Metal-Organic Frameworks in CO2 Cycloaddition with Epoxides

Subjects: Materials Science, Characterization & Testing

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The level of carbon dioxide in the atmosphere is growing rapidly due to fossil fuel combustion processes, heavy oil, coal, oil shelter, and exhausts from automobiles for energy generation, which lead to depletion of the ozone layer and consequently result in global warming. The realization of a carbon-neutral environment is the main focus of science and academic researchers of today. Several processes were employed to minimize carbon dioxide in the air, some of which include the utilization of non-fossil sources of energy like solar, nuclear, and biomass-based fuels. Consequently, these sources were reported to have a relatively high cost of production and maintenance. The applications of both homogeneous and heterogeneous processes in carbon capture and storage were investigated in recent years and the focus now is on the conversion of CO2 into useful chemicals and compounds. It was established that CO2 can undergo cycloaddition reaction with epoxides under the influence of special catalysts to give cyclic carbonates, which can be used as value-added chemicals at a different level of pharmaceutical and industrial applications. Among the various catalysts studied for this reaction, metal-organic frameworks are now on the frontline as a potential catalyst due to their special features and easy synthesis. Several metal-organic framework (MOF)-based catalysts were studied for their application in transforming CO2 to organic carbonates using epoxides. Here, we report some recent studies of porous MOF materials and an in-depth discussion of two repeatedly used metal-organic frameworks as a catalyst in the conversion of CO2 to organic carbonates

cycloaddition epoxides carbon dioxide metal-organic frameworks

1. Reaction Mechanism for the Production of Cyclic Carbonates from CO_2 and Epoxides

CO_2 conversion into cyclic carbonate compounds by cycloaddition reaction to epoxide is regarded as a method with economic advantages to attain a CO_2-neutral environment and to serve as a source for value-added chemicals. Various researchers reviewed the mechanism for cycloadding CO_2 into epoxides [1][2][3][4][5][6][7][8].

The process requires a robust acid catalyst to stimulate the epoxide substrate and the highly stable CO_2 double bond and thermodynamically facilitates the opening of the epoxide ring via nucleophilic co-catalyst (TBABr) attack forming an alkoxide as an intermediate, which subsequently combines with the CO_2-adduct to give the desired carbonates (**Figure 1**). The tetrabutylammonium bromide (TBABr) co-catalyst functions as a nucleophile to motivate the opening of the epoxide rings. The synergistic effect between the MOF catalyst and TBABr is therefore

crucial in attaining high catalytic performance [9][10]. The cycloaddition reaction of CO_2 with epoxides was extensively investigated using different potential catalysts [11][12][13][14][15][16][17][18][19][20][21][22].

