-67, which consequently explains the higher catalytic activity of ZIF-8 for the ring opening cyclodimerization of epichlorohydrin.

4. Conclusions

In this work, the high catalytic performance of ZIF-8 and ZIF-67 for one-step cyclodimerization of epichlorohydrin was demonstrated. No solvents or co-catalyst were mandatory for this reaction to proceed. Other MOFs such as UiO-66 and MIL-100; the known active catalysts for the cycloaddition of carbon dioxide to epoxides, were examined for the cyclodimerization of epichlorohydrin as well. However, the results revealed that they are not active for the cyclodimerization in the absence of solvents and co-catalyst. Hence, this portrays the importance of unique properties of ZIF-8 and ZIF-67 as catalysts for this reaction. To the best of our knowledge, this is the first report of using MOFs as an active catalyst for oligomerization of epoxide.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.arabjc.2017.09.011>.

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