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用于碳烃分离的共价有机框架

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摘要 碳烃化合物的高效分离不仅对石油化工行业具有重要的经济价值, 也对推动化工绿色转型和可持续发展具有深远的影响. 然而, 碳烃化合物相近的物理和化学性质为开发高效的分离技术带来了显著的挑战. 目前, 碳烃化合物分离主要依赖于能源密集型和成本高昂的精馏或萃取等技术. 开发基于不同碳烃化合物分子结构间细微差异的分离技术和新型分离材料, 为碳烃化合物的高效分离和利用提供了一种全新的解决方案. 共价有机框架材料(covalent organic frameworks, COFs)具有高度可调的孔结构和孔化学环境, 为碳烃化合物的分离和纯化提供了新的可能性. 本文主要概述了目前COFs材料用于分离纯化碳烃化合物的最新研究进展, 并对COFs材料在碳烃分离的未来发展趋势进行了展望, 为开发高效碳烃分离COFs材料提供了新研究思路.

关键词 共价有机框架, 碳烃化合物, 吸附, 分离

石油加工产物通常由各种碳烃化合物混合组成, 碳烃化合物的分离纯化是石油化工行业生产中极为重要的环节. 然而碳烃化合物特别是同系物之间结构差异小且通常具有相似的沸点, 使得基于沸点差异的分离方法难以实现碳烃化合物的高效分离[1,2]. 多孔材料吸附分离工艺较传统大规模工业蒸馏分离过程, 无相变过程, 在能耗和碳排放方面具有显著优势[3,4]. 设计和开发适宜的多孔吸附分离材料是实现碳烃化合物高效分离的关键, 理想的吸附材料不仅要具备高吸附容量以充分捕捉目标物, 还应拥有高选择性, 以确保在复杂体系中对特定组分的精准识别与分离[5].

共价有机框架(covalent organic frameworks, COFs)作为一种新兴的有机多孔材料, 是一类由有机结构单元通过共价键连接形成的具有二维或三维网络结构的结晶多孔聚合物[6~10]. COFs具有密度低、比表面积高、孔径与结构可调等特点, 近些年来在碳烃分离和纯化中表现出了优异的性能[11,12]. COFs相比于分子筛和多孔碳等传统吸附分离材料提供了更多的设计自由度和功能性, 表现出如下优势: (1) COFs的有机构筑单元库异常丰富, 可通过不同的组合方式产生几乎无限的结构和功能. (2) COFs的结构具有可裁剪性, 通过调整COFs有机构筑单元的长度与大小可以对COFs的孔径进行调节, 来实现不同分子尺寸物质的精确分离. (3) COFs易于功能化, 可将各种功能位点引入有机构筑单元或通过后修饰方法在COFs骨架引入额外的官能团, 可使其适用于不同的分离过程. 这些特性使COFs材料在分离领域具有巨大的发展潜力, COFs主客体化学中的π···π相互作用、C–H···π相互作用和酸碱相互作用等调节策略被证实可以有效分离多种碳烃化合物.

鉴于COFs在碳烃分离领域取得的显著进展, 本综述探讨了COFs的孔径、表面极性和稳定性的调控策略, 系统地介绍了近年来COFs在烷烃/烯烃、烯烃/炔

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烃、己烷异构体、芳烃/环烷烃以及C_8芳烃分离方向的研究进展, 并对其分离机理进行了相应的分析. 最后指出了COFs在碳烃分离领域面临的挑战和机遇, 为进一步开发新型的高效碳烃分离的COFs材料提供了研究思路.

1 用于碳烃分离的COFs的关键特性

COFs孔径是实现分子筛分的基本要素, 不同的孔径决定了COFs特定的应用场景. 迄今为止, 大部分已报道的COFs材料的孔径通常较大, 不足以通过分子筛分作用来实现小分子的精确分离, 而利用孔道调控策略将COFs孔道缩小至亚纳米级往往充满挑战[13]. 通常可通过改变有机单体的尺寸和几何形状来构筑不同孔径的COFs[14]. 另一种可行方法是利用共价接枝的方法在COFs网络骨架形成后将不同大小或者比例的官能团引入COFs孔壁中, 这种方法可突破COFs有机单体种类限制, 将COFs孔径范围进一步扩大[15,16].