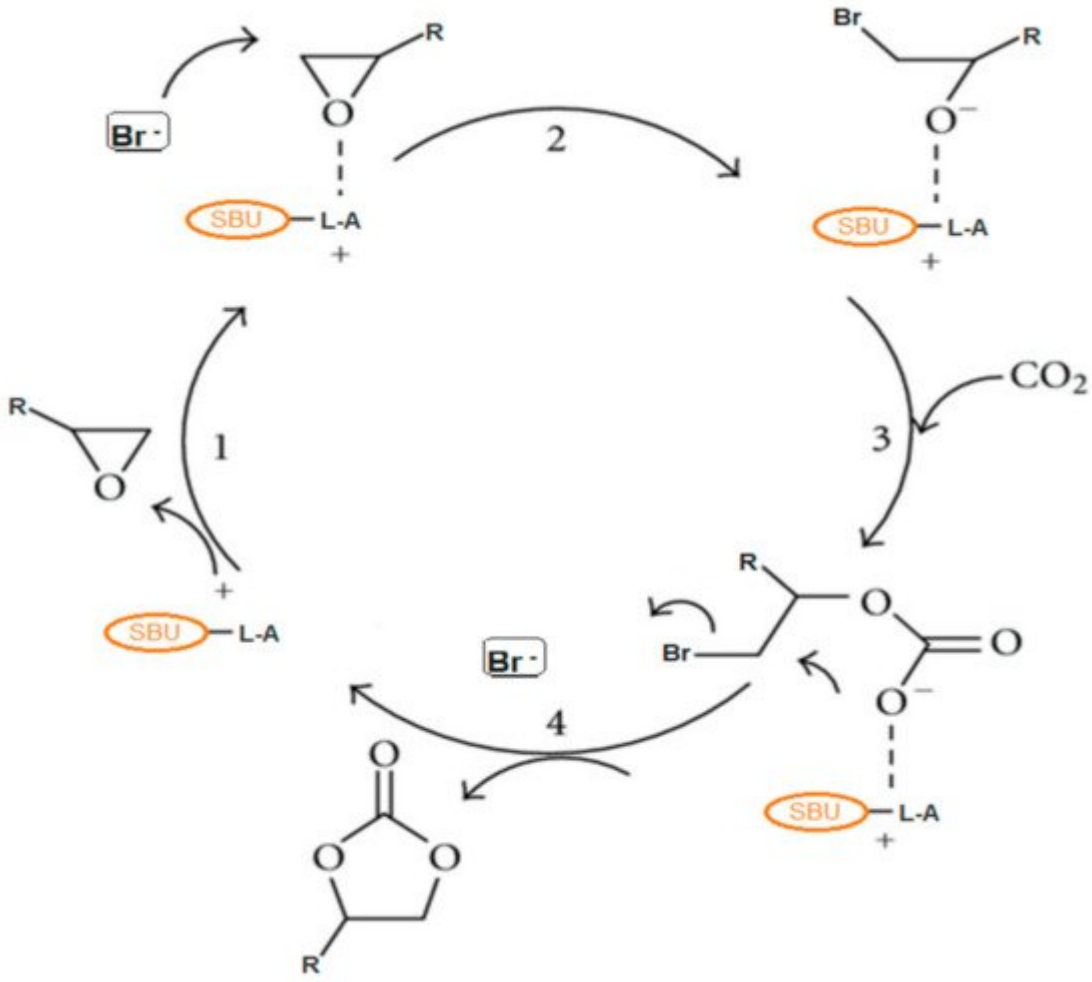

Figure 1. The general schematic reaction mechanism for CO_2 cycloaddition with epoxides catalyzed by a Lewis-acid catalyst MOF and TBABr co-catalyst presence.

The best route for the mechanism was identified as the one that begins with the epoxides ring opening before the addition of carbon dioxide. This therefore proved that the catalytic system in this process strongly depends on the opening of the epoxide ring [23]. The different method for epoxide activation by the MOF catalyst was categorized into four bases on the features of the MOF catalyst (**Figure 2**) as follows: (a) metal-organic frameworks (MOFs) with acidic secondary building units (SBUs) as the only active site, (b) MOFs with acidic linkers as metal active site catalyst, (c) MOFs with Lewis base linkers also acting as a nucleophile and Lewis acidic components, a binary catalytic system (d) MOFs with ionic linkers, where a single-component catalyst is used without the TBABr co-catalyst. The homogenous co-catalyst, tetrabutylammonium bromide (TBABr) would alone promote the epoxide ring-opening in (a and b) and the effort is reinforced in (c). The influence of Lewis-acidic component in SBUs or metal nodes of the MOFs, however, cannot be exempted as indicated (b–d) [22].

