基于正四面体构筑单元的多孔芳香骨架材料

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摘要 多孔芳香骨架(porous aromatic frameworks, PAFs)材料作为一类重要的多孔材料, 近十年取得了很大的研究进展. 这类材料具有超高的比表面积、轻的骨架密度、灵活的骨架可修饰性以及高的热化学稳定性, 被广泛地应用于气体吸附、分离、催化、传感等方面. 拓扑化学理论的引入使得PAFs材料的合成更具有目标性, 可以实现PAFs材料的定向设计合成. 具有高度对称性的正四面体基元是构筑高稳定性PAFs材料的理想单元, 可用于合成具有金刚石结构的高比表面多孔材料. 本文从2009年第1例PAFs材料、PAF-1的设计思想与定向合成出发, 分别讲述了PAFs材料的结构设计、合成策略、性质应用, 总结了基于正四面体基元的PAFs材料的研究进展, 以期合成高稳定性高比表面积的多孔材料提供一些思路.

关键词 多孔芳香骨架, 可控合成, 拓扑, 吸附, 分离, 催化

多孔材料由于其空旷的骨架结构和高的比表面积, 被广泛地应用于气体吸附、分离、主客体化学、催化以及光、电、磁微器件等领域. 按照结构的组成成分, 多孔材料包括由无机成分构成的沸石分子筛(zeolites)、无机-有机杂化的金属有机骨架(metal-organic frameworks, MOFs)和由纯有机组分构建的多孔有机骨架(porous organic frameworks, POFs)材料. POFs材料完全由C, H, N, O等轻元素通过共价键连接而成, 具有轻的骨架密度和高的稳定性, 是近年来多孔材料领域的研究热点.

金刚石(diamond), 一种完全由碳元素组成的无色晶体, 是目前自然界中存在的已知的最坚硬物质. 金刚石晶体中的每一个碳原子都以 sp^3 杂化形式与相邻的碳原子形成共价单键, 构成正四面体结构. 这种稳定的晶体结构, 使其具有非常大的硬度及高稳定性, 在室温条件下不会被任何酸碱腐蚀, 在纯氧中的燃点高达720~800℃. 金刚石结构以硬球堆积模型计

算的原子堆积因子(即空间堆积率)仅为0.34, 是常见晶体结构中堆积因子最小的. 但是由于金刚石中的C-C键长很小, 金刚石的原子密度很大, 是致密的原子晶体.

理论上, 如果将金刚石结构中的C-C共价键用刚性的苯环单元替换, 不仅会保持结构的金刚石拓扑, 同时苯环单元的加入将增加C-C键的长度, 使得结构中苯环的面与边充分地裸露出来, 从而提高材料的内比表面积, 得到高稳定性、高比表面积的多孔材料.

基于以上设计理念, 2009年, 本课题组^[1]将金刚石中的C-C键用不同长度的苯环单元进行替换, 通过材料模拟软件(Materials Studio)搭建了3个替换结构, 分别记作P1(1个苯环), P2(2个苯环)和P3(3个苯环)(图1(a)~(d)), 采用第一性原理与巨正则蒙特卡罗模拟结合的多尺度计算模拟方法, 模拟了3个模型材料的比表面积. 通过对比3个模型材料的比表面积与

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图1 金刚石(a), P1(b), P2(c), P3(d)的结构模型以及PAF-1在77 K下的氮气吸附等温线(吸附: ■, 脱附: □)和P2模型的模拟吸附等温线(红色方块)(e)^[1]

Figure 1 The structure of diamond (a), and models of P1 (b), P2 (c) and P3 (d). (e) N_2 sorption isotherms at 77 K of PAF-1 (adsorption: black square, desorption: empty square) and simulated N_2 sorption isotherms of model P2 (red square)^[1]

孔径尺寸,选择P2作为合成实验的目标多孔材料,利用沃尔曼偶联反应成功地合成了多孔芳香骨架材料PAF-1.

PAF-1具有超高的比表面积,其Langmuir(物理化学家Langmuir根据分子运动理论和一些假定提出的单分子层吸附理论)和BET(Brunauer, Emmett和Teller 3位科学家从经典统计理论推导出的多分子层吸附理论)比表面积分别为7100和5600 m^2/g .对比PAF-1的氮气吸附曲线与具有理想金刚石结构的P2模型的模拟氮气吸附曲线,我们发现合成的PAF-1材料与理论模型P2具有几乎一致的孔道性质(图1(e)),证明合成的PAF-1材料在一定程度上具有设计的理论模型P2结构. PAF-1还具有非常好的热稳定性,在空气中可稳定至520℃,在沸水中处理1周后,材料的氮气吸附性能几乎没有发生变化,说明PAF-1的骨架在热处理后依然得以保持. PAF-1的高比表面积及高稳定性使其具有良好的气体与液体吸附能力,其对氢气和二氧化碳的储存量均处于已知多孔材料报道结果前列.同时,由于PAF-1材料的芳香骨架特点,它对苯和甲苯也具有非常高的吸附量.

PAF-1的成功设计合成为多孔材料家族带来了新的一员:多孔芳香骨架(PAFs)材料.自2009年,百余种PAFs材料被合成出来,它们高的比表面积、低的骨架密度以及非常高的热稳定性和化学稳定性使其广泛地应用于吸附、分离、催化、传感等领域.同时,PAFs材料合成方法的多样性以及骨架可修饰的灵活性使材料的合成更有目标,为得到具有特定结构特

点与特性能的多孔材料提供了更大的可能,提高了该类材料在实际生产中的应用潜能^[2].

在PAF-1的合成实验中,具有正四面体构型的四溴四苯基甲烷被选择作为构筑PAF-1的结构基元.如果将该单元中每个苯环的对位用线性单元连接,则应该形成具有金刚石结构的多孔材料.利用沃尔曼偶联反应,具有与理论模型P2孔道性质一致的PAF-1被成功地合成出来.这说明具有正四面体结构的四苯基甲烷有机单体是构筑PAFs材料的理想单体^[3,4].通过调节连接单元的长度及结构,还可以有效地控制目标多孔材料的孔径尺寸^[5],向目标材料的骨架中引入多种多样的功能性基团^[6],从而使合成的材料具有预期的应用性质.

