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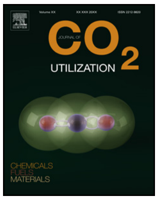

Review Article

Recent advances in the synthesis of covalent organic frameworks for CO_2 capture

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ABSTRACT

As a novel class of porous crystalline organic materials assembled from molecular building blocks, the synthetic strategies of covalent organic frameworks (COFs) allow for the design and construction of new crystalline materials since their properties can easily be tuned through appropriate selection of the building blocks and the linkage motif. Their fascinating and versatile properties have made them to emerge as a platform for functional explorations and applications in CO_2 capture. This review article addresses the synthetic strategies with special emphasis on dynamic covalent chemistry and potential application of COFs for CO_2 capture. Recent advancements in the synthesis of COFs, including the strategies and principles involved are discussed. Also discussed are strategies of introducing extra tools in COFs to enhance their crystallininty, porosity and chemical stability, which are important parameters in the applications of COFs for post-combustion capture of CO_2 in the CCS technology.

Contents

1. Introduction

The development of viable CO_2 storage systems has necessitated the needs for highly selective CO_2 capture materials suitable to selectively enrich CO_2 in preference to other gases in the flue gas stream, which contains N_2 (75–76%), CO_2 (15–16%), H_2O (5–7%), O_2 (3–4%), CO (20 ppm), SO_x (<800 ppm), and NO_x (<500 ppm) [1,2]. The anthropogenic emission of CO_2 is known to be the major source of global warming [3]. The global emissions of CO_2 by power plants and transportation sectors have been on the increase in the last decades [4], and have led to increased CO_2 build-up in the atmosphere. Carbon capture and storage (CCS) has been recognized as a technology capable of reducing the emissions of CO_2 up to 20% [3,5]. Therefore, materials suitable for CCS technology must have a high preference for adsorption of CO_2. Amine scrubbing,

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Nomenclature

N_2	Nitrogen
CO_2	Carbon dioxide
CH_4	Methane
H_2O	Water
Si	Silicon
$ZnCl_2$	Zinc (II) chloride
CF_3SO_3H	Trifluoromethane sulphonic acid
CCS	Carbon capture and storage
CLC	Chemical looping combustion
COFs	Covalent organic frameworks
MOFs	Metal organic frameworks
BDBA	1,4-benzene diboronic acid
HHTP	2,3,6,7,10,11-hexahydroxytriphenylene
BPDB	4,4′-biphenyl diboronic acid
BTBA	1,3,5-benzene triboronic acid
BzTDB	Benzo[*c*][1,2,5]-thiadiazole-4,7-diboronic acid
TDBPB	1,3,5-tris(4-dihydroxylborylphenyl) benzene
DPyDB	1,8-dihydropyrene-2,7-diboronic acid
TDBPPor	5,10, 15,20-tetrakis(4-dihydroxylborylphenyl) porphyrin
TDB	Thiophene-2,5-diboronic acid
TTDB	Thieno[2,3- *b*] thiophene-2,5-diboronic acid
BTDB	2,2′-bithiophene-5,5′-diboronic acid
BAPDB	2,5-bis(azidomethyl)-1,4-phenylene diboronic acid
TDBPT	1,1′,1″-tris(4-dihydroxyborylphenyl) tridecane
AnTol	Anthracene-2,3,6,7-tetraol
TPHol	Triphenylene-2,3,6,7,10,11-hexaol
TDBPM	1,1′,1″,1′”-tetrakis(4-dihydroxylborylphenyl) methane
TDBPS	1,1′,1″,1′”- tetrakis(4-dihydroxylborylphenyl) silane
TDBPE	1,1″.1″-tris(4-dihydroxylborylphenyl)ethane
CTFs	Covalent triazine frameworks
PCTFs	Porous covalent triazine frameworks
FCTFs	Fluorinated covalent triazine frameworks
MCTPs	Microporous covalent triazine polymers
DCB	1,4-dicyanobenzene or 1,2-dicyanobenzene
DCP_r	2,6-dicyanopyridine
DCT	2,5-dicyanothiophene
DCN	2,6-dicyano naphthalene
DCBP	4,4′-dicyanobiphenyl
$DCBP_r$	5,6′-dicyano-2,3′-bipyridine
BCBP	1,4-bis(4-cyanophenyl) benzene
TCB	1,2,4,5-tetracyanobenzene
NTB	4,4′,4″-nitrilotribenzonitrile
TCPB	1,3,5-tris(4-cyanophenyl) benzene
TrCB	1,3,5-tricyano benzene
ILCOF	Imine-linked COF
ACOF	Azine-linked COF
ALPs	Azo-linked polymers
MOPs	Microporous organic polymers
BILPs	Benzimidazole-linked polymers
RT-COF	Room temperature COF
IBTP	Imine benzothiazole
SQ-COPs	Squaraine-bridged covalent organic polymers
BTA	Benzene-1,2,4,5-tetraamine
BDA	Benzene-1,2diamine
TH	Terephthalohydrazide
TFPB	1,3,5-tris(4-formylphenyl)benzene
DFBP	4,4′-diformylbiphenyl
TFB	1,3,5-triformylbenzene
DETH	2,5-diethoxyterephthalohydrazide
TrFPT	1,3,5-tris(4-formylphenyl)triazine
TFPM	4,4′,4″,4′”-tetrakis(4-formylphenyl)methane
DFB	1,4-diformylbenzene
HATT	Hexaaminetritycene
TAA	Tetraaminoadamantane
TAPE	1,1′,2,2′-tetrakis(4-formylphenyl)ethane
NBA	4,4′,4″-nitrilotribenzoic acid
STBA	4,4′,4″,4′”-silanetetrayltetrabenzoic acid
TAPM	1,1′,1″,1′”-tetrakis (4-aminophenyl) methane
TAPB	1,2,4,5-tetrakis(4-aminophenyl)benzene
TrAPA	N,N’,N”-tris(4-aminophenyl)ammonia
DBDol	6,6′-diamino-1,1′-binaphthyl-2,2′-diol
TAPPor	1,4,7,10-tetrakis(4-aminophenyl)porphyrin
FPBA	4-formylphenylboronic acid
MC-COFs	Multi-component covalent organic frameworks
NLDFT	Non local density functional theory
TGA	Thermogravimetric analysis
NiPc	Nickel phthalocyanine
IAST	Ideal adsorption solution theory