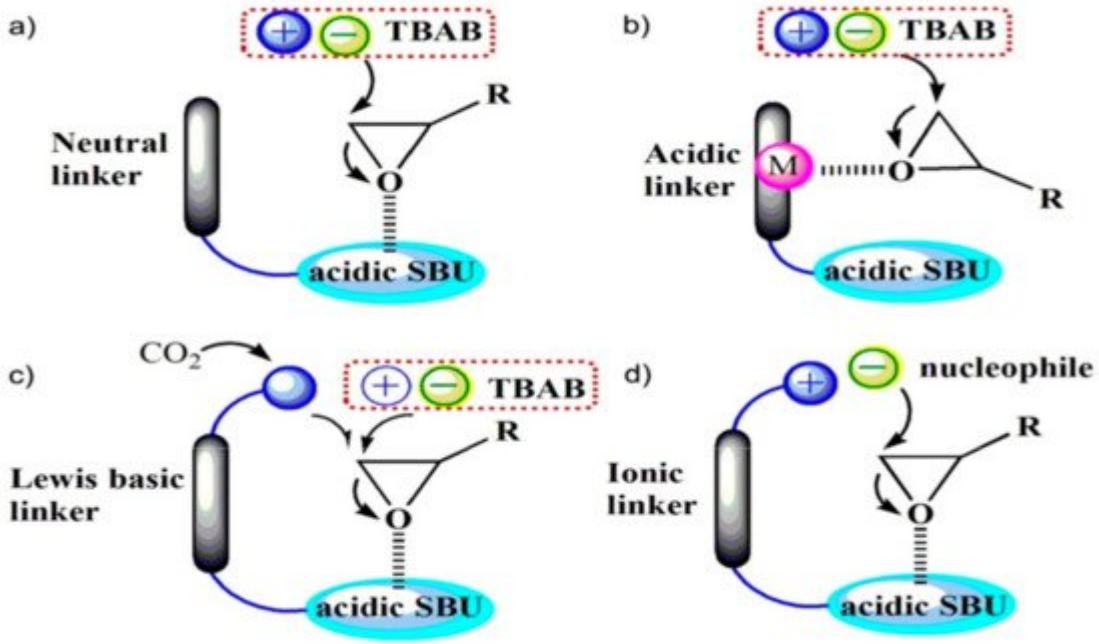

Figure 2. Epoxide activation modes by different MOF catalysts. (**a**) MOFs with acidic SBUs, (**b**) MOFs with acidic linkers, (**c**) MOFs with Lewis base linkers, (**d**) MOFs with ionic linkers. Reprinted with permission from Ref. [22]. Copyright 2019 Elsevier.

2. Metal-Organic Frameworks in CO_2 Cycloaddition with Epoxides

Metal-organic frameworks (MOFs) are a class of nanomaterials containing a cluster of metals and organic ligands (**Figure 3**) that attracted considerable attention because of their diverse topologies, tenability, and application in various fields (**Figure 4**) [24][25][26][27][28][29]. These nanoporous compounds have outstanding pore sizes of about 2 to 50 nm that have exhibited encouraging applications in adsorption [30][31][32][33][34][35], photocatalysis [36][37], and heterogeneous catalysis [1][38][39][40]. Different MOF materials were synthesized and employed as a catalyst in cycloaddition reaction of CO_2 with epoxides and were shown to have reasonable potentiality in their applications [41][42][43][7][7][44][45][46][47][48][49][50][51][52][53][54][55]. The studies in some recent MOF materials employed as a catalyst in the formation of cyclic organic carbonates from CO_2 and epoxides are summarized in **Table 1**.

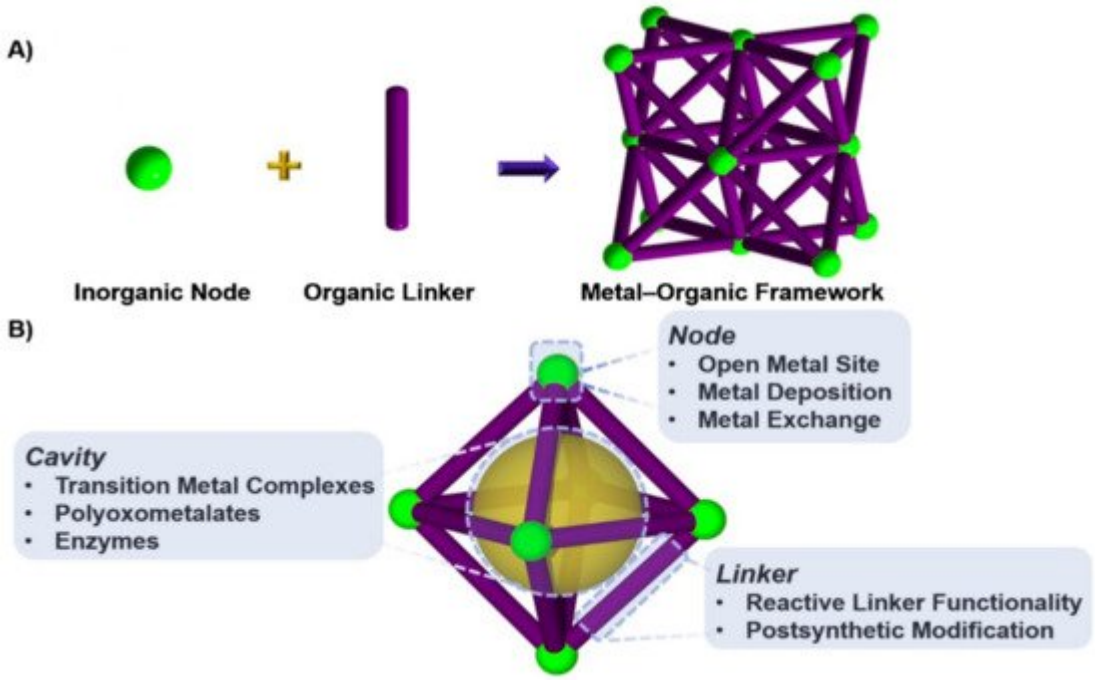

Figure 3. Special features of metal-organic frameworks: (**A**) Typical MOFs synthesis comprising inorganic nodes and organic linkers. (**B**) The accessibility of MOFs by modifying the node, linker, and content of the cavity. Reproduced with permission Ref. [28]. Copyright 2019 Elsevier.