本文主要介绍基于正四面体构筑单元的PAFs材料的设计合成及性质研究,将从该类材料的结构设计、合成策略及性能应用等方面进行归纳阐述,以期多孔材料的定向合成提供一些思路.同时,为了增加材料在实际生产中应用的可行性,本文还将介绍低成本PAFs材料的合成尝试及吸附性能研究.

1 拓扑导向的结构设计

拓扑学(topology)最早是指研究地形、地貌类似的有关学科,它只考虑物体间的位置关系而不考虑物体的形状和大小.拓扑学的提出及研究极大地推动了数学学科的发展,同时在物理学、化学、生物学等学科中也都有直接的应用.

20世纪末,Yaghi研究组^[7,8]成功地将拓扑学理论

应用到多孔材料的结构设计中,合成了一系列具有规则结构的MOFs材料,如具有 CaB_6 拓扑结构的经典MOF-5及IRMOF系列.之后,该理论被拓展到共价有机骨架的设计合成中,2007年,Yaghi研究组^[9]通过四硼酸四苯甲烷及其硅的类似物的自聚或共聚反应,合成了具有三维 ctn 或 bor 拓扑结构的晶型COF-102, 103, 105和108.2009年,具有类金刚石拓扑结构的PAF-1的成功设计合成更使得无定形多孔材料的定向合成不再只是设想^[1].

在拓扑学理论的指导下,PAFs材料的定向合成可以从2个方向实现:从下往上(bottom-up)和由上至下(top-down),如图2所示^[10,11].在从下往上的设计方法中,先选择刚性有机单体作为构筑基元,根据单体的结构特点,结合所选用的聚合反应条件,推测合成的PAFs材料可能具有的拓扑结构并模拟出理论模型.而由上至下方式,则是先挑选具有特定特点的拓扑结构,通过分析该拓扑结构的构成基元,选择与该基元具有类似结构的有机单体,并由基元的连接方式确定聚合反应,从而合成具有特定拓扑结构的多孔材料.PAF-1的设计合成就是采用了由上至下的设计思路.本文的其他例子大部分从具有正四面体结构的构筑基元出发,通过调整连接单元的长度及结构,向骨架中引入多种多样的功能性基团,从而达到材料的功能化,实现其在某些领域的特定应用.

2 多孔芳香骨架材料的制备

由上述拓扑导向的结构设计及定向合成思路,我们可知有机单体构筑基元及聚合反应是制备目标PAFs材料需要考虑的基本要素.

2.1 有机单体

图3归纳了目前报道的PAFs材料中所用的具有正四面体结构的有机单体,这类单体主要是四苯基

甲烷、四苯基硅烷、四苯基锆烷及其衍生物,它们对称性较高,有很好的刚性,聚合反应过程中不易变形,在合成的材料骨架中仍然可以保持其原有构型.通过向正四面体有机单体引入功能性基团,可以实现材料孔道结构及孔壁性质的调节.需要注意的是,引入的基团不能影响聚合反应的进行,并且在反应后还能保留下来,从而发挥其性质调控作用.此外,PAFs材料的改性还可以通过后修饰策略实现.正四面体中心为硼离子的带电荷有机单体LTIPB也被用来制备PAFs材料.

2.2 聚合反应

有机合成化学的多样性为PAFs材料的设计合成提供了丰富而灵活的选择.图4总结了应用于基于四面体构筑基块的PAFs材料的聚合反应.这些聚合反应可以分为两类:动态控制反应(dynamic controlled reactions)与动力学控制反应(kinetic controlled reactions).

动态控制反应为可逆反应,有机单体分子在反应过程中不断调整位置,确定最佳连接状态,最终合成稳定的晶型多孔骨架,硼酸基与羟基共聚脱水的反应(图4(a))即为此类反应.反之,在动力学控制反应中,共价键的形成是不可逆的,共价键一旦形成单体分子的位置便无法再调整,想要得到长程有序的结构是非常困难的.但是也正是因为共价键较难破坏,由该类反应得到的多孔材料稳定性通常较高^[12].这类反应包括,卤素基在Ni催化下的沃尔曼偶联反应(Yamamoto type Ullmann coupling reaction,图4(b))^[13,14], ZnCl_2 催化的氰基自聚反应(ZnCl_2 mediated nitrile cyclotrimerization,图4(c))^[15,16],硼酸基或硼酯基与卤素基在Pd催化下的铃木偶联反应(Suzuki coupling reaction,图4(d))^[17,18],炔基与卤素基在Pd催化下的菌头偶联反应(Sonogashira-Hagihara coupling

图2 (网络版彩色)PAFs材料(如PAF-1)的拓扑导向设计合成路线(从下往上和由上至下的方法)^[10]

Figure 2 (Color online) Topology-directed synthesis of PAF materials (PAF-1) via bottom-up and top-down approaches^[10]

图3 用于构筑PAFs材料的正四面体有机单体. PAF-n表示由对应单体合成的PAFs材料, 具体内容将在第3节讨论

Figure 3 Organic monomers with tetrahedral structure used to build PAF materials. PAF-n symbols refer to the PAF materials constructed from the corresponding monomer. These PAF materials will be discussed in detail in Section 3

reaction, 图4(e))^[19,20], FeCl₃或AlCl₃催化的傅氏反应(Friedel-Crafts reaction, 图4(f))^[21,22]与肖尔反应(Scholl reaction, 图4(g))^[23,24], 以及氨基与三聚氯氰脱去HCl的聚合反应(图4(h))^[25,26].

2.3 功能化策略

PAFs材料的功能化可以从3个方面实现^[27,28]: 改变连接单元长度或宽度调控孔径尺寸^[29-31]; 向有机单体引入官能团进行原位合成^[32-36]; 对合成的PAFs材料进行后修饰^[37-39].

