EDITORIAL

Polycarbonates and green chemistry
S. Guillaume and L. Mespouille, *J. Appl. Polym. Sci.* 2014,
DOI: 10.1002/app.40081

REVIEWS

Porous crystals as active catalysts for the synthesis of cyclic carbonates
M. Zhu and M. A. Carreon, *J. Appl. Polym. Sci.* 2014, **DOI: 10.1002/app.39738**

Renaissance of aliphatic polycarbonates: New techniques and biomedical applications
J. Xu, E. Feng and J. Song, *J. Appl. Polym. Sci.* 2014, **DOI: 10.1002/app.39822**

RESEARCH ARTICLES

Chemical modification of bisphenol A polycarbonate by reactive blending with ethylene carbonate
M. Colonna, C. Berti and M. Fiorini, *J. Appl. Polym. Sci.* 2014, **DOI: 10.1002/app.39820**

Synthesis and characterization of poly(ester carbonate)s by melt-phase interchange reactions of dihydroxy compounds with alkylene and arylene diphenyl dicarbonates containing ester groups
B. A. Sweileh, H. R. Al-Qalawi and H. A. Mohammad, *J. Appl. Polym. Sci.* 2014, **DOI: 10.1002/app.39904**

Terpolymerization of benzyl glycidyl ether, propylene oxide, and CO_2 using binary and bifunctional [rac-SalcyCo^{III}X] complexes and the thermal and mechanical properties of the resultant poly(benzyl 1,2-glycerol-co-propylene carbonate)s and poly(1,2-glycerol-co-propylene carbonate)s
H. Zhang and M. W. Grinstaff, *J. Appl. Polym. Sci.* 2014, **DOI: 10.1002/app.39893**

Synthesis of biodegradable high molecular weight polycarbonates from 1,3-trimethylene carbonate and 2,2-dimethyltrimethylene carbonate
M. Pastusiak, P. Dobrzynski, J. Kasperczyk, A. Smola and H. Janecze, *J. Appl. Polym. Sci.* 2014, **DOI: 10.1002/app.40037**

Propylene carbonate as a source of carbonate units in the synthesis of elastomeric poly(carbonate–urethane)s and poly(ester–carbonate–urethane)s
M. M. Mazurek, P. G. Parzuchowski and G. Rokicki, *J. Appl. Polym. Sci.* 2014, **DOI: 10.1002/app.39764**

Synthesis and properties of biodegradable multiblock poly(ester-carbonate) comprising of poly(L-lactic acid) and poly(butylene carbonate) with hexamethylene diisocyanate as chain-extender
J. Wang, L. Zheng, C. Li, W. Zhu, D. Zhang, G. Guan and Y. Xiao, *J. Appl. Polym. Sci.* 2014, **DOI: 10.1002/app.39158**

Effect of interfacial tension on the cell structure of poly(methyl methacrylate)/bisphenol A polycarbonate blends foamed with CO_2
P. Gong and M. Ohshima, *J. Appl. Polym. Sci.* 2014, **DOI: 10.1002/app.39228**

Flame retardancy and thermal properties of carboxyl-containing polysiloxane derivatives in polycarbonate
R. Song, L. Chang and B. Li, *J. Appl. Polym. Sci.* 2014, **DOI: 10.1002/app.39814**

**Clay-induced degradation during the melt reprocessing of waste polycarbonate**
M. U. de la Orden, D. P. C. Muñoz, V. Lorenzo and J. M. Urreaga, *J. Appl. Polym. Sci.* 2014, **DOI: 10.1002/app.39997**

Preparation and properties of polycarbonate microspheres containing tetanus toxoid vaccine
B. Hu, X.-J. Ke, G.-P. Yan, R.-X. Zhuo, Y. Wu, C.-L. Fan and Y.-J. Liu, *J. Appl. Polym. Sci.* 2014, **DOI: 10.1002/app.40048**

New thermogelling poly(ether carbonate urethane)s based on pluronics F127 and poly(polytetrahydrofuran carbonate)
X. J. Loh, H. X. Gan, H. Wang, S. J. E. Tan, K. Y. Neoh, S. S. J. Tan, H. F. Diong, J. J. Kim, W. L. S. Lee, X. Fang, O. Cally, S. S. Yap, K. P. Liong and K. H. Chan, *J. Appl. Polym. Sci.* 2014, **DOI: 10.1002/app.39924**
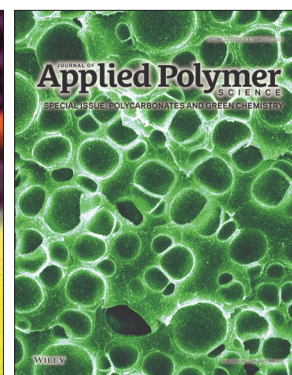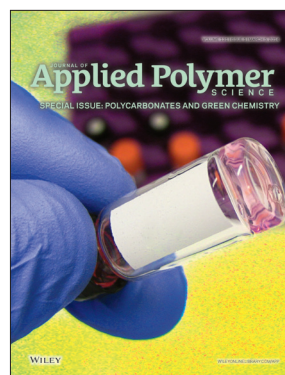
Porous Crystals as Active Catalysts for the Synthesis of Cyclic Carbonates

Minqi Zhu, Moises A. Carreon

Department of Chemical Engineering, University of Louisville, Louisville, Kentucky 40292
Correspondence to: M. A. Carreon (E-mail: macarr15@louisville.edu)

ABSTRACT: The utilization of CO_2 as a renewable raw material for the production of chemicals is an area of great societal importance. In particular, the catalytic conversion of CO_2 into cyclic carbonates, which are useful chemical intermediates used for the production of plastics and organic solvents, represents an appealing approach for the efficient use of CO_2. Microporous crystals, such as zeolites and metal organic frameworks, and ordered mesoporous phases have emerged as novel porous materials that combine highly desirable properties, such as uniform pores on the microscale and mesoscale, high surface areas, flexible chemistries, and exceptional thermal and chemical stability; this makes them ideal candidates for catalytic applications. In this review, representative examples demonstrating the catalytic ability of these porous materials for the synthesis of cyclic carbonates from CO_2 are presented. The fundamental structure/catalysis relationships of these porous phases in the conversion of CO_2 into cyclic carbonates are discussed. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39738.

INTRODUCTION

Cyclic carbonates are used as platform intermediates for electrolytes in lithium-ion batteries, green solvents, and polycarbonates.[1,2] Currently, cyclic carbonates (including polycarbonates) are manufactured with the highly toxic phosgene.[2] A green and alternative route for the synthesis of cyclic carbonates is the insertion reaction of CO_2 into the C—O bond of an epoxide (Figure 1). This route represents a very useful approach for effectively using CO_2 for the conversion of chemicals. The commercial production of cyclic carbonates uses nonexpensive catalysts, such as homogeneous quaternary ammonium salts.[3,4] However, the reaction in these commercial processes is typically carried out at elevated temperatures (453–473 K) and high pressures (50–80 bar). Therefore, there is a need and motivation to develop more efficient heterogeneous catalysts for the conversion of CO_2 into cyclic carbonates.

Organoantimony halides, zinc and aluminum complexes, and dialkyltin methoxide can catalyze this cycloaddition reaction.[5,6] However, these materials are toxic and sensitive to water and air; this causes handling problems and requirements for high temperatures and pressures for high conversion and selectivity. Nontoxic catalysts, including phthalocyanines,[7] porphyrines,[8–10] and Schiff bases,[11,12] catalyze this reaction with moderate to high carbonate yields but require the presence of a cocatalyst. Mg/Al oxide based catalysts have also demonstrated the ability

to catalyze the cycloaddition reaction.[13] However, a high loading of catalyst and a long reaction time were needed to observe reasonable carbonate yields. Ionic liquids (mainly, quaternary-ammonium-, phosphonium-, imidazolium-, or pyridinium-based cations with inorganic counter anions) have been successfully used for the cycloaddition of CO_2 to epoxides.[14–20] Typically, moderate to high conversions of the epoxide under mild conditions have been observed in the presence of these ionic liquids.

Microporous crystals, including zeolites and metal organic frameworks (MOFs), and mesoporous ordered oxides possess many desirable properties, which make them appealing for cycloaddition reactions. In general, these porous materials display (1) chemical and thermal stability; (2) moderate to high CO_2 uptakes; (3) an open porous structure for improved mass transfer; (4) accessible pore volumes; (5) acid sites, which are known as actives sites for cycloaddition reactions; and (6) high specific surface areas. Figure 2 shows representative structures of zeolites, MOFs, and mesoporous oxides. In the next paragraphs, we discuss relevant structural features of each of these porous materials. Then, we discuss several representative examples that demonstrate the catalytic ability of these porous materials for the synthesis of cyclic carbonates. Finally, the fundamental structure/catalysis relationships of these porous phases in the conversion of CO_2 into cyclic carbonates are highlighted.
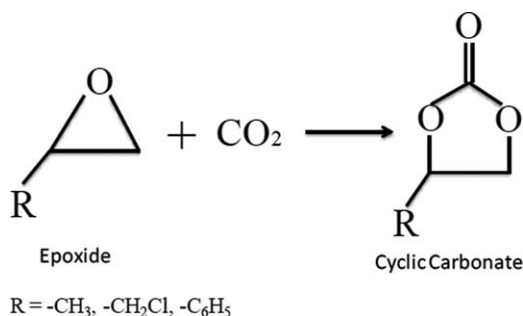
Figure 1. Insertion of carbon dioxide into the oxirane ring of an epoxide for the synthesis of cyclic carbonates.