Recent studies of some metal-organic framework materials as a catalyst for cycloaddition reaction (**Table 1**) reaffirmed that the cycloaddition reaction in most cases cannot proceed successfully without the presence of a co-catalyst. Tetra-n-butyl ammonium bromide (TBABr) was reported as the most effective co-catalyst among the various nucleophile components, TBAI, TBACl, and KI, and was identified to enhance epoxide ring opening in the reaction [45][56][57][58]. Some certain MOFs, however, were applied without the presence of a co-catalyst (**Table 1**, entry 17–20). Where this occured, the catalytic activity of MOFs were considered as a single component and were applied without the addition of TBABr. Nonetheless, based on the work studied, this type of reaction can only be successful under harsh reaction conditions of temperature and pressure (**Table 1**, entry 17–20) [59].

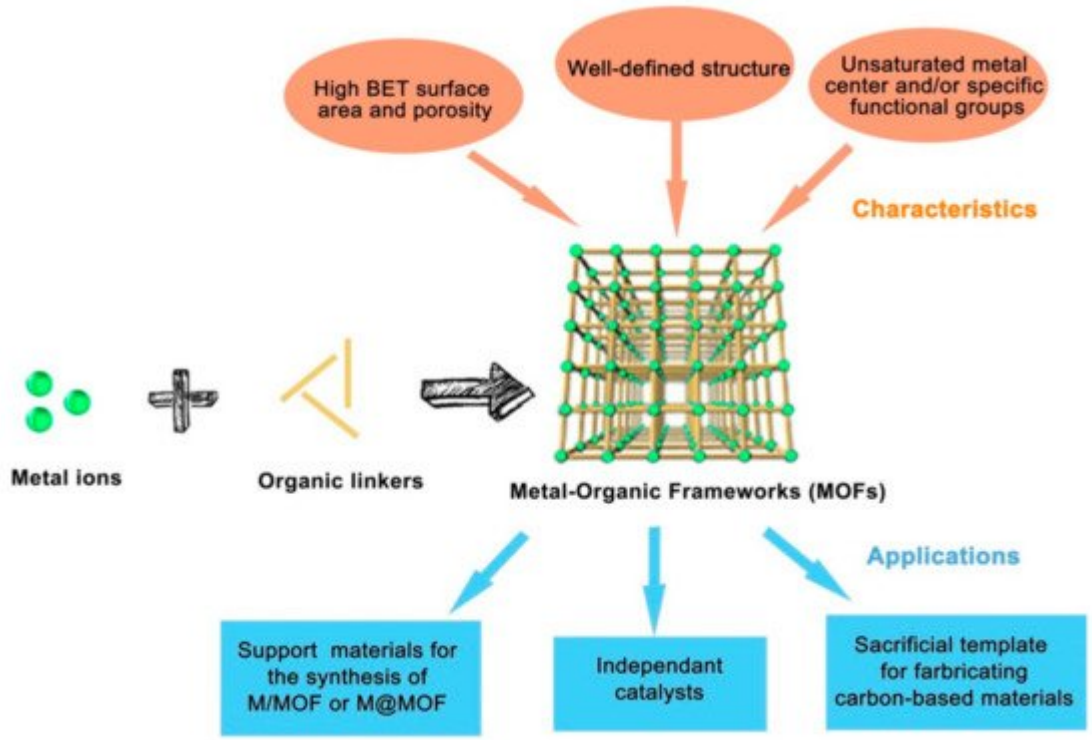

Figure 4. Illustration of MOF components, structure, characteristics, and mode of application. Reprinted with permission from Ref. [57]. Copyright 2018 Elsevier.

The addition of TBABr co-catalyst in most of the reported MOFs (**Table 1**, entry 1–16) further proved that the catalytic function of MOF catalysts in cycloaddition reaction works concurrently with the co-catalyst for successful conversion. Moreover, the catalyst/co-catalyst loading in the data entries (**Table 1**) was observed to be in relatively low percentage moles. The MOF catalytic materials were found to be active and were reused for at least three consecutive cycles in each case before losing their activity. All the reported MOFs (**Table 1**) were found to be effective at moderately ambient conditions, except for entry 17–20, which occured at relatively harsh conditions due to the absence of co-catalyst. Different epoxides such as propylene oxide, styrene oxide, and epichlorohydrin were found to undertake CO_2 cycloaddition under the influence of the MOF catalyst, as shown in **Table 1**.