通过调节连接单元的长度, 我们可以将材料的孔径延伸到介孔范围^[40], 如果连接单元过长, 聚合过程中则容易形成穿插结构而使得材料的孔径尺寸减小^[41,42]. 原位合成方法是合成带有功能性基团的PAFs材料最简便的手段, 通过一步聚合反应即可将官能团引入到材料骨架中, 从而使材料具有特定的性能(例如, 向骨架中引入杂原子或碱性基团可提高材料的二氧化碳吸附性能^[43-45]). 但是需要注意的是,

拟引入的功能性基团在聚合反应中不会被破坏或参与聚合反应而“失效”或影响材料骨架结构. 后修饰手段是提高材料功能性的更优异的方法, 它提供了更广泛的官能团接枝可能性, 并且在一定程度上可以实现可控修饰. 通过后修饰方法, 除了常见的官能团(如硝基、氨基、磺酸基等)^[46,47], 还可以向材料中引入金属离子和金属纳米粒子^[48-50]或大尺寸的功能性基团(如将酸性官能团与碱性官能团同时引入PAFs材料中作为异构级联催化平台)^[51]. 实现功能化策略的具体方法及效果将在第3节阐述.

3 多孔芳香骨架材料的应用

3.1 二氧化碳捕获

时下, 日益严重的全球变暖等气候问题成为人们广泛关注的问题, 而过量的二氧化碳排放被认为是引发该问题最重要的因素^[52]. 因此, 开发具有高效二氧化碳捕获性能的材料成为各国科研工作者研

图4 基于正四面体单元的PAFs材料的合成涉及的聚合反应类型. (a) 硼酸与二醇的共聚反应; (b) Ni_0 催化的沃尔曼偶联反应; (c) ZnCl_2 催化的氰基环三聚反应; (d) 卤素与硼酸基(d1)和硼酯基(d2)的铃木偶联反应; (e) Pd催化的菌头偶联反应; (f) FeCl_3 或 AlCl_3 催化的傅氏烷基化反应; (g) 路易斯酸催化的肖尔反应; (h) 氨基与三聚氯氰的聚合反应. X代表卤素原子

Figure 4 Representative coupling reactions used in the synthesis of PAFs based on tetrahedral units. (a) Co-condensation reaction between boronic acids and diols; (b) Ni_0 catalyzed Yamamoto type Ullmann coupling; (c) ZnCl_2 mediated nitrile cyclotrimerization; (d) Suzuki coupling reaction of halogen group with boronic acid group (d1) and boron ester group (d2); (e) Pd-mediated aryl-ethynyl (Sonogashira-Hagihara) coupling; (f) Friedel-Crafts reaction catalyzed with FeCl_3 or AlCl_3 with crosslinker agent; (g) Scholl reaction between two arene compounds with the aid of Lewis acid; (h) polycondensation of cyanuric chloride with amino-monomer. X refers to halogen atoms

研究的热点. 传统的二氧化碳捕获方法是利用氨溶剂与二氧化碳发生化学反应, 这种方法氨溶剂回收能耗大, 会造成更多的能源浪费^[53]. 反之, 依托于物理吸附作用的固体多孔材料则是更合适的二氧化碳捕获材料^[54,55]. 作为多孔材料家族重要的一员, PAFs材料高的比表面积、低的骨架密度以及骨架可修饰的灵活性及可控性使其在二氧化碳捕获中体现出更大的优势^[56].

影响材料二氧化碳储存量的因素包括温度与压力, 温度越高, 二氧化碳的储存量越低, 压力越大, 二氧化碳储存量越大; 材料的比表面积与孔容, 低压下, 这两个因素对材料的二氧化碳吸附量影响不大, 而当压力逐渐升高, 比表面积与孔容越大的材料吸附量越高; 孔径尺寸对低压下材料的二氧化碳吸附作用较大, 通常, 小孔径尺寸的材料具有更高的吸附量^[57,58]. 在298 K下, 当压力为40 bar(1 bar=0.1 MPa)时, 具有超高比表面积的PAF-1材料的二氧化碳储存量可以达到29.5 mmol/g^[1]. 在室温, 1 bar的条件下, 基于正四面体的PAFs材料的二氧化碳吸附量通常为5.2%~8.7%(重量百分比)^[59-64], 处于多孔材料对二氧化碳储存的前列. 通过向骨架中引入杂原子或官能团, 可以有效增加材料对二氧化碳的吸附作用从而提高其储存量. 通过简单的傅氏烷基化反应, 利用原位合成法将氨基、羟基官能团一步引入到材料骨架中, 合成了PAF-32-NH₂和PAF-32-OH, 其中羟基化的PAFs材料相比于无官能团的PAF-32, 其二氧化碳吸附量提高了约40%^[65]. 此外, 向骨架中引入轻金属离子也可以提高材料的二氧化碳储存量. 通过菌头偶联反应, 原位合成了具有羟基可修饰基团的PAF-18-OH, 然后采用后修饰策略, 利用羟基的活性与苯锂反应制备了Li离子修饰的PAF-18-OLi, 气体吸附结果证明修饰后的材料二氧化碳吸附能力大幅增加^[66]. 同样, 骨架中含有羧基官能团的PAF-26-COOH也被设计合成出来, 通过离子交换, Li, Na, K, Mg离子分别被引入骨架中, 这些金属离子具有不同的核外电子数和价态, 对二氧化碳分子的极化能力也不同, 表现出增强的二氧化碳吸附能力(图5)^[67]. 此外, 通过原位合成的方法将光响应型的偶氮官能团成功地接枝在材料骨架上, 合成了具有孔道性质可调的PAF-37, 在紫外光的照射下, 偶氮基团的顺式异构体显示出比反式异构体更高的二氧化碳吸附能力^[68].