ZEOLITES AND MESOPOROUS OXIDES: STRUCTURAL CHARACTERISTICS AND CATALYTIC PERFORMANCE

Zeolites (microporous crystalline aluminosilicate or silica polymorphs forming three-dimensional frameworks with uniformly sized pores of molecular dimensions) and ordered mesoporous materials (those exhibiting pore sizes in the ~2–50-nm range) are promising phases for the catalysis of the conversion of CO_2 into cyclic carbonates. For example, zeolite beta was found to have high catalytic activity in the cycloaddition reaction of CO_2 to epoxides to form cyclic carbonates.[21] Zeolite beta is a type of aluminosilicate molecular sieve consisting of a three-dimensional channel system composed by straight and zigzag channels with 12-membered rings as the minimum constricting apertures.[22] It has a large surface area of at least 600 m^2/g,[23] and the 12-membered ring has dimensions of 0.66×0.67 nm^2; however, the resulting pore size is 0.56×0.56 nm^2 because of the tortuous channel configuration.[24]

Zeolite beta exhibited high activity for catalyzing different oxiranes, such as epichlorohydrin, propene oxide, styrene oxide, and *n*-butene oxide, to cyclic carbonates with CO_2 as a raw material.[21] More importantly, this reaction did not require any cocatalyst or solvent. High yields of cyclic carbonates were obtained under mild reaction conditions (120°C and 6.9 bar). The zeolite beta catalyst maintained its excellent catalytic activity even after eight cycles; this confirmed the typical remarkable zeolite chemical and thermal stability. Researchers found that in the case of the as-synthesized catalyst, the template ion Et_4N^+ (which is an active alkyl group in one of the homogeneous quaternary ammonium halide catalysts) may have been responsible

for the superior catalytic activity of the as-synthesized zeolite beta. In addition, the as-synthesized zeolite beta also had a high adsorption of oxirane and a high amount of activated CO_2. Hence, the greater availability of activated reactant molecules could have also been another possible reason for the superior activity of the as-synthesized form of zeolite beta. Interestingly, when the organic template was removed by calcination, both the catalytic activity and selectivity for cyclic carbonates were drastically reduced.

MCM-41 (Mobil Crystalline Material (MCM) consisting on hexagonal amorphous mesoporous framework) is mesoporous material that was reported to catalyze the cycloaddition of CO_2 into epoxides to form cyclic carbonates.[25] It was first synthesized by Kresge et al.[26] in 1992. In its structure, amorphous silica forms hexagonal tubes with uniformly sized mesopores (pore diameter ≈3 nm). The width of the tubes can be controlled to be within 2 to 10 nm with template molecules of different lengths.[27] The tubes connect to each other through the sharing of the silica walls. MCM-41 has properties such as a high thermal and hydrothermal stability, uniform size and shape of the pores, and large surface area (~1000 m^2/g).[28] It is an interesting candidate for use as a catalyst for its thermal and hydrothermal stability, uniform size and shape of the pores, and large surface areas.[29–32] For the cycloaddition reaction, it was found that when MCM-41 was used as a catalyst, the carbonate yield increased with increasing temperature and pressure until it reached a maximum. The optimal conditions for higher carbonate yield were found to be 120°C and 6.9 bar. Noticeably, this reaction achieved high carbonate yields with less catalyst than most reported heterogeneous catalysts. The catalytic ability of MCM-41 decreased after the fifth cycle. According to X-ray diffraction patterns of recycled MCM-41, the catalyst started to lose its crystallinity after the fifth cycle; this could have been the reason for the reduced catalytic performance. It is also important to highlight that the catalyst was not calcined. The as-synthesized MCM-41 contained cetyltrimethylammonium cations as the template, which were likely to act as active sites for the cycloaddition reaction.

Titanium silicalite 1 (TS-1) was also studied for its catalytic ability in the synthesis of cyclic carbonate.[33] It is a crystalline zeotype material in which tetrahedral $[TiO_4]$ and $[SiO_4]$ units were arranged in an MFI (a typical zeolite topology) structure. TS-1 shows a three-dimensional system of channels having
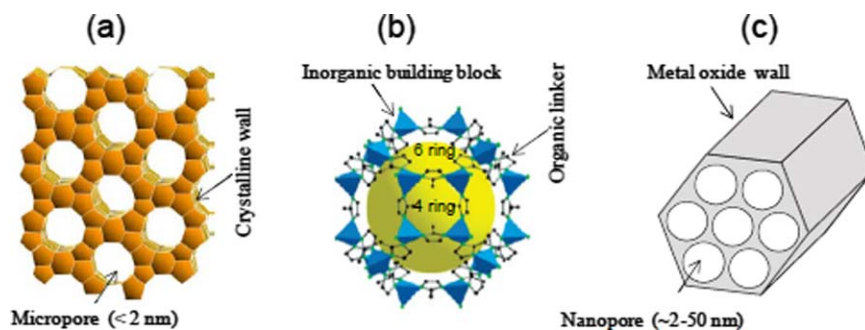
Figure 2. Typical structural representations of the (a) zeolite, (b) MOF, and (c) mesoporous oxide. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

molecular dimensions of 5.1–5.6 Å, which constitute the zeolitic micropores of the material. Two-channel systems (with a sinusoidal channel and a straight channel) are present in the TS-1 structure. However, TS-1 suffers from intercrystalline diffusion limitations because of its relatively small micropore size. To overcome this difficulty, mesoporous TS-1 with a pore size larger than 10 nm was synthesized by Lin et al.[34] The surface area of the meso TS-1 was in the range of 170–200 m^2/g.[35] It was improved to 649 m^2/g when a different synthesis route was used.[36] In the cycloaddition experiment, epoxides, such as epichlorohydrin, propylene oxide, and styrene oxide, were used as substrates to react with CO_2. High carbonate yields were observed at low temperature and pressure. The yield of the cyclic carbonate was greatly enhanced by the presence of a cocatalyst in the reacting solution. With TS-1 alone, the conversion of epichlorohydrin was 18.2 mol %, with a chloropropene carbonate selectivity of 87.4 mol % (120°C and 6.9 bar). The addition of N,N-dimethylaminopyridine (DMAP) enhanced the turnover frequency number by about five times. The effect of the temperature and pressure to the TS-1/DMAP catalyst system was studied by the cycloaddition of CO_2 to epychlorohydrin. The complete conversion of epichlorohydrin was achieved at 140–160°C with a high chloropropene carbonate selectivity. The conversion of epichlorohydrin increased with pressure and above 13.8 bar; however, the chloropropene carbonate yield decreased because of the formation of side products. Under the same conditions (120°C and 6.9 bar for 4 h), epichlorohydrin displayed better conversion and selectivity over the TS-1/DMAP catalyst system than those of styrene oxide and propylene oxide. The authors claimed that there was a synergic effect between that catalyst and the cocatalyst.[33] The nucleophilicity of the nitrogen or phosphorus atom (in the cocatalyst) is augmented by the electrophilic interaction of the Ti^{4+} ions with the epoxide. The synergism is lower with some cocatalysts, such as Ph_3P, DMAP, and pyridine, because the active complex formed during the cycloaddition reaction is larger than the pore diameter of TS-1, and hence, the complex may not form inside the TS-1 pores. With these bulkier cocatalysts, the reaction probably takes place mainly at titanium sites on the external surface of the particles, and hence, lower activities were observed.

Silico alumino phosphate molecular sieve-56 (SAPO-56) was evaluated for its catalytic activity in the conversion of epichlorohydrin to chloropropene carbonate by our group.[37] SAPO-56 is a crystalline microporous silicoaluminophosphate in which silicon substitutes for some of the phosphorus and aluminum atoms in the structural framework.[38] The AFX (a typical zeolite topology) topology of SAPO-56 is characterized by a three-dimensional structure with pore cages arranged in interconnected networks, with window (pore size) sizes of about 3.4 × 3.6 Å.[39] This leads to a surface area of about 400–450 m^2/g.[40] We found that yields to chloropropene carbonate almost doubled when smaller SAPO-56 crystals were used in the cycloaddition reaction. More specifically, when 3–4-μm crystals were used, the yield to chloropropene carbonate was 84.8%, whereas the yield to the carbonate was only 42.2% when crystals of about 50 μm were used. We proved experimentally that smaller crystals led to higher CO_2 uptakes and promoted the preferential adsorption of CO_2 in the surface of the

catalyst. In fact, we demonstrated that the yield of chloropropene carbonate was correlated with the CO_2 uptake. In addition, silica nanospheres present in the surface of the smaller SAPO-56 crystals may play a role as specific surface sites for the cycloaddition reaction.

The siliceous mesoporous material SBA-15 (mesoporous silica material with narrow pore size distribution between 5nm and 15 nm) possesses a regular two-dimensional array of tubular channels.[41,42] In comparison with other regular mesoporous materials, SBA-15 can be prepared with larger pores; this results in a more stable structure because of the thicker pore walls. It has an extremely high surface area (>700 m^2/g)[43] and well-defined pore size, which can be adjusted over a large range (2–20 nm). However, its catalytic activity is limited in the absence of a Lewis acid metal.[44] To overcome this limitation, the Ti-loaded hexagonal mesoporous SBA-15 (Ti-SBA-15) was synthesized for this purpose. In this particular example, the catalytic abilities of SBA-15 and Ti-SBA-15 were investigated.[44] Epichlorohydrin, propene oxide, and styrene oxide were used in the cycloaddition reaction. SBA-15 was weakly active under the studied reaction conditions. Under the same conditions, Ti-SBA-15 displayed a better catalytic ability than bare SBA-15 (~15 and 9%, respectively). The studies revealed that the Ti^{4+} ions increased the catalytic activity by enhancing the adsorption of the epoxide substrates. Increasing the surface concentrations of either CO_2 (by increasing the partial pressure of CO_2) or epoxides (by increasing the concentration of Lewis acid Ti^{4+} ions) enhanced the catalytic activity. Table I summarizes the relevant zeolites and mesoporous materials that have been used as catalysts for the synthesis of cyclic carbonates via the cycloaddition of epoxides and CO_2.