Table 1. Recent studies of MOF catalysts in CO_2 cycloaddition reaction to epoxides with reaction conditions.

Entry	MOF Material	Co-Catalyst	Catalyst: Cocatalyst Loading (mol%)	S_{BET} (m^2/g)	Epoxide	Press (atm)	Temp. (°C)	Time (h)	Selectivity (%)	Yield (%)	Isosteric Heat Q_{st} (Kj/Mol)	Reusability	Reference
1	Al(OH) (O_2C–CH=CH–CO_2)·$n$$H_2O$	TBABr	0.02:0.002	1169	ECH	10	50	6	97	95	23	4 cycles	[60]
2	Zn_2(Py)(Atz)$_2$·DMF·2H_2O	TBABr	0.1:0.1	764.5	PO	15	60	4	98	92	27.7	6 cycles	[40]
3	[In_2(L)(OH)$_2$]·2DMF·2H_2O	TBABr	0.5:0.2	1022	EBH	1	70	12	89	99	-	5 cycles	[61]
4	F-Mn-MOF-74	TBABr	0.1:0.031	20.83	SO	10	100	6	99	99	-	7 cycles	[62]

Entry	MOF Material	Co-Catalyst	Catalyst: Cocatalyst Loading (mol%)	S_{BET} (m^2/g)	Epoxide	Press (atm)	Temp. (°C)	Time (h)	Selectivity (%)	Yield (%)	Isosteric Heat Q_{st} (Kj/Mol)	Reusability	Reference
5	PCN-222(Co)@MTTB	TBABr	0.1:0.216		PO/ECH	1	50	20	98	>98	-	3 cycles	[51]
6	rho-ZMOF	TBABr	0.1:1.4	871	ECH	10	40	3	98	98	-	5 cycles	[54]
7	Co-MOF-2 {[Co(BDC)(L)]·$2H_2O$.xG}n	TBABr	1.8:2.5	6.8	SO/ECH	1	40	12	99	99	35.0	6 cycles	[44]
8	{[Zn(H_2O)(HL)]·$(DMF)_2$ $(H_2O)_2$}n	TBABr	0.25:0.232	945	PO	1	RT	48	-	76	-	-	[48]
9	MOF-5-MIX	TBABr	0.5:0.5	357	ECH	12	50	6	99	98	-	5 cycles	[63]
10	Ce-NU-1008	TBABr	0.02:0.002		SO	1	RT	20	95		-	3 cycles	[64]
11	Co-MOF-2 {[Co(BDC)(L)]·$2H_2O$·xG}n	KI	5.0:0.2	6.8	SEO	1	40	8	99	99	35.0	6 cycles	[65]
12	{[Ni_3HL(μ3-OH)$(H_2O)_2$]·3(H_2O)·DMA}n	TBABr	0.025:1.5	743.5	ECH	10	100	6	-	>99	-	5 cycles	[66]
13	[(Cu_2 BPDSDC·4DMF)·2DMF]n	TBABr	0.05:0.1	-	PO	25	80	5	98	99	-	4 cycles	[67]
14	{[$Co_6(OH)_2(H_2O)_4$ $(cpt)_9$](NO_3)$(DMF)_{13}$}	TBABr	0.1:2	873	PO	1	40	48	97	97	32	4 cycles	[68]
15	InDCPN-Cl	TBABr	0.05:5.00	997	SO	1	80	24	98	93	30	5 cycles	[16]
16	Ce-NU-1008	TBABr	0.002:0.02	910	SO	1	RT	20	95		-	-	[64]
17	MOF-5@Imidazolium iodide	-	-	277.9	SO	10	110	8	-	92	-	4 cycles	[69]
18	[$(CH_3)_2NH_2$][$M(COOH)_3$]	-	13.1	13.11	PO	20	120	6	100	98	-	3 cycles	[70]
19	Im-MnF [$C_3H_5N_2$][$Mn(COOH)_3$]	-	-	81.57	ECH	15	100	6	99	95	-	-	[71]
20	Pt/Mg-MOF-74	-		513	PO	17.5	150	4	77	44	-	3 cycles	[72]

Note: All pressure units are converted to the approximate atm value.