3.2 气体分离

PAFs材料由于其孔道性质可以进行可控调节, 被成功地应用到基于吸附的气体分离领域^[69]. 材料对混合气体的吸附分离能力主要体现在: 对其中一种气体具有选择性的优先吸附能力而对另外一种气体吸附能力较弱; 或者是材料对于不同气体的吸附量有明显差异^[70]. 通常, 我们利用下面3种方法来评估材料的气体分离能力: (1) 通过亨利法则(Henry's Law)计算在低压线性区($P < 0.1$ bar)不同气体吸附量的斜率比值来确定分离比; (2) 利用理想吸附溶液理论(ideal adsorbed solution theory, IAST)^[71]从单一组分的气体吸附等温线来模拟材料在混合气体中的吸附分离比; (3) 将材料填充在色谱分离柱中, 经过穿透实验(breakthrough)检测通过分离柱的气体组分来评判材料的分离能力.

鉴于二氧化碳捕获是当下研究关注的重点问题, 对PAFs材料的分离性能研究主要包括CO₂/N₂和CO₂/CH₄, 以上提到的分离效果评估方法在实验中都有应用. 本文着重介绍基于四硼酸基四苯基甲烷的MCOF-1材料对烃类小分子的分离^[72]. 利用CH₄, C₂H₄, C₂H₆, C₃H₈的分子动力学直径为4~6 Å的特点, 设计合成了孔径尺寸为6.4 Å的MCOF-1材料. 由于孔道大小的限制及材料对C₂, C₃烷烃具有较高吸附的影响, IAST计算结果及混合气体穿透实验都显示MCOF-1具有很高的烷烃分离能力, 其中, 由IAST方法计算出的MCOF-1的C₃H₈/CH₄分离比超过了1800, 说明材料能够很容易进行丙烷和甲烷的分离(图6).

3.3 液体小分子吸附

正四面体构筑基块主要的结构单元是苯环, 以此基块制备的PAFs材料对芳香性液体小分子很可能有较好的吸附性能. 在298 K, 苯和甲苯的饱和蒸气压下, PAF-1对苯的吸附量为1301 mg/g, 对甲苯的吸附量为1357 mg/g, 超过了大部分多孔材料^[1]. 正四面体中心由4个苯环单元连接的PAF-11, 由于其连接单元太长, 结构发生了穿插, Langmuir比表面积仅为952 m²/g, 但是它的结构中有更多的苯环, 因此对苯和甲苯的吸附量也达到了874和780 mg/g^[29].

同时, PAFs材料的疏水性使得材料对水的吸附作用较弱. 对合成的一些PAFs材料(如PAF-8^[60], PAF-11^[29]等)进行甲醇、水蒸气吸附测试, 结果显示

图5 (网络版彩色)PAF-26s的合成路线及其二氧化碳吸附曲线。(a) 利用四(4-乙炔基苯)甲烷合成PAF-26-COOH和PAF-26-COOM的示意图;(b) 273 K下PAF-26s的二氧化碳吸附曲线;(c) PAF-26s的二氧化碳吸附热^[67]

Figure 5 (Color online) Synthetic route and CO₂ sorption of PAF-26s. (a) Schematic representation of the synthesis of PAF-26-COOH and PAF-26-COOM using tetrakis(4-ethynylphenyl)methane; (b) CO₂ sorption isotherms at 273 K of PAF-26s; (c) CO₂ isosteric heats of adsorption for PAF-26s^[67]

PAFs材料对水的吸附量远远低于对甲醇的吸附值, 结合该类材料高的热稳定性和化学稳定性, PAFs材料有可能在醇水分离中有一定的实际应用价值。

3.4 碘单质的吸附与释放

核能是非常重要的未来能源之一, 只需消耗少量的核燃料就可产生大量的电能, 具有传统燃料能源不可比拟的优势^[73,74]。但是, 核废料中的放射性核物质(比如碘单质)的安全存储是影响核能应用的重要问题^[75]。通过选择带电荷的正四面体构筑单元LTIPB, 利用菌头偶联反应与四炔基四苯基甲烷合成了新型荷电PAFs材料PAF-25^[76]。该策略将带电荷的中心、丰富的炔键整合到材料骨架中, 加之骨架本身有大量的苯环, 这些独特的结构有利于增加骨架与碘分子的相互作用, 使其成为优秀的碘捕获材料。实验证明, 1 g PAF-25材料可以吸附2.6 g碘单质, 是目前最高的碘单质吸附值(图7)。此外, 利用铃木偶联

反应合成的带电荷PAFs材料PAF-21和PAF-22, 也具有可逆的碘单质捕获能力, 可在富集碘单质的过程中循环使用^[77]。

3.5 催化

PAFs材料高的稳定性及灵活的可修饰性使其在催化方面也有广泛的应用。利用一种新的合成策略特别设计了具有氨基锚点的PAFs材料PAF70-NH₂, 该材料具有多级孔结构, 并且其介孔孔径分布较窄(图8)。通过后修饰的方法, 相当大尺寸的硫脲基团很容易地被共价固载到PAF70-NH₂的孔里, 得到一种新的具有硫脲基团的材料PAF70-thiourea^[78]。PAF70-thiourea可以催化NBS氧化醇的反应, 与对应的均相催化剂相比, 表现出了更高的催化活性。PAF70-thiourea还具有完全再循环的能力, 在现有的催化体系中至少可以经历36次循环而催化活性没有降低的趋势。利用PAF70-NH₂的刚性骨架及介孔结构, 还制备了

图6 (网络版彩色)MCOF-1的合成及气体分离性质。(a) MCOF-1的合成路径;(b) 298 K, 101 kPa条件下, MCOF-1的烃类小分子气体混合物的吸附分离比预测图;(c) 298 K下, MCOF-1的模拟穿透实验^[72]

Figure 6 (Color online) Synthesis of MCOF-1 and its gas separation properties. (a) Synthetic route of MCOF-1; (b) IAST predicted equimolar gas mixture adsorption selectivities of small hydrocarbon molecules for MCOF-1 at 298 K and 101 kPa; (c) simulated breakthrough experiment of MCOF-1 at 298 K^[72]