cryogenic cooling and chemical-looping combustion (CLC) have been the established technologies over the years for CO_2 capture, which, however have some limitations, including increasing energy requirements of a power plant by 25–40% [1,6], disposal and formation of toxic byproducts during high temperature regeneration step of amine scrubbing technology. Moreover, amine solutions decompose over time leading to decrease in their CO_2 capturing capacity with time [7]. In addition, volatility, toxicity and corrosivity of amine solutions limit their applications in real-world applications due to environmental concerns [7].

Recently, porous solid materials such as activated carbons [8,9], zeolite [10,11], metal organic frameworks (MOFs) [12–14], covalent organic frameworks (COFs) [15–17] and amine modified porous silica [18–20] have been extensively studied as CO_2 adsorbents. The main advantages of these solid adsorbents include their longevity and regenerability at moderate temperatures. Most importantly, COFs are promising because of their chemical and thermal stabilities as well as synthetic versatility, giving rise to a wide variety of functional and structural designs.

COFs are constructed by linking well defined organic building units through strong covalent bonds such as C—C, C—N, C—O, B—O, C=N and C—Si [21,22]. Since the pioneering work of Yaghi and co-workers in 2005[21], the rapid development in this research area has attracted worldwide attention and numerous chemical architectures with one-dimensional (1-D) to extended 2-D and 3-D structures have been constructed by assembling the diverse building units with different functionalities in different ways [23]. COFs are usually synthesized by reversible condensation reactions where the reversability originates from the hydrolysis back reaction. Their synthesis include but not limited to the following organic reactions, viz; the formation of B—O (boronate, boroxine and borosilicate) [24,25], C=N (imine, hydrazine, and squaraine) [26–30], C—N (triazine and imidization) [31,32], B—N (borazine) [33] and N—N (azodioxides) [34] bond linkages. Therefore, a lot of synthetic strategies have been developed for the synthesis of COFs of different dimensions and with different textural properties. Compared with other crystalline porous solid adsorbents (inorganic zeolites and hybrid MOFs), COF materials possess the advantage of low density, high permanent surface areas, high chemical and thermal stability, columnar π-stacking structure, tunable pore size and structure and versatile covalent combination of building units. All these advantages have attracted considerable interest of scientific community in COFs, thereby