MOFS: STRUCTURAL CHARACTERISTICS AND CATALYTIC PERFORMANCE

Several MOFs have been effectively used as catalysts in the cycloaddition of CO_2 into epoxides to form cyclic carbonates. For example, zeolitic imidazolate framework-8 (ZIF-8) is a highly desirable material for this purpose. ZIF-8 is a microporous crystalline material, in which Zn atoms are linked through N atoms by ditopic imidazolate (Im^-) or functionalized Im^- links to form neutral frameworks and to provide tunable nanosized pores formed by four- and six-membered rings. ZIF-8 has large pores of 1.16 nm that are accessible through small apertures of 0.34 nm and a cubic space group (I-43 m) with unit cell dimensions of 1.632 nm.[7,8,11]

Previously, our group studied the catalytic activity of ZIF-8 in the conversion of CO_2 to chloropropene carbonate[45] and styrene carbonate.[46] In both reactions, no cocatalysts or solvents were required. In the cycloaddition reaction of CO_2 to epichlorohydrin, ZIF-8 catalysts displayed high epichlorohydrin conversions and moderate to high selectivities to chloropropene carbonate at reaction temperatures as low as 70°C. The conversion of epichlorohydrin increased as the temperature increased, reaching a maximum of about 100% at 100°C, whereas the selectivity to chloropropene carbonate decreased. The highest chloropropene carbonate yield was observed at 80°C. However,

Applied Polymer SCIENCE

Table I. Representative Zeolites and Ordered Mesoporous Materials Used as Catalysts for the Synthesis of Cyclic Carbonates

Catalyst	Surface area (m^2/g)	Epoxide	Main product	Reaction conditions	Solvent	Cocatalyst	Yield to carbonate (%)	Reference
Zeolite beta	520	Propene oxide	Propene carbonate	120°C, 6.9 bar, 5 h	CH$_3$CN	None	100	21
Zeolite beta	520	Styrene oxide	Styrene carbonate	120°C, 6.9 bar, 8 h	CH$_3$CN	None	96.3	21
Zeolite beta	520	Epichlorohydrin	Chloropropene carbonate	120°C, 6.9 bar, 3 h	DMF	None	97.6	21
Zeolite beta	520	n-Butane oxide	n-Butane carbonate	120°C, 6.9 bar, 5 h	CH$_3$CN	None	67	21
Zeolite beta	451	Epichlorohydrin	Chloropropene carbonate	100°C, 7 bar, 4 h	None	None	81	51
TS-1	400	Epichlorohydrin	Chloropropene carbonate	160°C, 6.9 bar, 4 h	CH$_2$Cl$_2$	DMAP	91.4	33
TS-1	400	Epichlorohydrin	Chloropropene carbonate	120°C, 6.9 bar, 4 h	CH$_2$Cl$_2$	Pyridine	67.8	33
TS-1	400	Epichlorohydrin	Chloropropene carbonate	120°C, 6.9 bar, 4 h	CH$_2$Cl$_2$	Bu$_4$NBr	51.7	33
TS-1	400	Epichlorohydrin	Chloropropene carbonate	120°C, 6.9 bar, 4 h	CH$_2$Cl$_2$	Bu$_4$PBr	66.7	33
TS-1	400	Epichlorohydrin	Chloropropene carbonate	120°C, 6.9 bar, 4 h	CH$_2$Cl$_2$	Ph$_3$P	18.5	33
SAPO-56	400–450	Epichlorohydrin	Chloropropene carbonate	100°C, 10 bar, 4 h	None	None	84.8	37
MCM-41	972	Epichlorohydrin	Chloropropene carbonate	120°C, 6.9 bar, 3 h	DMF	None	100	25
MCM-41	972	Propene oxide	Propene carbonate	120°C, 6.9 bar, 5 h	CH$_3$CN	None	90.1	25
MCM-41	972	Styrene oxide	Styrene carbonate	120°C, 6.9 bar, 8 h	None	None	89.2	25
MCM-41	972	n-Butane oxide	n-Butane carbonate	120°C, 6.9 bar, 5 h	CH$_3$CN	None	86.3	25
SBA-15	871	Epichlorohydrin	Chloropropene carbonate	120°C, 6.9 bar, 4 h	None	None	9.3	44
SBA-15	390	Epichlorohydrin	Chloropropene carbonate	100°C, 10 bar, 4 h	None	None	10	51
Ti-SBA-15	40–119	Epichlorohydrin	Chloropropene carbonate	120°C, 6.9 bar, 4 h	CH$_3$CN	None	14.7	44

the catalyst lost its activity after one use, probably because of the combination of high temperature, high pressure, and the poisoning/blocking of the pores by the carbonaceous product.

In the experiment of converting CO_2 and styrene oxide to styrene carbonate, the ZIF-8 crystals displayed catalytic activity even at temperatures as low as 50°C and yielded styrene carbonate as the only product at temperatures of 100°C or lower. Polymerization took place when the reaction temperature was above 110–115°C. At 80°C and 7 bar for 5 h, the yield to styrene carbonate only decreased slightly from about 39.4% (fresh) to about 37% (recycled). In addition, we found that the styrene carbonate yield increased with increasing temperature and increasing time within a certain range (<9 h and ≤100°C). The highest yield (>70%) was observed at 100°C and 7 bar for 8.5 h.

Lewis acid sites are known to catalyze the reaction of CO_2 with epoxides to give cyclic carbonates and other precursors of polycarbonate.[21,44,47] The Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy of adsorbed pyridine revealed the presence of both Brönsted and Lewis acid sites. The basic sites were associated with the imidazole groups in the ZIF-8 structure, which tend to attract more CO_2 to be trapped in the vacant space inside the pores. It is likely that solids having both Lewis acid sites and basic sites on their surface will have enhanced activity for this cycloaddition reaction. Therefore, our group postulated that ZIF-8 displayed enhanced catalytic activity because of its high CO_2 uptake, and the presence of Lewis acid sites in its framework. It is likely that the Lewis acid sites (associated with Zn ions) played an important role in catalyzing the cycloaddition of CO_2 to epichlorohydrin. In addition, the polar nature of ZIF-8 (i.e., the presence of the basic nitrogen atoms of the imidazole ligand) favored the binding and activation of the polar carbon–oxygen bonds of CO_2. The presence of both the Zn(II) acid sites and the N basic moieties (in adjacent locations) from the imidazole linker in ZIF-8 probably facilitated the adsorption of CO_2 on the solid surface and its further conversion to the carbonate.

MOF-74 (Metal Organic Framework-74) is another microporous material that has been used as a catalyst in the cycloaddition reaction of CO_2 and epoxides. The crystal structure of MOF-74 is built around a one-dimensional honeycomb motif with pores 1.1–1.2 nm in diameter and helical chains of edge-condensed metal–oxygen coordination octahedrals located at the intersections of the honeycomb, in which the metal is square–pyramidally coordinated. One of the six oxygen atoms coordinated to the metal comes from a solvent water molecule, and the MOF-74 structure develops coordinatively unsaturated (open) metal sites in Lewis acidity upon the removal of the solvent molecules attached to the metal sites by heating *in vacuo*.[48] Co-MOF-74 and Mg-MOF-74 can be prepared by the replacement of the typical zinc atoms with cobalt and magnesium in the MOF-74 structure. Both of these two MOFs have a high surface area (∼1300 and 1500 m^2/g, respectively, for Co-MOF-74 and Mg-MOF-74)[48,49] and large pore volume (11–12 Å).[50]

Co-MOF-74 demonstrated excellent catalytic performance in the cycloaddition of CO_2 to styrene oxide at 2.0 MPa and 100°C with close to 100% selectivity to carbonate.[48] This partic-

ular MOF displayed a surface area of 1300 m^2/g and a high CO_2 adsorption capacity (288 mg/g). No appreciable effect of the catalyst particle size was detected, and Co-MOF-74 could be reused three times without a loss of catalytic activity and with no structural deterioration. The authors suggested that the six oxygen atoms (five oxygen atoms from the ligand and one from H_2O used as the solvent) located around cobalt atoms functioned as a base, whereas the open metal cobalt functioned as a Lewis acid.[48] The Lewis base site activated CO_2, which then attacked styrene oxide adsorbed on the Lewis acid site.

The catalytic performance of Mg-MOF-74 was also investigated for the cycloaddition reaction.[49] Like Co-MOF-74, Mg-MOF-74 also demonstrated excellent catalytic performance in the cycloaddition of CO_2 to styrene oxide under relatively mild reaction conditions (2.0 MPa and 100°C) with close to 100% selectivity to carbonate. Mg-MOF-74 could be reused three times without a loss of catalytic activity and with no structural deterioration. The authors identified Lewis base and Lewis acid sites in the MOF structure.[49] The former activated CO_2, which subsequently attacked the styrene oxide adsorbed on the latter. Although most heterogeneous catalysts, despite a strongly acidic nature, need a cocatalyst, such as a quaternary ammonium salt to compensate for the inherent problem of low basicity, Mg-MOF-74 functioned exceptionally well without additives. The authors proposed that the five oxygen atoms from the organic linkers located around magnesium atoms could function as a base despite low basicity, whereas open metal magnesium is well known to function as a Lewis acid site.