3. MIL-101 Based MOFs in CO_2 Cycloaddition with Epoxides

MIL-101 is one of the repeatedly reported MOF materials with a high potential catalytic activity for the conversion of CO_2 to cyclic carbonates. This was ascribed to its possession of Lewis-acid sites due to Cr^{2+} present at the metal center [65] and structural flexibility, which allows its modifications by substituting different functional groups in the

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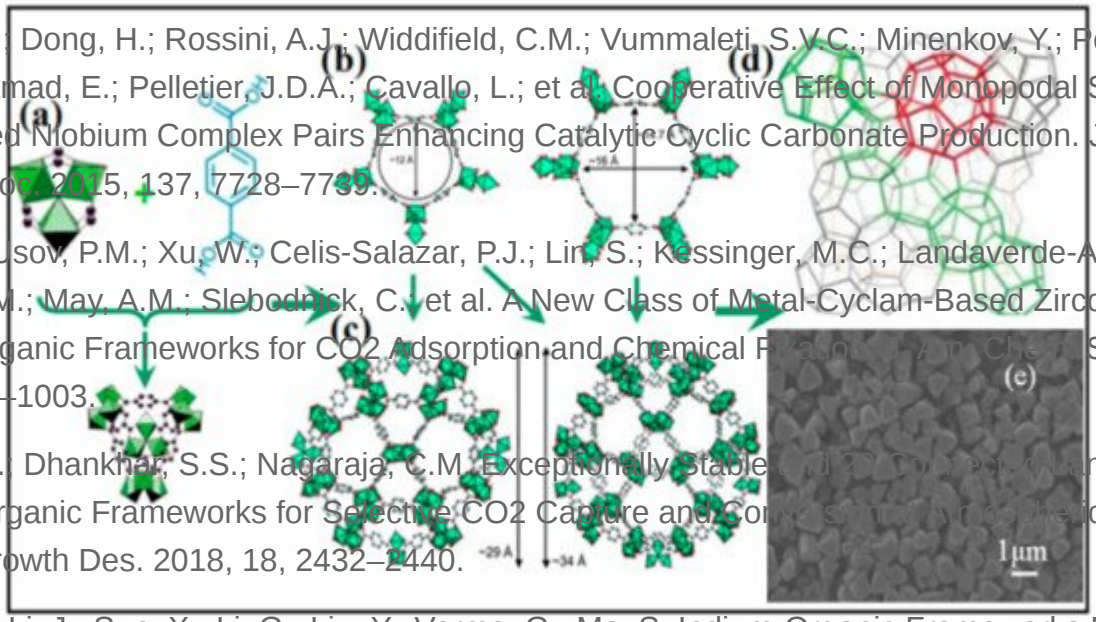

Figure 5. Synthesis and structural elucidation of MIL-101(Cr): (**a**) The formation of the hybrid super tetrahedron by the cluster chromium metal building unit and the btc ligand; (**b**) Small pentagonal and larger hexagonal window (**c**) The two mesoporous cages; (**d**) 3D schematic representation of the MTN zeotype architecture (small cages are highlighted in green and large one is highlighted in red); (**e**) Morphology showing clear octahedral shape with an average crystal size of ~1.0 μm [84].