图7 (网络版彩色)PAF-25的结构片段和碘捕获性能。(a) PAF-25的结构基本单元;(b) PAF-25碘捕获前后的颜色变化图片;(c) 将吸附碘分子的PAFs材料浸泡在乙醇中的碘释放过程^[76]

Figure 7 (Color online) PAF-25 and its iodine capture abilities. (a) Representative structure basic unit of PAF-25. (b) Photographs showing the color change before and after iodine capture of PAF-25. (c) Progress of iodine release from PAF-25 when the containing iodine PAF materials were immersed in ethanol^[76]

具有很高Pd固载量的PAF70-Pd, 该材料在铃木偶联反应的过程中表现出了极高的催化活性(0.1 mg的催化剂可以催化产出4.6 g的产品)和显著的择形性^[79]。

这些工作促进了介孔PAF材料的发展及其在催化和其他领域的应用。

卟啉环是仿生催化中一类重要的研究对象, 将

图8 (网络版彩色)PAF70-NH₂, PAF70-thiourea^[78]和PAF70-Pd的合成路线图^[79]

Figure 8 (Color online) Synthetic route of PAF70-NH₂, PAF70-thiourea^[78] and PAF70-Pd^[79]

卟啉环与PAFs材料结合, 不仅提供了新的构筑基元, 也增加了材料的功能位点. 通过四硼脂四苯基甲烷与四溴四苯基卟啉的 Suzuki 偶联反应合成了 PAF-76^[80]. 然后, 利用卟啉环与过渡金属离子的络合作用将金属 Fe, Mn, Zn 离子引入到骨架中, 合成的 PAF-76s 在苯乙烯催化氧化的实验中具有优异的催化性能.

3.6 传感检测

荧光淬灭分析法是一种灵敏且容易操作的分析方法, 被广泛应用于传感方面. 采用四硼酸四苯基甲烷构筑基块制备了具有良好荧光性能的 PAF-14^[81], PAF-15^[82], 它们在二氯甲烷中的荧光量子产率分别为 37.5% 和 14%. 当材料吸附硝基苯、2,4-二硝基甲苯和 2,4,6-三硝基甲苯后, 材料的荧光淬灭展现了良好

的检测灵敏度.

带有咪唑基团的正四面体构筑基元被用来制备具有电活性的PAFs材料PAF-39^[83]. 利用PAF-39制备的电极材料具有较好的过氧化氢还原性能, 加入葡萄糖、麦芽糖等干扰物后材料的还原性能基本不变, 可用于过氧化氢检测.

3.7 低成本PAFs材料

2.2节列举了制备正四面体多孔芳香骨架材料采用的聚合反应, 从中可以看到大部分聚合反应都是由过渡金属或贵金属催化的, 这类催化剂价格昂贵, 大大限制了材料在实际生产中的应用, 而其中由廉价氯化铁、氯化铝催化的反应则更有应用价值. 通过简单经济的傅氏烷基化反应和肖尔反应, 合成了一系列低成本PAF材料PAF-7-9^[59,60], PAF-32s^[65], PAF-42-44^[84]. 这些材料都具有较高的比表面和高的稳定

性, 同时, 对于PAF-32s, 还可以通过原位合成的方法将氨基、羟基官能团一步引入骨架中, 从而提高材料的气体吸附性能.

4 结论

以上主要介绍了基于正四面体构筑基元的PAFs材料的设计合成与性质探索研究. 从中可以看到, 以四苯基四苯甲烷为代表的正四面体有机单体, 可以被广泛地应用于PAFs材料的合成中. 通过采用丰富的聚合反应, 合成的PAFs材料在吸附、分离、催化、传感等不同领域都展现出优异的性能. 而低成本反应的开发更提高了该类材料在实际生产中应用的可能性. 未来, 具有高比表面、高稳定性及灵活可控修饰性的PAFs材料会得到更多研究者的关注, 更多具有优异性能的PAFs材料将被合成出来并广泛地应用到各个领域.

参考文献

- 1 Ben T, Ren H, Ma S Q, et al. Targeted synthesis of a porous aromatic framework with high stability and exceptionally high surface area. *Angew Chem Int Ed*, 2009, 48: 9457–9460
- 2 Zhu G S, Ren H. Porous organic frameworks: Design, synthesis and their advanced applications. In: *SpringerBriefs in Green Chemistry for Sustainability*. Berlin: Springer Nature, 2015
- 3 Holst J R, Cooper A I. Ultrahigh surface area in porous solids. *Adv Mater*, 2010, 22: 5212–5216
- 4 Holst J R, Stockel E, Adams D J, et al. High surface area networks from tetrahedral monomers: Metal-catalyzed coupling, thermal polymerization, and “click” chemistry. *Macromolecules*, 2010, 43: 8531–8538
- 5 Lu W G, Yuan D Q, Zhao D, et al. Porous polymer networks: Synthesis, porosity, and applications in gas storage/separation. *Chem Mater*, 2010, 22: 5964–5972
- 6 Lu W, Yuan D, Sculley J, et al. Sulfonate-grafted porous polymer networks for preferential CO₂ adsorption at low pressure. *J Am Chem Soc*, 2011, 133: 18126–18129
- 7 Eddaoudi M, Rosi N, Vodak D, et al. Systematic design of pore size and functionality in isorecticular MOFs and their application in methane storage. *Science*, 2002, 295: 469–472
- 8 Yaghi O M, O’Keeffe M, Ockwig N W, et al. Reticular synthesis and the design of new materials. *Nature*, 2003, 423: 705–714
- 9 El-Kaderi H M, Hunt J R, Mendoza-Cortes J L, et al. Designed synthesis of 3D covalent organic frameworks. *Science*, 2007, 316: 268–272
- 10 Zou X Q, Ren H, Zhu G S. Topology-directed design of porous organic frameworks and their advanced applications. *Chem Commun*, 2013, 49: 3925–3936
- 11 Ren H, Zhu G S. Porous organic frameworks: Synthetic strategy and their applications. *Acta Chim Sin*, 2015, 73: 587–599
- 12 McKeown N B, Budd P M. Exploitation of intrinsic microporosity in polymer-based materials. *Macromolecules*, 2010, 43: 5163–5176
- 13 Rose M, Bohlmann W, Sabo M, et al. Element-organic frameworks with high permanent porosity. *Chem Commun*, 2008, (21): 2462–2464
- 14 Zhou G, Baumgarten M, Müllen K. Arylamine-substituted oligo(ladder-type pentaphenylene)s: Electronic communication between bridged redox centers. *J Am Chem Soc*, 2007, 129: 12211–12221
- 15 Kuhn P, Antonietti M, Thomas A. Porous, covalent triazine-based frameworks prepared by ionothermal synthesis. *Angew Chem Int Ed*, 2008, 47: 3450–3453
- 16 Ren H, Ben T, Wang E S, et al. Targeted synthesis of a 3D porous aromatic framework for selective sorption of benzene. *Chem Commun*, 2010, 46: 291–293
- 17 Chen L, Honsho Y, Seki S, et al. Light-harvesting conjugated microporous polymers: Rapid and highly efficient flow of light energy with a porous polyphenylene framework as antenna. *J Am Chem Soc*, 2010, 132: 6742–6748