The catalytic activity of $Cu_3(BTC)_2$ (Cu based microporous metal organic framework) was demonstrated by our group in the synthesis of chloropropene carbonate from CO_2 and epichlorohydrin.[51] $Cu_3(BTC)_2$ has a three-dimensional twisted boracite framework composed of binuclear copper paddle-wheel units bridged by three-connecting benzene-1,3,5-tricarboxylate (btc) ligands.[52] The framework contains three different types of pores. One unit cell includes eight such small pores. The octahedral holes of an face centered cubic (fcc) structure are a little larger, the inner surface of which is constructed from benzene rings of the trimesic acid with the sixfold axis of the rings pointing toward the pore center. The third type of pore is even larger, having the hydrogen atom of the trimesic linker pointing toward the pore center. Only the third type of pores has open copper coordination sites pointing into the pore. The pore diameter for these three types of pores are 4.9, 10.5, and 12.2 Å, respectively.[53] This MOF has a high Brunauer-Emmett-Teller (BET) surface area in the 1200–2100 m^2/g range.[54]

No solvents or cocatalysts were required for this cycloaddition reaction. The catalysts displayed moderate epoxide conversions and moderate selectivities to chloropropene carbonate at 100°C. $Cu_3(BTC)_2$ was catalytically selective to chloropropene carbonate only at 100°C. Only diols of the epoxide and dimers of epichlorohydrin were observed below 100°C. The chloropropene carbonate yield at 100°C was about 33%. The yield to chloropropene carbonate decreased from about 33% to about 23% when it was reused after the first reaction. The X-ray diffraction of the recycled catalyst showed that the $Cu_3(BTC)_2$ structure

was preserved; however, its framework had a greater degree of local structural disorder. Therefore, the reduced activity of recycled catalyst could be attributed, in part, to this local structural disorder and to active site/pore blocking by residual carbonaceous deposits formed during the reaction.

We proposed that the Lewis acid copper(II) sites played an important role in catalyzing the cycloaddition of CO_2 to epichlorohydrin. In addition, the partial positive charges on the unsaturated copper metal sites of $Cu_3(BTC)_2$ promoted the binding and activation of the polar carbon–oxygen bonds of carbon dioxide; this resulted in high CO_2 adsorption capacities. In fact, unsaturated cooper metal sites have been identified by theoretical and experimental investigations as CO_2 adsorption sites.[55] The CO_2 adsorption capacities for $Cu_3(BTC)_2$ ranged from 8.0 to 12.7 mol/kg at room temperature and 15 bar.[56–58] Therefore, the copper acid sites promoted the adsorption of carbon dioxide on the solid surface and its further conversion to the carbonate.

Chromium terephthalates (e.g., Cr-MIL-101 (chromium based metal organic frameworks) and Fe-MIL-101 (iron based metal organic frameworks)) were reported to effectively catalyze the cycloaddition of CO_2 to epoxides to yield cyclic carbonates.[59,60] These MOFs have a unique mesoporous zeotype architecture with mesoporous cages and microporous windows, which renders a giant cell volume and huge surface area. They are built up by a hybrid supertetrahedral building unit, which consists of Cr_3O/Fe_3O trimers and 1,4-benzenedicarboxylic acids.[61] The supertetrahedra are microporous with an 8.6-Å free aperture. The four vertices and six edges of the tetrahedra are occupied by the trimers and organic linkers, respectively. MIL-101 has a free diameter of 29 Å, which is accessible through a pentagonal window with a 12-Å aperture, and a large cage with a free diameter of 34 Å, which is accessible through both hexagonal and pentagonal windows with a 14.7×16 Å^2 aperture.[62] Both materials possess huge surface areas (typically, 3200–3900 and 1.4–2.1 m^2/g, respectively).[61]

The catalytic performance of Cr-MIL-101 in the coupling reaction of epoxides with CO_2 produced cyclic carbonates under solvent-free conditions.[59] At 8–100 atm of CO_2 and 70–80°C, moderate yields of the cyclic carbonates were observed. Interestingly, the reaction proceeded effectively under milder conditions (8 atm and 25°C) when tetrabutylammonium bromide (TBABr) was added as a cocatalyst to Cr-MIL-101. In the Cr-MIL-101/TBABr catalytic system, the reaction rate increased with increasing amounts of both catalyst and cocatalyst and with increasing reaction temperature, and the high level of selectivity (90–95%) was retained. Under optimal reaction conditions, propylene and styrene carbonates were obtained with yields of 82 and 95%, respectively. However, the catalytic activity decreased after several reuses because of the loss of the Cr-MIL-101 regular porous structure, pore blockage, and poisoning of active sites with the reaction products.

The authors suggested that Cr-MIL-101 was an effective catalyst for this reaction because it possessed an extremely high surface area and pore volume; was resistant to air, water, and common solvents; and had a fairly good thermal stability (up to

300°C).[59] Furthermore, this MOF was able to adsorb large amounts of gases, including CO_2. They proposed that the epoxide first coordinated on a metal center; this was followed by epoxide ring opening under the action of TBABr. Then, the oxygen anion of the open ring (nucleophilic) interacted with CO_2 (electrophilic) to form the carbonate anion, which was converted into the final cyclic carbonate.

Fe-MIL-101 was active and highly selective in the synthesis of propylene (yield to propylene carbonate = 87.3%) and styrene carbonates (yield to styrene carbonate = 81.84%).[60] The MIL-101/TBABr system showed an excellent catalytic ability for the cycloaddition reaction of CO_2 and epoxides. The authors suggested that Fe-MIL-101 could be a suitable catalyst because it is a functional porous coordination polymer that possesses a unique combination of properties (e.g., extremely high surface areas, crystalline open structures, and tunable pore size and functionality). Fe-MIL-101 is composed of isolated metal atoms or clusters linked by polydentate organic ligands; this results in a rigid porous network. An important feature of Fe-MIL-101 is a high content of active metal sites; all of them are uniformly spatially distributed and are accessible for reagents, provided the size of pore entrances allows the penetration of the reactant molecules.

Another reported catalyst for this type of reaction is MOF-5. In the MOF-5 structure, octahedral $Zn_4O(CO_2)_6$ clusters are linked by phenylene rings (from H_2BDC) to form a cubic structure with open pores. The core of the cluster consists of a single O atom bonded to four Zn atoms to form a regular Zn_4O tetrahedron. Each edge of each Zn tetrahedron is then capped by a —CO_2 group to form a $Zn_4(O)(CO_2)_6$ cluster.[63] The thermal stability of MOF-5 is as high as 350°C.[64] It also has a very porous and crystalline structure with a high surface area (which varies from 600 to 4000 m^2/g, depending on the synthesis method)[65] and a pore size of 0.7–0.8 nm.[66]

The catalytic activity of MOF-5 was studied in the synthesis of various cyclic carbonates under mild conditions in the presence of various quaternary ammonium salts.[67] No organic solvent was necessary in the reaction. MOF-5 displayed an excellent ability to catalyze the cycloaddition reaction when n-Bu_4NBr was added as a cocatalyst. The yields to propene carbonate were as high as 97.6% under 2 MPa and 50°C. No decrease in the catalytic activity was observed after three uses (the catalytic activity was 96% for both the second and third reactions). Both the unique structure of MOF-5 and the Lewis acid sites inside the structure contributed to the conversion of the epoxides to the cyclic carbonates. The authors proposed that the coupling reaction was initiated by the coordination of the Zn_4O clusters in MOF-5 as a Lewis acid site with the oxygen atom of the epoxide, and this step could activate the epoxy ring.[67] Second, the Br^- generated from the n-BuN_4Br attacked the less hindered carbon atom of the coordinated epoxides; this was followed by the ring-opening step. Then, the oxygen anion of the opened epoxy ring interacted with the CO_2, and this could form an alkylcarbonate anion, which was converted into the corresponding cyclic carbonate through the ring-closing step. The synergistic effect of MOF-5 and n-BuN_4Br was believed to be the main

Table II. Representative MOFs Used as Catalysts for the Synthesis of Cyclic Carbonates