孔道表面的极性也是影响COFs分离的重要因素, 孔道表面的极性基团(羧基、磺酸基和F原子等)或非极性官能团(如烷基、烷氧基等)能够调节COFs与客体分子间的相互作用, 在分子分离中起着至关重要的作用. 基于COFs结构可预设计性和易于官能化特点, 通常可选取不同极性的结构单元构筑COFs或采用合成后修饰法在COFs骨架中引入不同极性官能团来调控COFs的极性[17,18].

COFs的稳定性是影响碳烃分离工艺稳定性的关键因素之一, 稳定性高的COFs有助于提高分离过程的效率和经济性. COFs大多由热力学控制的可逆聚合反应形成, 导致其在部分苛刻环境中稳定性欠佳[19]. 为进一步提高COFs的稳定性, 可合理选择COFs的有机单体, 以强度和稳定性更高的共价键如碳碳双键[20~22]、芳醚键[23,24]等连接构筑单元. 另一种方法是通过化学后修饰的方法将共价键转化为更稳定的共价键, 如亚胺键可被转化为稳定性更高的酰胺键[25]、吡啶环[26]等. 此外, 还可以通过在COFs层内或层间引入氢键来保护敏感的化学键或稳定结构单元的构象来提高COFs整体稳定性[27,28].

特别值得关注的是, 无论是通过结构预设计还是合成后修饰这两种策略调节COFs的性能时, 可能都会导致其孔径、表面极性以及稳定性发生相应变化. 这些变化之间可能相互促进, 形成正向的协同效应, 但同样可能引发一些非预期的负面效果. 因此, 在实际应用过程中, 必须对实验条件进行精确的调控, 并细致地平衡这些变化之间的关系, 以期达到最优的性能调整策略.

2 COFs在碳烃分离中的应用进展

2.1 烷烃/烯烃分离

乙烯和丙烯作为石化行业中需求量最大的基础化工原料, 其生产主要依赖于石油裂解, 产物中不可避免地会存在一定量的烷烃. 据估计每年用于烯烃与烷烃分离的能耗约占全球总能耗的0.3%, 开发烯烃与烷烃的高效分离技术对于现代化工可持续发展具有重要意义[29].

张振杰课题组[30]采用自下而上的[8+2]构建方法设计并合成了一系列具有有序的微孔结构和非极性/惰性孔环境的3D COFs(NKU-21, -22和-23), 可以选择性地从C_2H_4/C_2H_6混合物中吸附乙烷(图1(a)). NKU-21由于具有更窄的孔道可诱导更强的客体-骨架作用, 因此在室温下具有最高的乙烷吸附量(97.9 $cm^3\ g^{-1}$). 室温下动态穿透实验结果显示, NKU-21的穿透时间更长并可以从9/1的乙烯/乙烷混合气体中单次吸附分离得到纯度>99.99%的聚合级乙烯(图1(b), 1(c)).

通过合成后修饰在COFs中引入金属离子与不饱和烯烃产生π电子络合作用增强对烯烃分子的吸附, 可有效地提升烷烃/烯烃分离能力. 姜忠义课题组[31]通过在COF纳米孔道中负载高密度Ag^+与丙烯分子形成较强的π-络合作用, 促进了丙烯分子沿着纳米孔道表面快速扩散而减少了丙烷的传输. SCOF-Ag/聚酰亚胺复合膜的丙烯的渗透系数为75 barrer, 丙烯/丙烷的选择性高达35. 罗峰课题组[32]发现在含有磺酸基团的COF-ECUT-1中掺入少量钠离子可将其C_2H_2/C_2H_4选择性由6.33提升至9.41. 密度泛函理论计算结果显示, 这种选择性提升是由COF孔道中锚定的Na^+与C_2H_2分子间更强的Na-π相互作用力所造成的.

在COFs骨架中引入路易斯碱性位点后吸附质既可以与苯环间通过C–H···π相互作用吸附也可与路易斯碱性位点间通过C–H···N相互作用而吸附, 从而协同增强COFs对吸附质的选择性吸附能力. Hong课题组[33]利用线性二醛和哌嗪缩合制备了碱性叔胺基连接的KUF-3. 由于KUF-3富含芳香环和路易斯碱位点加之适宜的孔径大小, 可选择性分离C_2H_4/C_2H_6混合气中的C_2H_6, 分离后乙烯纯度>90%, 乙烯处理能力为