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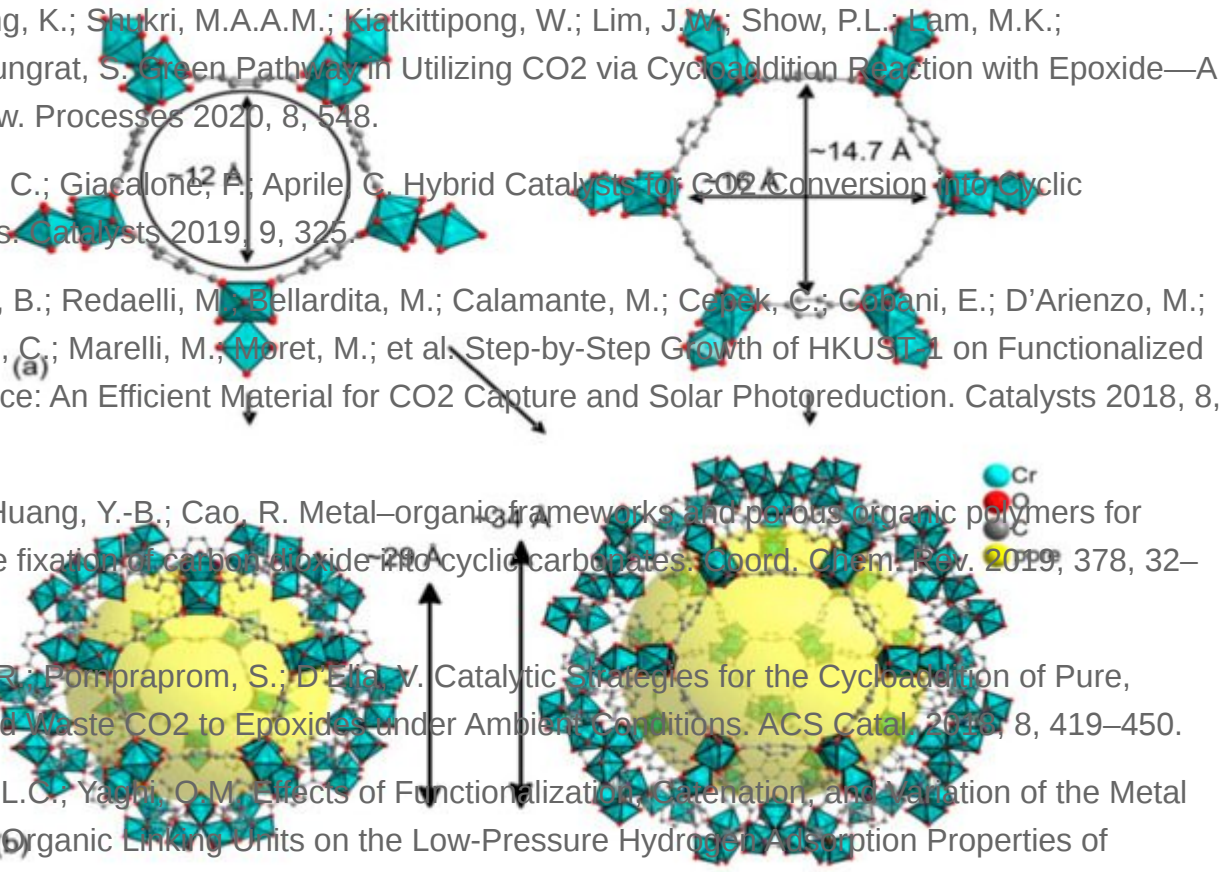

Figure 6. Trinuclear chromium building units and the bridging bdc ligands forming pentagonal and hexagonal rings (**a**) assembled into mesoporous cages (**b**) and mesoporous cages of yellow spheres with diameters of 29 or 34 Å, respectively. Reprinted with permission from Ref. [83]. Copyright 2016 Elsevier.

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4. HKUST-1 for CO_2 Cycloaddition with Epoxides

Another group of porous material that attracted the attention of researchers as a potential catalyst for CO_2 cycloaddition with epoxides is HKUST-1 (Hong Kong University of Science and Technology) and also referred to as MOF-199 or Cu-based 1,3,5-benzenetricarboxylate (BTC). It was first synthesized in 1999 using copper(II) ion (Cu^{2+}) as metal center and BTC ligand to give a light blue powder (**Figure 7**) [38][91][92], it was also reported using other metals with +2 oxidation state such as Cr^{2+} [93], Ni^{2+} [94], Zn^{2+} [95], Fe^{2+}, Co^{2+} [96][97], and as bimetallic with two different metals at the center while maintaining the structure [98]. HKUST-1 material has a molecular formula $[Cu_3(BTC)_2(H_2O)_3]$ and morphological structure with a sound level of thermal stability (**Figure 8**) and a capacity for chemical functionalization of the channel linings with face-centered-cubic crystals comprising a 3D intersecting system with big square-shaped pores (9 Å by 9 Å) of a continuous network through $Cu(OAc)_4$ paddle wheel SBU, as in **Figure 9**. The open metal sites in the HKUST-1 structure provides the basis for CO_2 adsorption property [99][100]. The large porous structure can also be used to create effective heterogeneous catalysts as templates to construct dynamic heterogeneous system by encapsulation of other nanomaterials to form composites. The resultant composite material can preserve the original properties of the HKUST-1, while gaining additional unique properties that can be applied in different applications [25][101][102][103][104].

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Figure 7. Schematic illustration of HKUST-1 synthesis and structural elucidation. Reprinted with permission from Ref. [92]. Copyright 2019 Elsevier.