Catalyst	Surface area (m^2/g)	Epoxide	Main product	Reaction conditions	Solvent	Cocatalyst	Yield to carbonate (%)	Reference
Co-MOF-74	1314	Styrene oxide	Styrene carbonate	100°C, 2 MPa, 4 h	Chlorobenzene	None	96	48
Mg-MOF-74	1525	Styrene oxide	Styrene carbonate	100°C, 2 MPa, 4 h	Chlorobenzene	None	96	49
Mg-MOF-74	1525	Styrene oxide	Styrene carbonate	100°C, 2 MPa, 4 h	Chlorobenzene	None	94	73
$Cu_3(BTC)_2$	995	Epichlorohydrin	Chloropropene carbonate	100°C, 7 bar, 4 h	None	None	33	51
$Cu_3(BTC)_2$	995	Styrene oxide	Styrene carbonate	100°C, 2 MPa, 4 h	Chlorobenzene	None	48	73
IRMOF-3	2580	Styrene oxide	Styrene carbonate	100°C, 2 MPa, 4 h	Chlorobenzene	None	33	73
Cr-MIL-101	3200-3900	Propene oxide	Propene carbonate	25°C, 8 bar, 24 h	None	TBABr	81.9	60
Cr-MIL-101	3200-3900	Styrene oxide	Styrene carbonate	25°C, 8 bar, 48 h	None	TBABr	95.1	60
Cr-MIL-101	3200-3900	Cyclohexene oxide	Cyclohexene carbonate	25°C, 8 bar, 64 h	None	TBABr	0.5	60
Cr-MIL-101	3270	Styrene oxide	Styrene carbonate	25°C, 8 atm, 48 h	None	TBABr	95	59
Cr-MIL-101	3270	Propene oxide	Propene carbonate	25°C, 8 atm, 24 h	None	TBABr	82	59
Cr-MIL-101	3270	Cyclohexene oxide	Cyclohexene carbonate	25°C, 8 atm, 64 h	None	TBABr	5	59
Fe-MIL-101	3200-3900	Propene oxide	Propene carbonate	25°C, 8 bar, 24 h	None	TBABr	87.3	60
Fe-MIL-101	3200-3900	Styrene oxide	Styrene carbonate	25°C, 8 bar, 54 h	None	TBABr	81.8	60
MIL-101	3098	Styrene oxide	Styrene carbonate	100°C, 2 MPa, 4 h	Chlorobenzene	None	63	73
MOF-5	—	Propylene oxide	Propylene carbonate	50°C, 6 MPa, 4 h	None	n-Bu$_4$NBr	97.6	67
MOF-5	—	Propylene oxide	Propylene carbonate	90°C, 6 MPa, 2 h	None	KI	98	68
MOF-5	—	Propylene oxide	Propylene carbonate	90°C, 6 MPa, 2 h	None	KI/K$_2$CO$_3$	98	68
MOF-5	—	1,2-Epoxy-3-phenoxypropane	Phenoxymethyl ethylene carbonate	90°C, 6 MPa, 2 h	None	KI	97	68
MOF-5		Epichlorohydrin	Chloropropene carbonate	90°C, 6 MPa, 4 h	None	KI	94	68
MOF-5		Styrene oxide	Styrene carbonate	90°C, 6 MPa, 7 h	None	KI	95	68
MOF-5		Cyclohexene oxide	Cyclohexene carbonate	90°C, 6 MPa, 24 h	None	KI	20	68
MOF-5		Styrene oxide	styrene carbonate	50°C, 0.1 MPa, 3 h	None	n-Bu$_4$NBr	92	67
MOF-5	3208	Styrene oxide	Styrene carbonate	100°C, 2 MPa, 4 h	Chlorobenzene	None	1	73
UIO-66	970	Styrene oxide	Styrene carbonate	100°C, 2 MPa, 4 h	Chlorobenzene	None	94	73
ZIF-8	1173	Epichlorohydrin	Chloropropene carbonate	80°C, 7 bar, 4 h	None	None	43.7	45
ZIF-8	~860	Styrene oxide	Styrene carbonate	100°C, 7 bar, 8.5 h	None	None	72	46
ZIF-8	1173	Epichlorohydrin	Chloropropene carbonate	100°C, 7 bar, 4 h	None	None	33	51
ZIF-8	1602	Styrene oxide	Styrene carbonate	100°C, 2 MPa, 4 h	Chlorobenzene	None	11	73
MIXMOF	~800	Propylene oxide	Propylene carbonate	160°C, 2.2.1 (CO$_2$: PO), 3 h	None	NEt$_4$Br	89	74
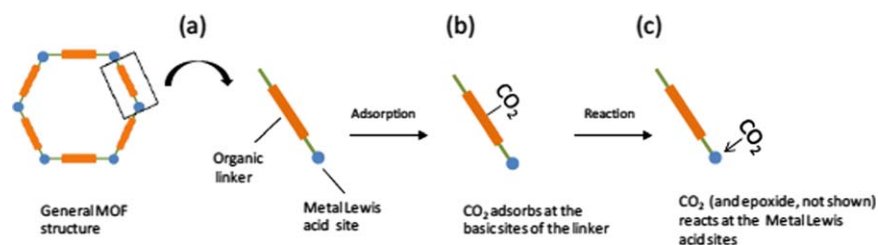
Figure 3. (a) General MOF structure, (b) CO_2 adsorbing at the basic organic unit sites, and (c) adsorbed CO_2 (together with the epoxide) reacting at the metal Lewis acid sites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reason for the high catalytic activity of the catalytic system under mild conditions. The same group reported MOF-5/KI as an effective catalyst for the cycloaddition of CO_2 and propene oxide to produce propene carbonate.[68]

MOF UIO-66 (zirconium containing porous solid) has a crystal structure with one octahedral cage and two adjacent tetrahedral cages forming a cubic unit.[69] The vertex is based on a $Zr_6O_4(OH)_4$ octahedron, which forms lattices by 12-fold connection through a 1,4-benzene dicarboxylate (BDC) linker.[70] The octahedral and tetrahedral have cavities of 11 and 8 Å, which are accessible via triangular windows of 5–7 Å.[71] It has a high surface area of about 1175 m^2/g.[72] The catalytic ability of UIO-66 was compared with different MOFs (Mg-MOF-74, MIL-101, CuBTC (copper(II)-benzene-1,3,5-tricarboxylate), ZIF-8, IRMOF-3, and MOF-5) in the conversion of styrene oxide to styrene carbonate under the same conditions (100°C, 2 MPa, and 1 h) in chlorobenzene solvent.[73] Styrene carbonate was found to be the only product. A high yield of styrene carbonate (94%) was observed when UIO-66 was used as the catalyst. Under the same reaction conditions with the same amount of catalyst, UIO-66 showed the best catalytic performance among the MOF samples tested. The catalytic activities of these MOFs were in the following order: UIO-66 > Mg-MOF-74 > MIL-101 > CuBTC > IRMOF-3 > ZIF-8 > MOF-5. The high surface area and the Lewis acid sites inside the UIO-66 contributed to its high catalytic activity.

A series of MIXMOF (a series of MOFs consisting of Zn_4O tetrahedras and different amounts of two different linkers) materials, which were based on MOF-5 and the corresponding IRMOF series, were studied for the catalytic conversion of CO_2 and epoxides to carbonates.[74] These MOFs had the same structure as MOF-5 and IRMO-3. More specifically, the BDC linkers were partially (from 0 to 90%) substituted by 2-aminobenzene-1,4-dicarboxylate (ABDC) as a functionalized linker bearing an amino side group, which could act as a weak basic site. The Langmuir surface area of the pure MOF-5 was determined to be 1250 m^2/g, whereas the 20 and 40% MIXMOFs had a decreased surface area of about 800 m^2/g. The decrease of the surface area was in agreement with the incorporation of ABDC molecules, which possessed additional side groups that reduced the total accessible pore volume.

The combination of 40% MIXMOF and NEt_4Br (tetraethylammonium bromide) (as a cocatalyst) resulted in an enhanced activity (propene carbonate yield = 63%). In addition, a higher

activity was observed with the bromides (NEt_4Br = 63%, NBu_4Br (tetrabutylammonium bromide) = 49%) as compared to chloride/iodine salts. The observed results were in contrast to literature reports in which iodides were found to be the best promoters (in accordance to the increasing nucleophilicity).[75,76] However, in the presence of microporous MIXMOFs, the diffusion of the large iodide might be hampered; this would explain the slightly reduced activity compared to the bromides. The authors found that the catalytic activity of the MIXMOF series increased with the content of ABDC. For instance, the propene carbonate yield increased from 44 to 63% when 40% MIXMOF was used instead of pure MOF-5 (0% ABDC). The authors believed that the catalyst was effective because of the active metal center and the basic NH_2 sites.[74] They speculated that the unsaturated Zn species at the surface of the framework might have been accessible for substrate activation. In addition, the higher number of basic NH_2 sites led to an increased activity of the resulting catalysts. Table II summarizes the relevant MOFs that have been used to catalyze the synthesis of cyclic carbonates via the cycloaddition of epoxides and CO_2. Figure 3 shows the hypothetical adsorption sites and reaction sites for several MOFs in the conversion of CO_2 into cyclic carbonates.

The suggested reaction mechanism for the conversion of CO_2 and epoxides to cyclic carbonates over MOFs is illustrated in Figure 4. First, CO_2 is adsorbed on a basic site, and the epoxide
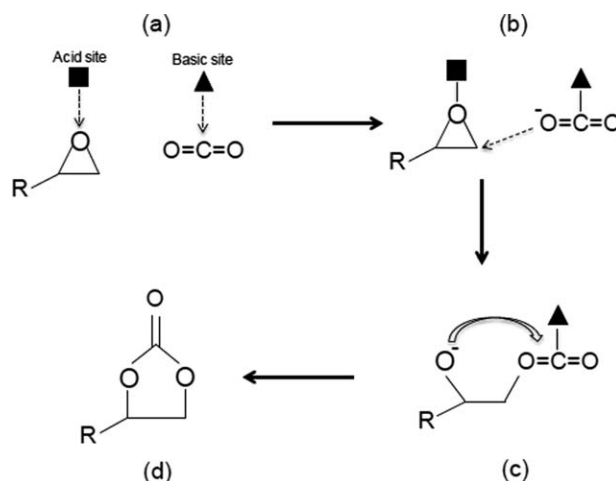
Figure 4. Suggested reaction mechanism for the catalytic conversion of CO_2 and epoxides to cyclic carbonates over MOFs: (a) adsorption steps, (b) nucleophilic attack, (c) ring opening, and (d) ring closure.
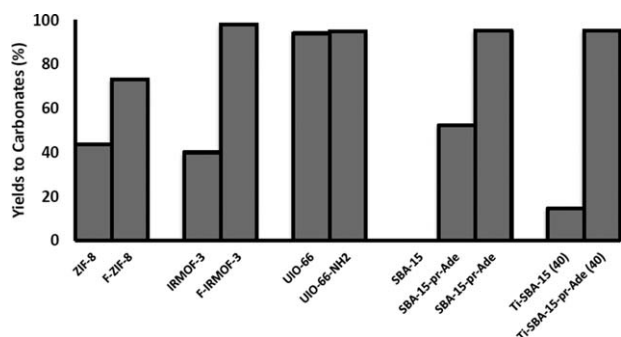
Figure 5. Comparison between the yields to carbonates of nonfunctionalized versus functionalized porous catalysts. Reaction conditions for ZIF-8 and functionalized ZIF-8: 18 mmol of epichlorohydrin, 100 mg of catalyst, 80°C, 7 bar, and 4 h. Reaction conditions for IRMOF-3 and functionalized IFMOF-3: PO (29 g, 500 mmol), initial pressure = 2 MPa, and 140°C. CH_3I was used as a cocatalyst when pure IRMOF-3 was tested. Reaction conditions for UIO-66 and UIO-66–NH_2: 10 mL of chlorobenzene, 5 mmol of SO, 100°C, 2 MPa, and 4 h. Reaction conditions for SBA-15, Ti-SBA-15, functionalized SBA-15, and functionalized Ti-SBA-15: 100 mg of catalyst, 18 mmol of epoxide, 120°C, and 6.9 bar.

is adsorbed on an adjacent acid site (typically Lewis acid sites). The nucleophilic attack of the δ^- charge of CO_2 should lead to a high ring strain in the epoxide-promoting ring opening. Finally, when CO_2 is desorbed from the basic site, ring closure takes place, and the cyclic carbonate is formed. This mechanism is in agreement with that reported recently.[73] The reaction mechanism over mesoporous oxides has been reported earlier[44,47] and, similar to the mechanism over MOFs, involves the activation of the epoxide on the acid sites and the activation of CO_2 on the basic sites. The activated CO_2 is then inserted into the epoxide ring, and this leads to the formation of the cyclic carbonate.