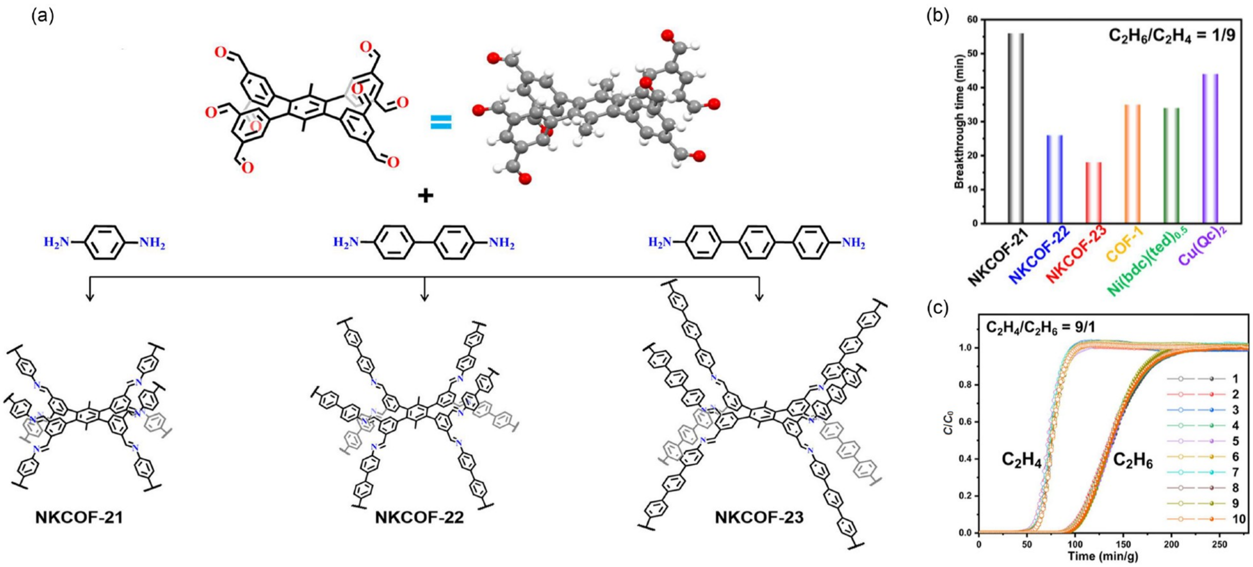

图 1 (网络版彩色)NKCOF-21, -22和-23的合成示意图和C_2H_4/C_2H_6混合气分离性能图[30]. (a) NKCOF-21, -22和-23的合成与结构示意图; (b) 不同吸附质的C_2H_4/C_2H_6混合气(9:1, v/v)穿透时间对比图; (c) 以NKCOF-21为吸附质的C_2H_4/C_2H_6混合气(9:1, v/v)的十次穿透实验曲线

Figure 1 (Color online) Illustration of synthetic procedures and C_2H_4/C_2H_6 separation performance of NKCOF-21, -22, and -23[30]. (a) Synthesis and structure of NKCOF-21, -22, and -23; (b) experimental breakthrough time intervals of C_2H_4/C_2H_6 mixtures (9:1, v/v) for different adsorbents; (c) ten cycles of experimental breakthrough curves of C_2H_4/C_2H_6 mixtures (9:1, v/v) for NKCOF-21

2.24 L kg^{-1}. 汪成课题组[34]采用含吡啶基团的单体2,3,5,6-四-(4-甲酰基苯基)吡啶(2,3,5,6-tetrakis-(4-formylphenyl)pyridine, TPP)与四(4-氨基苯基)甲烷(tetra(4-aminophenyl)methane, TAPM)缩合制备得到了高乙烷吸附能力的3D-TPP-COF. 与结构类似但由不含吡啶基团的1,2,4,5-四-(4-甲酰基苯基)苯(1,2,4,5-tetrakis-(4-formylphenyl)benzene, TPB-H)所合成的3D-TPB-COF-H相比, 3D-TPP-COF由于可与乙烷分子间形成额外的C–H···N相互作用, 因而具备更高的C_2H_6吸附量和C_2H_4/C_2H_6吸附选择性.

2.2 烯烃/炔烃分离

石脑油裂解产烯烃的过程中发生过度脱氢会生成炔烃, 烯烃中的存在痕量炔烃会导致烯烃聚合终止从而影响聚烯烃的质量. 工业上一般采用催化加氢去除炔烃杂质, 但这一工艺存在催化剂的贵金属用量大、过度加氢等不足[35].