- 18 Chen L, Yang Y, Jiang D. CMPs as scaffolds for constructing porous catalytic frameworks: A built-in heterogeneous catalyst with high activity and selectivity based on nanoporous metalloporphyrin polymers. *J Am Chem Soc*, 2010, 132: 9138–9143
- 19 Nicolaou K C, Bulger P G, Sarlah D. Palladium-catalyzed cross-coupling reactions in total synthesis. *Angew Chem Int Ed*, 2005, 44: 4442–4489
- 20 Jiang J X, Trewin A, Su F, et al. Microporous poly(tri(4-ethynylphenyl)amine) networks: Synthesis, properties, and atomistic simulation. *Macromolecules*, 2009, 42: 2658–2666
- 21 Lee J Y, Wood C, Bradshaw D, et al. Hydrogen adsorption in microporous hypercrosslinked polymers. *Chem Commun*, 2006, (25): 2670–2672
- 22 Schmidt J, Weber J, Epping J D, et al. Microporous conjugated poly(thienylene arylene) networks. *Adv Mater*, 2009, 21: 702–705
- 23 King B T, Kroulik J, Robertson C R, et al. Controlling the scholl reaction. *J Org Chem*, 2007, 72: 2279–2288
- 24 Yang Y, Yuan L Y, Shan B W, et al. Twisted polycyclic arenes from tetranaphthylidiphenylbenzenes by controlling the scholl reaction with substituents. *Chem Eur J*, 2016, 22: 18620–18627
- 25 Zhao H Y, Jin Z, Su H M, et al. Targeted synthesis of a 2D ordered porous organic framework for drug release. *Chem Commun*, 2011, 47: 6389–6391
- 26 Patel H A, Karadas F, Canlier A, et al. High capacity carbon dioxide adsorption by inexpensive covalent organic polymers. *J Mater Chem*, 2012, 22: 8431–8437
- 27 Pei C Y, Ben T, Qiu S L. Great prospects for PAF-1 and its derivatives. *Mater Horiz*, 2015, 2: 11–21
- 28 Dawson R, Cooper A I, Adams D J. Nanoporous organic polymer networks. *Prog Polym Sci*, 2012, 37: 530–563
- 29 Yuan Y, Sun F, Ren H, et al. Targeted synthesis of a porous aromatic framework with a high adsorption capacity for organic molecules. *J Mater Chem*, 2011, 21: 13498–13502
- 30 Hmadeh M, Lu Z, Liu Z, et al. New porous crystals of extended metal-catecholates. *Chem Mater*, 2012, 24: 3511–3513
- 31 Wu X J, Wang R, Yang H J, et al. Ultrahigh hydrogen storage capacity of novel porous aromatic frameworks. *J Mater Chem A*, 2015, 3: 10724–10729
- 32 Ben T, Pei C, Zhang D, et al. Gas storage in porous aromatic frameworks (PAFs). *Energy Environ Sci*, 2011, 4: 3991–3999
- 33 Dawson R, Ratvijitvech T, Corker M, et al. Microporous copolymers for increased gas selectivity. *Polym Chem*, 2012, 3: 2034–2038
- 34 Weston M H, Farha O K, Hauser B G, et al. Synthesis and metalation of catechol-functionalized porous organic polymers. *Chem Mater*, 2012, 24: 1292–1296
- 35 Zhang Y M, Li B Y, Williams K, et al. A new microporous carbon material synthesized via thermolysis of a porous aromatic framework embedded with an extra carbon source for low-pressure CO₂ uptake. *Chem Commun*, 2013, 49: 10269–10271
- 36 Patel H A, Je S H, Park J, et al. Unprecedented high-temperature CO₂ selectivity in N-2-phobic nanoporous covalent organic polymers. *Nat Commun*, 2013, 4: 1357–1364
- 37 Li B Y, Sun Q, Zhang Y M, et al. Functionalized porous aromatic framework for efficient uranium adsorption from aqueous solutions. *ACS Appl Mater Interfaces*, 2017, 9: 12511–12517
- 38 Lyndon R, Konstas K, Evans R A, et al. Tunable photodynamic switching of DArE@PAF-1 for carbon capture. *Adv Funct Mater*, 2015, 25: 4405–4411
- 39 Van Humbeck J F, McDonald T M, Jing X F, et al. Ammonia capture in porous organic polymers densely functionalized with bronsted acid groups. *J Am Chem Soc*, 2014, 136: 2432–2440
- 40 Jing X F, Sun F X, Ren H, et al. Targeted synthesis of micro-mesoporous hybrid material derived from octaphenylsilsesquioxane building units. *Micropor Mesopor Mater*, 2013, 165: 92–98
- 41 Uribe-Romo F J, Hunt J R, Furukawa H, et al. A crystalline imine-linked 3D porous covalent organic framework. *J Am Chem Soc*, 2009, 131: 4570–4571
- 42 Yuan Y, Liu J, Ren H, et al. Synthesis and characterization of germanium-centered three-dimensional crystalline porous aromatic framework. *J Mater Res*, 2012, 27: 1417–1420
- 43 Dawson R, Cooper A I, Adams D J. Chemical functionalization strategies for carbon dioxide capture in microporous organic polymers. *Polym Int*, 2013, 62: 345–352
- 44 McDonald T M, D'Alessandro D M, Krishna R, et al. Enhanced carbon dioxide capture upon incorporation of *N,N'*-dimethylethylenediamine in the metal-organic framework CuBTtri. *Chem Sci*, 2011, 2: 2022–2028
- 45 Garibay S J, Weston M H, Mondloch J E, et al. Accessing functionalized porous aromatic frameworks (PAFs) through a *de novo* approach. *CrystEngComm*, 2013, 15: 1515–1519
- 46 Merino E, Verde-Sesto E, Maya E M, et al. Mono-functionalization of porous aromatic frameworks to use as compatible heterogeneous catalysts in one-pot cascade reactions. *Appl Catal A Gen*, 2014, 469: 206–212