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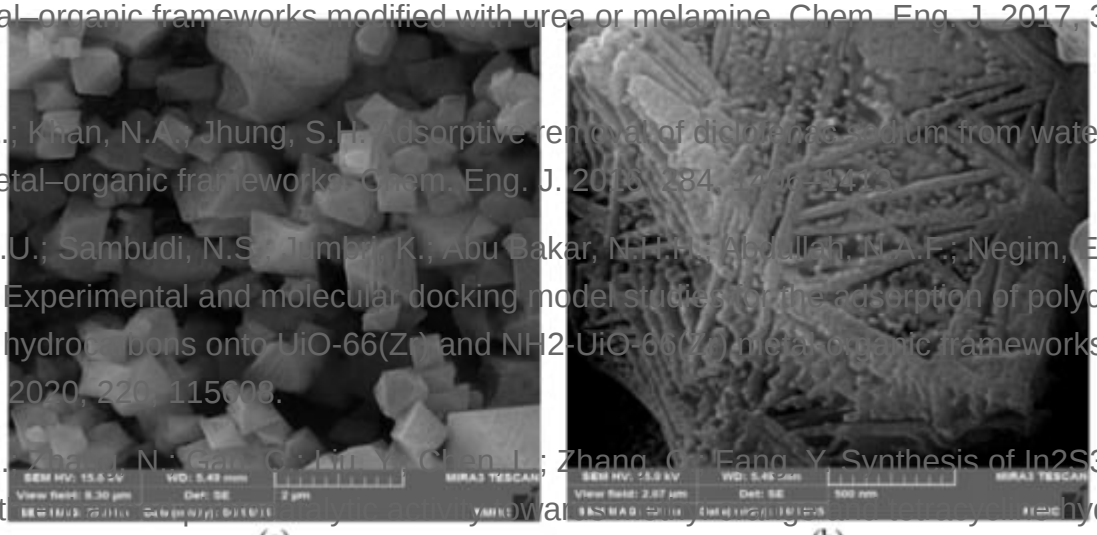

Figure 8. FESEM micrographs of HKUST-1 in different scales: (**a**) 2 µm, (**b**) 500 nm. Reprinted with permission from Ref. [92]. Copyright 2019 Elsevier.

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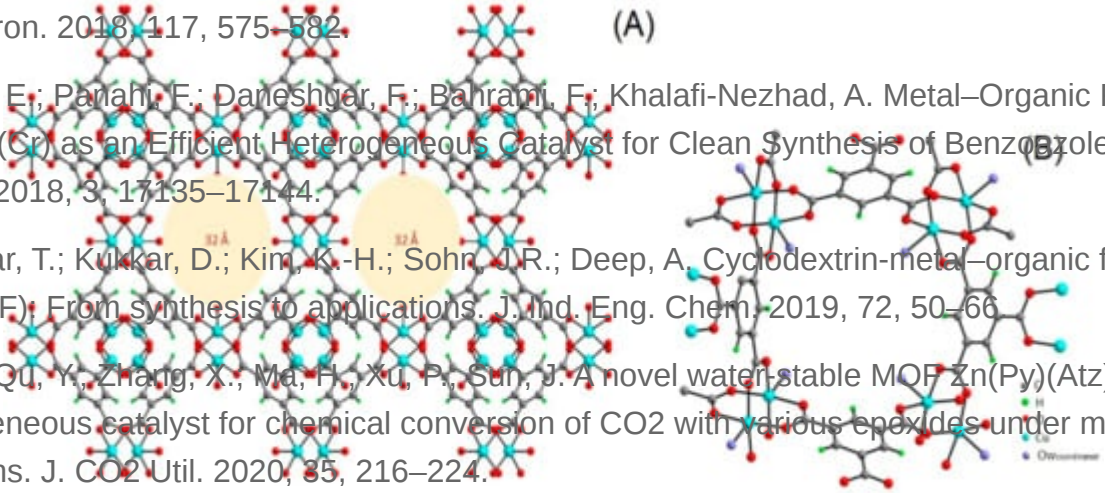

Figure 9. (**A**) Structure of HKUST-1. (**B**) Paddle-wheel secondary building unit (SBU). Reprinted with permission from Ref. [165]. Copyright 2019 Elsevier.

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Abbreviations

MOFs	Metal-organic frameworks
TBABr	Tetrabutyl ammonium bromide
SBU	Secondary Building Unit
SO	Styrene Oxide
PO	Propylene oxide
ECH	Epichlorohydrin
EBH	Epibromohydrin
SEO	Spiro-Epoxy Oxindole
BTC	1,3,5-benzenetricarboxylate
HKUST	Hong Kong University of Science and Technology
RT	Room temperature
KI	potassium iodide
Å	Aperture

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