2D COFs层与层之间通过π-π相互作用堆积形成3D结构, 层间堆积模式的改变可显著影响COFs稳定性、孔隙率和气体吸附性能等化学和物理性质. 张振杰课题组[36]采用调节剂辅助法和溶剂热法调控酰亚胺COF的层间堆叠方式, 分别得到了ABC和AA堆积的2D NKCOF-11. 得益于更小的孔径和更高密度的结合位点, ABC堆积COF相较于AA堆积COF具有更高的C_2H_2吸附容量, 对C_2H_2/CO_2和C_2H_2/C_2H_4混合气具有更优异的分离能力, 可选择性地去除C_2H_2且具有良好的可回收性.

与金属有机框架(metal organic frameworks, MOFs)[37]、氢键有机框架(hydrogen-bonded organic frameworks, HOFs)[38]和多孔有机分子笼(porous organic cages, POCs)[39]的“开门效应”现象类似, 当COFs材料骨架具备一定的柔性时, 客体分子与骨架相互作用可诱导其孔道尺寸和结构发生变化产生“呼吸效应”实现烯烃/炔烃的分离. 汪成课题组[40]发现柔性三维FCOF-5(图2(a))在吸附多种气体分子(如CO_2, C_2, C_3)时展现出独特的“S型”吸脱附曲线(图2(b)). 相关原位表征技术证实了C–O单键在压力诱导下可发生构象变化, 导致COF骨架由收缩向膨胀状态转变, 气体吸附急剧升高. 基于不同气体的开口压力差异, FCOF-5可从丙烯/丙炔混合气体中高效提纯丙烯, 且经过5次循环穿透实验分离性能无明显衰退(图2(c)).

COFs具有易于官能化的特点, 在COFs骨架中引入不同特性的官能团来调节COFs骨架与客体分子间相互作用, 是提高COFs材料烯烃/炔烃分离能力的有效途

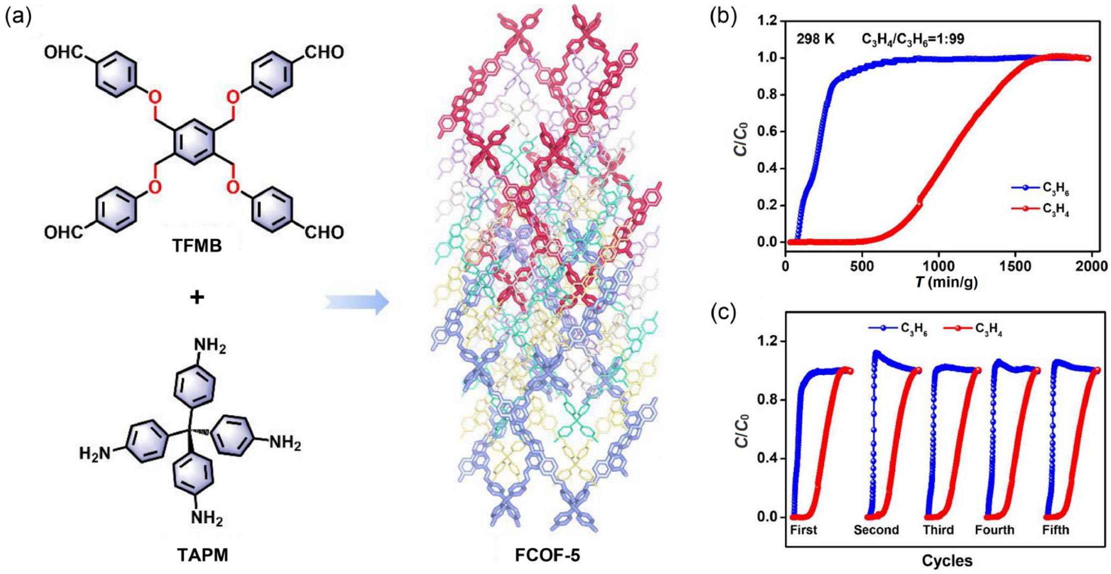

图 2 (网络版彩色)FCOF-5的结构示意图和C_3H_4/C_3H_6分离性能图[40]. (a) FCOF-5的结构示意图; (b) C_3H_4/C_3H_6 (1:99 v/v)混合气在FCOF-5上的穿透曲线; (c) C_3H_4/C_3H_6 (1:99 v/v)混合气在FCOF-5上的五次循环穿透曲线

Figure 2 (Color online) Schematic structure and C_3H_4/C_3H_6 separation performance of FCOF-5[40]. (a) Schematic structure of FCOF-5; (b) breakthrough profiles for binary C_3H_4/C_3H_6 (1:99 v/v) gas mixtures on FCOF-5; (c) five cycle breakthrough curves for binary C_3H_4/C_3H_6 (1:99 v/v) gas mixtures on FCOF-5