- 47 Xiang Z H, Wang D, Xue Y H, et al. Paf-derived nitrogen-doped 3D carbon materials for efficient energy conversion and storage. *Sci Rep*, 2015, 5: 8307–8314
- 48 Li B Y, Zhang Y M, Krishna R, et al. Introduction of pi-complexation into porous aromatic framework for highly selective adsorption of ethylene over ethane. *J Am Chem Soc*, 2014, 136: 8654–8660
- 49 Lee S, Barin G, Ackerman C M, et al. Copper capture in a thioether-functionalized porous polymer applied to the detection of Wilson's disease. *J Am Chem Soc*, 2016, 138: 7603–7609
- 50 Dong Y, Das S, Zhu L K, et al. Standout electrochemical performance of SnO₂ and Sn/SnO₂ nanoparticles embedded in a KOH-activated carbonized porous aromatic framework (PAF-1) matrix as the anode for lithium-ion batteries. *J Mater Chem A*, 2016, 4: 18822–18831
- 51 Zhang Y M, Li B Y, Ma S Q. Dual functionalization of porous aromatic frameworks as a new platform for heterogeneous cascade catalysis. *Chem Commun*, 2014, 50: 8507–8510
- 52 Orr J, Fabry J V, Aumont O, et al. Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. *Nature*, 2005, 437: 681–686
- 53 Boot-Handford M E, Abanades J C, Anthony E J, et al. Carbon capture and storage update. *Energy Environ Sci*, 2014, 7: 130–189
- 54 Choi S, Drese J H, Jones C W. Adsorbent materials for carbon dioxide capture from large anthropogenic point sources. *ChemSusChem*, 2009, 2: 796–854
- 55 Lin L C, Berger A H, Martin R L, et al. In silico screening of carbon-capture materials. *Nat Mater*, 2012, 11: 633–641
- 56 Das S, Heasman P, Ben T, et al. Porous organic materials: Strategic design and structure-function correlation. *Chem Rev*, 2017, 117: 1515–1563
- 57 Liu Y Y, Wang Z Y U, Zhou H C. Recent advances in carbon dioxide capture with metal-organic frameworks. *Greenhouse Gases Sci Technol*, 2012, 2: 239–259
- 58 Sumida K, Rogow D L, Mason J A, et al. Carbon dioxide capture in metal-organic frameworks. *Chem Rev*, 2012, 112: 724–781
- 59 Cui P, Jing X F, Yuan Y, et al. Synthesis of porous aromatic framework with friedel-crafts alkylation reaction for CO₂ separation. *Chin Chem Lett*, 2016, 27: 1479–1484
- 60 Cui P, Jing X F, Ren H, et al. Porous aromatic frameworks: Synthesis via Friedel-Crafts alkylation reaction and gas sorption property. *Chin J Inorg Chem*, 2015, 31: 1855–1859
- 61 Wang W, Ren H, Sun F X, et al. Synthesis of porous aromatic framework with tuning porosity via ionothermal reaction. *Dalton Trans*, 2012, 41: 3933–3936
- 62 Yuan R R, Ren H, Yan Z J, et al. Robust tri(4-ethynylphenyl)amine-based porous aromatic frameworks for carbon dioxide capture. *Polym Chem*, 2014, 5: 2266–2272
- 63 Wang W, Yan Z J, Yuan Y, et al. Target synthesis of a novel porous aromatic framework for efficient CO₂ capture. *Acta Chim Sin*, 2014, 72: 557–562
- 64 Wang W, Yuan Y, Sun F X, et al. Novel porous aromatic framework with excellent separation capability of CO₂ in N₂ or CH₄. *Chem Res Chin Univ*, 2014, 30: 1018–1021
- 65 Jing X F, Zou D L, Cui P, et al. Facile synthesis of cost-effective porous aromatic materials with enhanced carbon dioxide uptake. *J Mater Chem A*, 2013, 1: 13926–13931
- 66 Ma H P, Ren H, Zou X Q, et al. Novel lithium-loaded porous aromatic framework for efficient CO₂ and H₂ uptake. *J Mater Chem A*, 2013, 1: 752–758
- 67 Ma H P, Ren H, Zou X Q, et al. Post-metalation of porous aromatic frameworks for highly efficient carbon capture from CO₂+N₂ and CH₄+N₂ mixtures. *Polym Chem*, 2014, 5: 144–152
- 68 Yuan R R, Ren H, He H M, et al. Targeted synthesis of porous aromatic frameworks with stimuli-responsive adsorption properties. *Sci China Mater*, 2015, 58: 38–43
- 69 Zou X, Zhu G. Microporous organic materials for membrane-based gas separation. *Adv Mater*, 2018, 30: 1700750
- 70 Li J R, Sculley J, Zhou H C. Metal-organic frameworks for separations. *Chem Rev*, 2012, 112: 869–932
- 71 Myers A L, Prausnitz J M. Thermodynamics of mixed-gas adsorption. *AIChE J*, 1965, 11: 121–127
- 72 Ma H P, Ren H, Meng S, et al. A 3D microporous covalent organic framework with exceedingly high C₃H₈/CH₄ and C₂ hydrocarbon/CH₄ selectivity. *Chem Commun*, 2013, 49: 9773–9775
- 73 Vienna J D. Nuclear waste vitrification in the united states: Recent developments and future options. *Int J Appl Glass Sci*, 2010, 1: 309–321
- 74 Kintisch E. Congress tells DOE to take fresh look at recycling spent reactor fuel. *Science*, 2005, 310: 1406–1406
- 75 Ewing R C, von Hippel F N. Nuclear waste management in the united states-starting over. *Science*, 2009, 325: 151–152
- 76 Yan Z, Yuan Y, Tian Y, et al. Highly efficient enrichment of volatile iodine by charged porous aromatic frameworks with three sorption sites. *Angew Chem Int Ed*, 2015, 54: 14215