Although some MOFs have shown to be catalytically active in the CO_2 cycloaddition reaction to cyclic carbonates, there are still important challenges, such as the synthesis cost and stability, which need to be addressed to use MOFs as robust catalysts for this and other practical catalytic conversions. The cost of the organic linkers and solvents needed to synthesize MOFs is higher than that of, for example, the chemicals needed to synthesize zeolites. In addition, many of these organic linkers have not been commercialized on a large scale yet and can only be synthesized on the laboratory scale. As suggested earlier,[77] to reduce the cost of synthesizing MOFs, scaling up the synthesis process would be a future viable option. In addition to the cost issues, stability issues may limit the use of MOFs as catalysts. For instance, several MOFs can adsorb a large amount of water and compromise the stability of the MOF.[78] A straightforward approach to mitigating water effects on the stability of MOFs is to make MOFs with hydrophobic surfaces.

FUNCTIONALIZED MOFs AND ZEOLITES/MESOPOROUS OXIDES: STRUCTURAL CHARACTERISTICS AND CATALYTIC PERFORMANCE

Organic cations containing typically amino group functionalities have a high affinity for CO_2. Therefore, the incorporation of amino groups into the surface of porous crystals or mesoporous

oxides promote CO_2 adsorption and, in principle, should improve the catalytic performance for the cycloaddition reaction. Herein, the concept of *functionalization* refers to the grafting or anchoring of amino-based compounds in the surface of porous materials. Several research groups have demonstrated the successful surface functionalization of porous crystals and mesoporous oxides and their improved catalytic performance in the synthesis of cyclic carbonates. In the next paragraphs, we briefly describe specific examples of functionalized porous crystals and mesoporous phases used as catalysts in the synthesis of cyclic carbonates.

Ethylenediamine was used earlier to functionalize MOFs.[72,79,80] Our group reported the catalytic ability of functionalized ZIF-8 in the synthesis of chloropropene carbonate.[45] After ethylenediamine was introduced to the ZIF-8 structure, both the conversion and yield to chloropropene carbonate were enhanced. According to the CO_2 adsorption isotherms, the functionalized ZIF-8 displayed a higher CO_2 uptake, which explained the enhanced conversion and yield to chloropropene carbonate.

The isoreticular metal organic framework 3 (IRMOF-3) has a cubic structure very similar to MOF-5. The only difference is that 2-aminoterephthalic acid is used as a linker to synthesize IRMOF-3.[81] The functionalized IRMOF-3 can be synthesized by the treatment of the pure IRMOF-3 crystals with 3 equiv of methyl iodide (CH_3I) at room temperature for 2–6 days. CH_3I coordinates with the —NH_2 group in the linker to form a new group, —$NH_x(CH_3)_{3-x}I$ (where $x = 1$, 2, or 3). The surface area of the functionalized IRMOF-3 varies from 89 to 132 m^2/g, depending on the ratio of functionalization.[81] The functionalized IRMOF-3 was tested for the solventless synthesis of propene carbonate.[81] There was barely any propene carbonate formed over pure IRMOF-3. When a cocatalyst, CH_3I, was added, the carbonate yield was improved; however, it was still poor. On the other hand, the functionalized IRMOF-3 had excellent activity, selectivity, and reusability. Also, the reaction time was reduced from 5 to 2.5 h and less. The effects of the reaction temperature, pressure, and time on the yield of propylene carbonate were tested. The yield of propene carbonate increased from 62 to 98% with changing initial pressure from 1 to 2 MPa and was then kept almost constant with the initial pressure increasing further to 5.0 MPa. In addition, the effect of time was also investigated. The propene carbonate yield decreased from 98 to 92% when the reaction time was reduced from 1.5 to 1 h. That means that the reaction mostly took place in the 1st h. The authors suggested that Zn_4O and I^- were active sites, and they played the role of activating and opening the epoxy ring, respectively.[81] In addition, functionalized isoreticular metal organic framework-3 (F-IRMOF-3) also had the group of —NH_2, which could activate the epoxy ring through the hydrogen bond.[82,83] The coordination of the oxygen atom of the epoxide with Zn_4O or the hydrogen of —NH_2 in F-IRMOF-3 led to the polarization of C—O, whereas I^- attacked the less sterically hindered carbon atom to open the epoxide ring. Then, the oxygen anion interacted with CO_2 to form an alkylcarbonate anion, which was converted to the corresponding cyclic carbonate.

UIO-66–NH_2 (amino-functionalized UiO-66) was synthesized to improve the catalytic activity by the grafting of the —NH_2

Table III. Representative Functionalized MOFs and Mesoporous Materials Used as Catalysts for the Synthesis of Cyclic Carbonates

Catalyst	Surface area (m²/g)	Epoxide	Main product	Reaction conditions	Solvent	Cocatalyst	Yield to carbonate (%)	Reference
Functionalized zeolitic imidazolate framework-8 (F-ZIF-8)	1096	Epichlorohydrin	Chloropropene carbonate	80°C, 7 bar, 4 h	None	None	73.1	45
F-IRMOF-3 4 days	108	Propene oxide	Propene carbonate	140°C, 2 MPa, 1.5 h	None	None	98	81
F-IRMOF-3 6 days	89	Propene oxide	Propene carbonate	140°C, 2 MPa, 1.5 h	None	None	98	81
UIO-66–NH$_2$	970	Styrene oxide	Styrene carbonate	100°C, 2 MPa, 4 h	Chlorobenzene	None	96	73
UIO-66–NH$_2$	970	Hexene oxide	(R)-Hexene carbonate	100°C, 2 MPa, 3 h	Chlorobenzene	None	97	73
SBA-15-pr-NH$_2$	871	Epichlorohydrin	Chloropropene carbonate	120°C, 6.9 bar, 4 h	None	None	32.9	44
SBA-15-pr-Ade (mesoporous SBA-15 in which 3-chloropropyltriethoxysilane molecules connect to Si atoms of the mesoporous structure, and to adenine molecules)	390	Epichlorohydrin	Chloropropene carbonate	120°C, 6.9 bar, 4 h	None	None	52.2	44
Ti-SBA-15-pr-Ade (Ti-SBA-15-pr-Ade is similar to SBA-15-pr-Ade, but a certain amount of Si atoms are replaced by Ti atoms)	40–119	Propene oxide	Propene carbonate	120°C, 6.9 bar, 6 h	None	None	95.3	44
Ti-SBA-15-pr-Ade	40–119	Styrene oxide	Styrene carbonate	120°C, 6.9 bar, 8 h	None	None	89	44

group in the MOF structure.[73] The functionalization of UIO-66 increased the catalytic ability of UIO-66 to a certain extent in the conversion of styrene oxide to styrene carbonate under similar reaction conditions. UIO-66–NH$_2$ could be reused three times without a loss of catalytic activity in a truly heterogeneous mode without structural deterioration, and it also exhibited excellent cycloaddition activities for different epoxide substrates as well. UIO-66–NH$_2$, having both high populations of Lewis acid and base sites, showed superior catalytic performance in the cycloaddition of CO$_2$ to epoxide under relatively mild conditions.

Adenine-functionalized SBA-15 and Ti-SBA-15 were synthesized to improve the catalytic performance compared that of the as-synthesized catalysts.[44] Both the surface area and pore diameter of Ti-SBA-15 showed a slight decrease to 627 m^2/g and 6.7 nm, respectively. Epichlorohydrin, propene oxide, and styrene oxide were used in the cycloaddition reaction. Solvents and cocatalysts/promoters like DMAP and quaternary ammonium salts, which are usually essential with conventional catalyst systems, could be avoided with the use of adenine-modified Ti-SBA-15 catalysts. A yield of 94% cyclic carbonate was achieved when the functionalized Ti-SBA-15 was used as a catalyst in the reaction.

The authors found that the amine-functionalized Ti-SBA-15 exhibited excellent catalytic performance in the conversion of CO$_2$ and epoxides to cyclic carbonates.[44] They proposed that Ti^{4+} ions (acid sites) could enhance the adsorption and surface concentration of the epoxides, and the basic sites of amines were able to activate CO$_2$ for the insertion of CO$_2$ into epoxides molecules. When the Ti^{4+} ions and the basic amine functionalities coexisted on the surface of the functionalized Ti-SBA-15, activated CO$_2$ molecules and Lewis acid-bound epoxides were generated simultaneously, and the condensation reaction occurred; this led to the cyclic carbonates. This was the reason for the increase in the catalytic activity with Ti content and with the surface concentration of the activated CO$_2$. Figure 5 compares the carbonate yields for pure versus functionalized MOFs. Relevant examples of functionalized porous phases used as catalysts in the synthesis of cyclic carbonates are shown in Table III.

Although, this mini review covers mainly porous crystals, it is important to mention that conjugated microporous polymers (porous materials with an extended π-conjugation in an amorphous organic framework) are effective catalysts for the conversion of CO$_2$ into cyclic carbonates.[84] For instance, cobalt- and aluminum-coordinated conjugated microporous polymers were reported to catalyze the CO$_2$ conversion to cyclic carbonates.[84] In particular, these polymers showed exceptional catalytic activity in the conversion of propylene oxide to propylene carbonate under mild experimental conditions. High surface areas ($\sim$800–965 m^2/g, with an average pore size of 0.5 nm) and huge CO$_2$ uptakes were associated with the improved catalytic performance.