径之一. 韦张文课题组[41]利用2,4,6-三甲酰基间苯三酚(2,4,6-triformylphloroglucinol, Tp)和2-硝基-1,4-苯二胺(2-nitro-1,4-phenylenediamine, Pa-NO_2)合成了NO_2官能化的微孔COF材料TpPa-NO_2. COF骨架中的亚胺键H原子、羰基氧原子和硝基官能团与C_2H_4间具有较强的亲和力, 导致TpPa-NO_2可选择性地从C_2H_2/C_2H_4或$C_2H_2/C_2H_4/CO_2$混合气中分离出C_2H_4. 朱广山课题组[42]将异喹啉-5,8-二胺(isoquinoline-5,8-diamine, IQD)与Tp缩合制备了一种具有超微孔结构N-O官能化的TP-IQD-COF, 吸附测试和理论计算表明其骨架中相邻的羰基和异喹啉基团可以选择性吸附C_2H_2.

2.3 己烷异构体分离

己烷异构体的选择性分离生产高辛烷值汽油在石化行业占据重要地位. 己烷由正己烷、2-甲基戊烷、3-甲基戊烷、2,3-二甲基丁烷和2,2-二甲基丁烷五种研究辛烷值(research octane number, RON)差异较大的同分异构体所组成. 工业上采用5A沸石分子筛实现正己烷与其支链异构体的选择性分离可有效提升汽油品质, 但是其正己烷吸附容量低且无法分离单/双支链烷烃, 导致其应用受阻[43]. 因此, 开发新型吸附剂用于提高己烷异构体分离效率具有良好的发展前景.

当COFs材料的孔径与吸附分子动力学直径接近时, 吸附分子与孔道会产生强烈的范德华相互作用力, 可有效存储和分离客体分子. 然而2D COFs的孔径通常超过0.7 nm, 与己烷异构体的动力学直径(4.3~6.2 Å)差异较大较难实现尺寸筛分[43,44]. 黄宁课题组[44]首先采用4,4′-(2,3,6,7-四羟基蒽-9,10-二基)二苯甲醛(4,4′-(2,3,6,7-tetrahydroxyanthracene-9,10-diyl)dibenzaldehyde, DBAAn)和1,3,5-苯三硼酸(1,3,5-benzenetriboronic acid, BTBA)反应制备了介孔DBAAn-BTBA-COF, 然后再采用孔道切割策略将结构匹配的刚性单体六氨基苯基苯(hexaaminophenyl benzene, HAPB)插入至预构筑的DBAAn-BTBA-COF骨架中, 成功将其转化为超微孔DBAAn-BTBA-HAPB-COF(图3(a)). 由于己烷异构体动力学直径接近COF的楔形和超微孔一维通道平均直径(0.65 nm), 加之己烷异构体与COF孔道间范德华相互作用差异, 使COF能够高效地分离五种己烷异构体. 等摩尔比例的五种己烷异构体混合物经过以DBAAn-BTBA-HAPB-COF为吸附剂的固定床后, 洗脱混合物的RON值可达99 (图3(b)). 该课题组[45]的另一工作将碳硼烷对二醛(diformyl-*p*-carborane, DFCB)分别与1,3,5,7-四氨基金刚烷(1,3,5,7-tetraaminoadamantane, TAA)和TAPM缩合得到了3D网状结构的TAA-DFCB-