- 77 Yan Z J, Yuan Y, Liu J, et al. Targeted syntheses of charged porous aromatic frameworks for iodine enrichment and release. *Acta Chim Sin*, 2016, 74: 67–73
- 78 Sun J S, Jing L P, Tian Y Y, et al. Task-specific design of a hierarchical porous aromatic framework as an ultrastable platform for large-sized catalytic active site binding. *Chem Commun*, 2018, 54: 1603–1606
- 79 Jing L P, Sun J S, Sun F, et al. Porous aromatic framework with mesopores as a platform for a super-efficient heterogeneous Pd-based organometallic catalysis. *Chem Sci*, 2018, 9: 3523–3530
- 80 Meng S, Zou X Q, Liu C F, et al. Synthesis and catalytic properties of new metalloporphyrin-based porous organic framework materials with single and accessible sites. *ChemCatChem*, 2016, 8: 2393–2400
- 81 Yuan Y, Ren H, Sun F X, et al. Sensitive detection of hazardous explosives via highly fluorescent crystalline porous aromatic frameworks. *J Mater Chem*, 2012, 22: 24558–24562
- 82 Yuan Y, Ren H, Sun F X, et al. Targeted synthesis of a 3D crystalline porous aromatic framework with luminescence quenching ability for hazardous and explosive molecules. *J Phys Chem C*, 2012, 116: 26431–26435
- 83 Yuan R R, Gu Y, Ren H, et al. Porous aromatic framework as an efficient metal-free electrocatalyst for non-enzymatic H_2O_2 sensing. *Chem Eur J*, 2017, 23: 9467–9471
- 84 Li L N, Ren H, Yuan Y, et al. Construction and adsorption properties of porous aromatic frameworks via AlCl_3 -triggered coupling polymerization. *J Mater Chem A*, 2014, 2: 11091–11098

Summary for “基于正四面体构筑单元的多孔芳香骨架材料”

Porous aromatic frameworks derived from tetrahedral units

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Porous aromatic frameworks (PAFs), an important class of porous materials, have gained worldwide attentions and been greatly developed since the first PAF material PAF-1 was successfully designed and synthesized in 2009. More than 100 PAF materials with specific functionalities were synthesized and reported in the last decade. The high surface areas, light skeleton densities and high thermal and chemical stabilities make PAF materials good candidates in various applications, such as gas sorption and separation, catalysis, sensor and host-guest chemistry.

The design of PAF-1 came from the structure of diamond, the most stable substance existing in the nature at present. The carbon atoms in diamond are covalently bonded with four adjacent carbon atoms by sp^3 hybridization to form tetrahedral units. This special structure makes diamond the hardest material. However, the short length of C–C bond results in a compact structure of diamond. Conceptually, if the C–C bonds were replaced with rigid linear units, the resulting material should not only retain the diamond structure but also present increasing internal surface area. By employing Ullmann coupling reaction of tetrakis(4-bromophenyl)methane, PAF-1 with ultrahigh surface area as well as high thermal and chemical stability was synthesized. The structural information of PAF-1 was obtained by various characterizations, which is consistent with P2 model structure simulated from diamond topology. Thus, tetrahedral building units are good candidates to construct PAFs with high surface area and high stabilities.

Reticular chemistry was introduced into the design of porous materials in the end of 20th century, and has been well developed and employed with the concept of topology. Via the bottom-up and top-down ways, PAF materials derived from tetrahedral units may possess diamond-like structure thus they would exhibit high thermal stabilities. By adjusting the length of linkages between tetrahedral units, PAFs with tunable pore sizes can be targeted synthesized, which might even extend to mesopore range. *In-situ* synthesis and post-modification methods bring more possibilities for the functionalization of PAF materials. Various functional groups such as $-NH_2$, $-COOH$, $-OH$ can be embedded in PAFs' skeletons. Metal cations can be introduced in the pores of PAF materials by ion-exchange method. Besides, metal nanoparticles would also be encapsulated in PAF materials with large pore size and specific interaction sites.

In this review, we summarized the targeted synthesis of PAF materials derived from tetrahedral units with the guide of reticular chemistry and demonstrated the functionalization strategy. Meanwhile, the applications of PAF materials, including CO_2 sorption and separation, small liquid molecule adsorption, iodine capture, catalysis and sensor were presented and the effect factors were discussed in detail. In addition, cost-effective PAF materials were synthesized with cheap catalysts such as $FeCl_3$ and $AlCl_3$ to expand their applications in practice.

The above achievements opened up new avenues for the targeted synthesis of porous materials with high surface areas and high stabilities and provided insights for the materials design with specific functionalities.

porous aromatic framework, targeted synthesis, topology, sorption, separation, catalysis

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