CONCLUDING REMARKS AND OUTLOOK

As revealed in the previously discussed studies, in the reaction between CO$_2$ and an epoxide to form cyclic carbonates, the

surface features of the solid catalyst, such as acidity (the presence of acid sites) and adsorption selectivity (presence of basic sites), and the textural features, such as surface area, pore size, and pore volume, play a critical role in the overall catalytic performance of these porous phases. Of all the discussed porous phases, it is likely that because of its highly desirable tunable and flexible structural, textural, morphological, and compositional properties, MOFs may find more opportunities to be used as catalysts in the conversion of carbon dioxide into cyclic carbonates. In particular, biometal organic frameworks (Bio-MOFs),[85–95] a subclass of MOFs having in their framework structure a basic organic biomolecule, represent ideal candidates as catalysts for the synthesis of carbonates from CO_2. Bio-MOFs are microporous materials in which rigid biomolecules, such as nucleobases, saccharides, peptides, and amino acids, have been used as building blocks to form an MOF. Other biomolecules that have been used to synthesize Bio-MOFs have been reviewed.[86] Bio-MOFs are attractive phases to be used as catalysts for CO_2 conversion to carbonates because of the presence of Lewis acid sites in their frameworks (in most cases, exposed metal sites), remarkably high CO_2 adsorption capacity (because of the presence of basic linkers), and high chemical stability, which in principle would translate into robust catalysts that could be recycled without losing catalytic activity.

Several examples of the potential of Bio-MOFs to catalyze diverse chemical reactions have been reported. For example, amino-acid-based Bio-MOFs [Ni_2(L-asp)-(4,4-bipyridine)·$2H_2O$] displayed enantioselective sorption capabilities of small chiral diols and catalytic activity in the methanolysis of cis-2,3-epoxy-butane.[96] The bio-MOF Zn_2(BDC)(L-lac) dimethylformamide (DMF) (where L-lac = lactic acid) has shown a high enantioselective adsorption capability to sulfoxides.[97] Therefore, Bio-MOFs may be very appealing catalytic phases for the conversion of CO_2 into carbonates.

Porous crystals such as zeolites and MOFs that possess highly desirable and tunable structural, textural, morphological, and compositional properties are particularly attractive materials to be used as catalytic phases in the conversion of CO_2 and epoxides into cyclic carbonates. In this article, we have reviewed the progress made on the catalytic ability of these materials for the conversion of CO_2 to carbonates. Zeolites seem to be more robust catalytic phases for this particular reaction because most of them can be recycled without loss in their catalytic activity. However, these porous crystals need to show reasonable activity temperatures above 100°C. On the other hand, MOFs have been shown to be active for this reaction at temperatures as low as 50°C. However, their recyclability is generally limited. In addition, compared to zeolites, MOFs are more expensive to synthesize. Therefore, two important criteria to be addressed before MOFs can be used (beyond the laboratory scale) as cost-effective catalysts for the conversion of CO_2 and epoxides into cyclic carbonates are (1) the synthesis of MOFs in bulk at a reasonable cost and (2) the improvement of their stabilities. With regard to the first issue, novel synthesis approaches including an activation step and the alternate use of cheap organic linkers may help to alleviate the typical high cost of synthesizing MOFs.

With regard to stability, the design of MOFs with hydrophobic surfaces may be one way to improve their solvothermal stability and, therefore, to enhance their recyclability properties. We anticipate that these catalytic microporous crystals will lead to a fundamental understanding of the relationships between the molecular structure and catalytic properties of a broad range of relevant chemical reactions involving the conversion of CO_2 into useful chemicals.

ACKNOWLEDGMENTS

REFERENCES

1. Encyclopedia of Chemical Processing and Design; McKetta, J. J., Cunningham, W. A., Eds.; Marcel Decker: New York **1984**; Vol. *20*, p 177.

2. Behr, A. *Angew. Chem. Int. Ed.* **1988**, *27*, 661.

3. Fukuoka, S.; Kawamura, M.; Komiya, K.; Tojo, M.; Hachiya, H.; Hasegawa, K.; Aminaka, M.; Okamoto, H.; Fukawa, I.; Konno, S. *Green Chem.* **2003**, *5*, 497.

4. *Filtration Ind. Anal.* **1999**, *27*, 2.

5. Darensbourg, D. J.; Holtcamp, M. W. *Coord. Chem. Rev.* **1996**, *153*, 155.

6. Shaikh, A. A. G.; Sivaram, S. *Chem. Rev.* **1996**, *96*, 951.

7. Ji, D.; Lu, X.; He, R. *Appl. Catal. A* **2000**, *20*, 329.

8. Aida, T.; Ishikawa, M.; Inoue, S. *Macromolecules* **1986**, *19*, 8.

9. Kruper, W. J.; Dellar, D. V. *J. Org. Chem.* **1995**, *60*, 725.

10. Paddock, R. L.; Hiyama, Y.; McKay, J. M.; Nguyen, S. T. *Tetrahedron Lett.* **2004**, *9*, 2023.

11. Paddock, R. L.; Nguyen, S. T. *J. Am. Chem. Soc.* **2001**, *123*, 11498.

12. Darensbourg, D. J.; Yarbrough, J. C. *J. Am. Chem. Soc.* **2002**, *124*, 6335.

13. Yamaguchi, K.; Ebitani, K.; Yoshida, T.; Yoshida, H.; Kaneda, K. *J. Am. Chem. Soc.* **1999**, *121*, 4526.

14. Peng, J. J.; Deng, Y. Q.; New. *J. Chem.* **2001**, *25*, 639.

15. Kim, H. S.; Kim, J. J.; Kim, H.; Jang, H. G. *J. Catal.* **2003**, *220*, 44.

16. Kawanami, H.; Sasaki, A.; Matsui, K.; Ikushima, Y. *Chem. Commun.* **2003**, 896.

17. Kim, Y. J.; Varma, R. S. *J. Org. Chem.* **2005**, *70*, 7882.

18. Sun, J.; Zhang, S. *J. Tetrahedron Lett.* **2008**, *49*, 3588.

19. Sun, J.; Ren, J. Y.; Zhang, S. J.; Cheng, W. G. *Tetrahedron Lett.* **2009**, *50*, 423.

20. Yang, Z. Z.; He, L. N.; Miao, C.; Chanfreau, S. *Adv. Synth. Catal.* **2010**, *352*, 2233.

21. Srivastava, R.; Srinivas, D.; Ratnasamy, P. *Appl. Catal. A* **2005**, *289*, 128.

22. Newsam, J. M.; Treacy, M. M. J.; Koetsier, W. T.; De Gruyter, C. B. *Proc. R. Soc. Lond. A.* **1988**, *420*, 375.

23. Shamshoum, E. S. U.S. Pat. 5,256,392 A (**1993**).

24. Barcia, P. S.; Silva, J. A. C.; Rodrigues, A. E. From Zeolites to Porous MOF Materials—The 40th Anniversary of International Zeollite Conference 2007: Proceedings of the 15th International Zeolite Conference, Beijing, People's Republic of China, Aug 2007; Elsevier: New York; p 955.

25. Srivastava, R.; Srinivas, D.; Ratnasamy, P. *Tetrahedron Lett.* **2006**, *47*, 4213.

26. Kresge, C. T.; Leonovicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710.

27. Koh, C. A.; Nooney, R.; Tahir, S. *Catal. Lett.* **1997**, *47*, 199.

28. Janicke, M. T.; Landry, C. C.; Christiansen, S. C.; Birtalan, S.; Stucky, G. D.; Chmelka, B. F. *Chem. Mater.* **1999**, *11*, 1342.

29. Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schimitt, K. D.; Chu, C. T.-W.; Oslon, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834.

30. Chen, C. Y.; Li, H. X.; Davis, M. E.; *Micropor. Mater.* 1993, *2*, 17.

31. Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C. U.S. Pat. 5,098,689 (**1992**).

32. Beck, J. S. U.S. Pat. 5,057,296 (**1991**).

33. Srivastava, R.; Srinivas, D.; Ratnasamy, P. *Catal. Lett.* **2003**, *91*, 133.

34. Lin, M.; Shu, X.; Wang, X.; Zhu, B. U.S. Pat. 6475465 B2 (**2002**).

35. Kim, S.-H.; Lee, C.-Y.; Kim, G. *J. Stud. Surf. Sci. Catal.* **2005**, *407*.

36. Serrano, D.; Sanz, R.; Pizarro, P.; Moreno, I. *Chem. Commun.* **2009**, 1407.

37. Xie, Z.; Zhu, M.; Nambo, A.; Jasinski, J. B.; Carreon, M. A. *Dalton Trans. J. Inorg. Chem.* **2013**, *42*, 6732.

38. Wilson, S. T.; McGuire, N. K.; Blackwell, C. S.; Bateman, C. A.; Kirchner, R. M.; *Stud. Surf. Sci. Catal.* **1995**, *98*, 9.

39. Xu, R.; Pang, W.; Yu, J.; Huo, Q.; Chen, J. Chemistry of Zeolites and Related Porous Materials, Synthesis and Structure; Wiley: Hoboken, NJ, **2007**; p 45.

40. Jeon, H.-Y.; Shin, C.-H.; Jung, H.-J.; Hong, S.-B. *Appl. Catal. A* **2006**, *305*, 70.

41. Zhao, D. Y.; Feng, J. L.; Huo, Q. S.; Melosh, N.; Fredrickson, G. H.; Chmelka, B. F.; Stucky, G. D. *Science* **1998**, *279*, 548.

42. Zhao, D. Y.; Huo, Q. S.; Feng, J. L.; Chmelka, B. F.; Stucky, G. D. *J. Am. Chem. Soc.* **1998**, *120*, 6024.

43. Katiyar, A.; Yadav, S.; Smirniotis, P. G.; Pinto, N. G. *J. Chromatogr. A* **2006**, *1122*, 13.

44. Srivastava, R.; Srinivas, D.; Ratnasamy, P. *J. Catal.* **2005**, *233*, 1.

45. Miralda, C. M.; Macias, E. M.; Zhu, M.; Ratnasamy, P.; Carreon, M. A. *Am. Chem. Soc. Catal.* **2012**, *2*, 180.

46. Zhu, M.; Srinivas, D.; Bhogeswararao, S.; Ratnasamy, P.; Carreon, M. A. *Catal. Commun.* **2013**, *32*, 36.

47. Srivastava, R.; Srinivas, D.; Ratnasamy, P. *Micropor. Mesopor. Mater.* **2006**, *90*, 314.

48. Cho, H.-Y.; Yang, D.-A.; Kim, J.; Jeong, S.-Y.; Ahn, W.-S. *Catal. Today* **2012**, *185*, 35.

49. Yang, D.-A.; Cho, H.-Y.; Kim, J.; Yang, S.-T.; Ahn, W.-S. *Energy Environ. Sci.* **2012**, *5*, 6465.

50. Bae, Y.-S.; Lee, C. Y.; Kim, K. C.; Farha, O. K.; Nickias, P.; Hupp, J. T.; Nguyen, S. T.; Snurr, R. Q. *Angew. Chem. Int. Ed.* **2012**, *51*, 1857.

51. Macias, E. E.; Ratnasamy, P.; Carreon, M. A. *Catal. Today* **2012**, *198*, 215.

52. Chui, S. S. Y.; Lo, S. M. F.; Charmant, J. P. H.; Orpen, A. G.; Williams, I. D. *Science* **1999**, *283*, 1148.

53. Getzschmann, J.; Senkovska, I.; Wallacher, D.; Tovar, M.; Fairen-Jimenez, D.; Duren, T.; Van Baten, J. M.; Krishna, R.; Kaskel, S. *Micropor. Mesopor. Mater.* **2010**, *136*, 50.

54. Perez-Mayoral, E.; Cejka, J. *Chem. Cat. Chem* **2011**, *3*, 157.

55. Grajciar, L.; Wiersum, A. D.; Llewellyn, P. L.; Chang, J.-S.; Nachtigall, P. *J. Phys. Chem. C* **2011**, *115*, 17925.

56. Wang, Q. M.; Shen, D.; Bulow, M.; Lau, M. L.; Deng, S.; Fitch, F. R.; Lemcoff, N. O.; Semanscin, J. *Micropor. Mesopor. Mater.* **2002**, *55*, 217.

57. Millward, A. R.; Yaghi, O. M. *J. Amer. Chem. Soc.* **2005**, *127*, 17998.

58. Liang, Z.; Marshall, M.; Chaffee, A. L. *Energy Fuels* **2009**, *23*, 2785.

59. Zalomaeva, O. V.; Chibiryaev, A. M.; Kovalenko, K. A.; Kholdeeva, O. A.; Balzhinimaev, B. S.; Fedin, V. P. *J. Catal.* **2013**, *298*, 179.

60. Maksimchuk, N. V.; Zalomaeve, O. V.; Skobelev, I. Y.; Kovalenko, K. A.; Fedin, V. P.; Kholdeeva, O. A. *Proc. R. Soc. A* **2012**, *468*, 2017.

61. Ferey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F.; Dutour, J.; Surble, S.; Margiolaki, I. *Science* **2005**, *309*, 2040.

62. Chen, Y. F.; Babarao, R.; Sandler, S. I.; Jiang, J. W. *Langmuir* **2010**, *26*, 8743.

63. Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276.

64. Hafizovic, J.; Bjorgen, M.; Olsbye, U.; Dietzel, P. D. C.; Bordiga, S.; Prestipino, C.; Lamberti, C.; Lillerud, K. P. *J. Am. Chem. Soc.* **2007**, *129*, 3612.

65. Chen, B.; Wang, X.; Zhang, Q.; Xi, X.; Cai, J.; Qi, H.; Shi, S.; Wang, J.; Yuan, D.; Fang, M. *J. Mater. Chem.* **2010**, *20*, 3758.

66. Graham, A. J.; Allan, D. R.; Muszkiewicz, A.; Morrison, C. A.; Moggach, S. A. *Angew. Chem. Int. Ed.* **2011**, *50*, 11138.

67. Song, J.; Zhang, Z.; Hu, S.; Wu, T.; Jiang, T.; Han, B. *Green Chem.* **2009**, *11*, 1031.

68. Song, J.; Zhang, B.; Jiang, T.; Yang, G.; Han, B. *Front. Chem. China* **2011**, *6*, 21.

69. Valenzano, L.; Civalleri, B.; Chavan, S.; Bordiga, S.; Nilsen, M. H.; Jakobsen, S.; Lillerud, K. P.; Lamberti, C. *Chem. Mater.* **2011**, *23*, 1700.

70. Cavka, J. H.; Jakobsen, S.; Olsbye, U.; Guillou, N.; Lamberti, C.; Bordiga, S.; Lillerud, K. P. *J. Am. Chem. Soc.* **2008**, *130*, 13850.

71. Cunha, D.; Gaudin, C.; Colinet, I.; Horcajada, P.; Maurin, G.; Serre, C. *J. Mater. Chem. B* **2013**, *1*, 1101.

72. Pinto, M. L.; Dias, S.; Pires, J. *Appl. Mater. Interfaces* **2013**, *5*, 2360.

73. Kim, J.; Kim, S.-N.; Jang, H.-G.; Seo, G.; Ahn, W. S. *Appl. Catal. A* **2013**, *453*, 175.

74. Kleist, W.; Jutz, F.; Maciejewski, M.; Baiker, A. *Eur. J. Inorg. Chem.* **2009**, 3552.

75. Sun, J.; Fujita, S.; Zhao, F.; Arai, M. *Green Chem.* **2004**, *6*, 613.

76. Jutz, F.; Grunwaldt, J.-D.; Baiker, A. *J. Mol. Catal. A* **2008**, *279*, 94.

77. Liu, J.; Thallapally, P. K.; McGrail, B. P.; Brown, D. R.; Liu, J. *Chem. Soc. Rev.* **2012**, *41*, 2308.

78. Kusgens, P.; Rose, M.; Senkovska, I.; Frode, H.; Henschel, A.; Siegle, S.; Kaskel, S. *Micropor. Mesopor. Mater.* **2009**, *120*, 325.

79. Hwang, Y. K.; Hong, D.-Y.; Chang, J.-S.; Jhung, S. H.; Seo, Y.-K.; Kim, J.; Vimont, A.; Daturi, M.; Serre, C.; Ferey, G. *Angew. Chem. Int. Ed.* **2008**, *47*, 4144.

80. Demessence, A.; D'Alessandro, M.; Foo, M. L.; Long, J. R. *J. Am. Chem. Soc.* **2009**, *131*, 8784.

81. Zhou, X.; Zhang, Y.; Yang. X.; Zhao, L.; Wang, G. *J. Mol. Catal. A* **2012**, *361–362*, 12.

82. Morris, W.; Taylor, R. E.; Dybowski, C.; Yaghi, O. M.; Gacia-Garibay, M. A. *J. Mol. Struct.* **2011**, *1004*, 94.

83. Sun, J.; Ren, J. Y.; Zhang, S. J.; Cheng, W. G. *Tetrahedron Lett.* **2009**, *50*, 423.

84. Xie, Y.; Wang, T.-T.; Liu, X.-H.; Zou, K.; Deng, W.-Q. *Nature* **2013**, *4*, 1960.

85. An, J.; Fiorella, R.; Geib, S. J.; Rosi, N. L. *J. Am. Chem. Soc.* **2009**, *131*, 8401.

86. An, J.; Geib, S. J.; Rosi, N. L. *J. Am. Chem. Soc.* **2009**, *131*, 8376.

87. An, J.; Geib, S. J.; Rosi, N. L. *J. Am. Chem. Soc.* **2010**, *132*, 38.

88. An, J.; Rosi, N. L. *J. Am. Chem. Soc.* **2010**, *132*, 5578.

89. An, J.; Shade, C. M.; Chengelis-Czegan, D. A.; Petoud, S.; Rosi, N. L. *J. Am. Chem. Soc.* **2011**, *133*, 1220.

90. Smaldone, R. A.; Forgan, R. S.; Furukawa, H.; Gassensmith, J. J.; Slawin, A. M. Z.; Yaghi, O. M.; Stoddart, J. F. *Angew. Chem. Int. Ed.* **2010**, *49*, 8630.

91. Rabone, J.; Yue, Y. F.; Chong, S. Y.; Stylianou, K. C.; Bacsa, J.; Bradshaw, D.; Darling, G. R.; Berry, N. G.; Khimyak, Y. Z.; Ganin, A. Y.; Wiper, P.; Claridge, J. B.; Rosseinsky, M. *J. Science* **2010**, *329*, 1053.

92. Anokhina, E. V.; Jacobson, A. J. *J. Am. Chem. Soc.* **2004**, *126*, 3044.

93. Vaidhyanathan, R.; Bradshaw, D.; Rebilly, J. N.; Barrio, J. P.; Gould, J. A.; Berry, N. G.; Rosseinsky, M. *J. Angew. Chem. Int. Ed.* **2006**, *45*, 6495.

94. Zhu, P.; Gu, W.; Cheng, F. Y.; Liu, X.; Chen, J.; Yan, S. P.; Liao, D. Z. *Cryst. Eng. Commun.* **2008**, *10*, 963.

95. Imaz, I.; Rubio-Martinez, M.; An, J.; Sole-Font, I.; Rosi, N. L.; Maspoch, D. *Chem. Commun.* **2011**, *47*, 7287.

96. Ingleson, M. J.; Perez-Barrio, J.; Bacsa, J.; Dickinson, C.; Park, H.; Rosseinsky, M. *J. Chem. Commun.* **2008**, 1287.

97. Dybtsev, D. N.; Nuzhdin, A. L.; Chun, H.; Bryliakov, K. P.; Talsi, E. P.; Fedin, V. P.; Kim, K. *Angew. Chem. Int. Ed.* **2006**, *45*, 916.