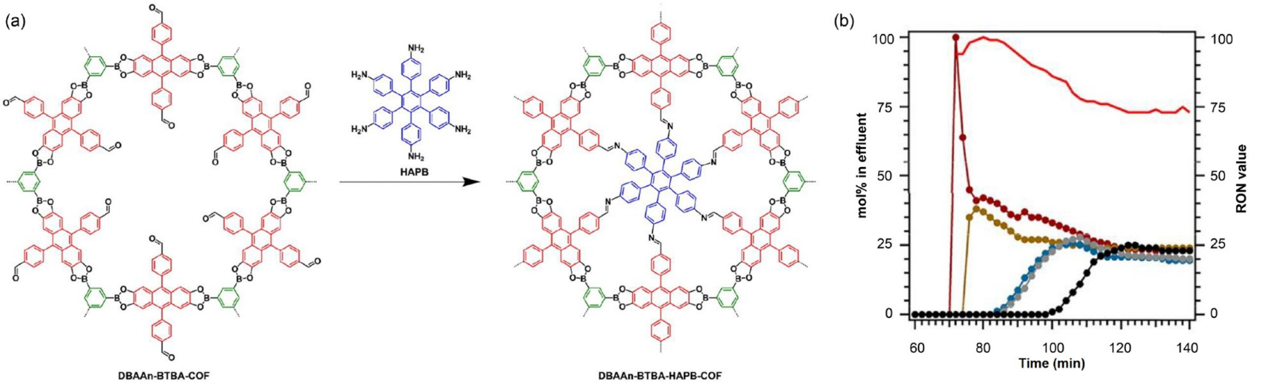

图 3 (网络版彩色)DBAAn-BTBA-HAPB-COF的后修饰合成路线和己烷异构体分离性能[44]. (a) 孔道切割法制备DBAAn-BTBA-HAPB-COF; (b) 373 K和1 atm下5种等摩尔己烷异构体混合物的穿透曲线

Figure 3 (Color online) Post-synthetic route of DBAAn-BTBA-HAPB-COF and its breakthrough results of hexane isomers[44]. (a) Reaction scheme of DBAAn-BTBA-HAPB-COF through pore partition strategy; (b) breakthrough curves for equimolar mixtures of five hexane isomers at 373 K and 1 atm

COF和TAPM-DFCB-COF, B与H的电负性差异使得两种COFs可通过B-H$^{\delta-}$···H$^{\delta+}$-C相互作用吸附和分离己烷异构体. 静态吸附实验结果表明TAA-DFCB-COF和TAPM-DFCB-COF的吸附能力都随着烷烃支化程度的增加而降低, 吸附选择性因子分别为5.70和2.23. 等摩尔比例的五种己烷异构体气态穿透实验结果显示, 两种COFs为吸附剂可以有效提升产品的RON值至100, 其分离因子分别为1.2和1.3, 其性能可与已报道的多孔材料如$Fe_2(BDP)_3$[46](BDP = 1,4-benzenedipyrazolate, 1,4-苯二吡唑盐)、Zr-abtc[47](abtc = 3,3′,5,5′-azobenzene-tetracarboxylate, 3,3′,5,5′-偶氮苯四羧酸盐)和Al-bttotb[48](bttotb = 4,4′,4″-(benzene-1,3,5-triyltris(oxy))tribenzoicacid, 4,4′,4″-(苯基-1,3,5-三氧代)-苯甲酸)相媲美.

2.4 芳烃/环烷烃分离

芳烃加氢制环烷烃产物中残余的芳烃杂质通常采用恒沸精馏和萃取精馏的方法去除, 但芳烃/环烷烃沸点接近容易形成共沸物(如苯与环己烷的沸点分别为80.1和80.8℃), 导致过程复杂且所需能耗大[49]. 吸附分离过程由于能耗低被认为是分离芳烃/环烷烃最具有前景的技术之一.

大多数COFs含有丰富的芳环和极性基团, 有利于增强其与芳烃的亲和力, 可实现芳烃的优先识别吸附. Navarro课题组[50]发现COF-300相较于同构的LZU-111具有更高的柔性, 可与客体苯分子通过π-π相互作用诱导COF骨架形变从而容纳更多苯, 致使COF-300相较于LZU-111具有更高的苯/环己烷吸附选择性. 方千荣课题组[51]采用平面六边形和三棱柱形构筑单元制备得到了JUC-641和JUC-642两种三维COFs(图4(a)). 两种COFs均表现出对苯更高的吸附量(图4(b), (c)), 室温下JUC-641和JUC-642动态穿透实验得到的苯/环己烷分离系数分别为1.80和1.91(图4(d), (e)). 与JUC-641相比, JUC-642由于骨架中存在大量极性氟原子增强了与客体苯分子间的相互作用, 因此展现出了更好的苯/环己烷分离性能. 章跃标课题组[52]采用多元(multivariate, MTV)构筑策略在COF-300结构中引入了多种极性各异可变比例的官能团, 以调节COFs在气体和有机蒸汽吸附过程中的灵活性和动态响应. MTV-COF在苯和环己烷选择性分离中实现了动态协同作用, 性能优于相应的纯单功能材料. 贲腾课题组[53]采用[8+8]亚胺缩合方法开发了一种新型三维COF TUS-88, 298 K下等摩尔比的苯/环己烷的动态穿透实验显示出TUS-88具有优异的苯/环己烷选择性(2.46). 理论计算结果表明TUS-88框架中丰富的共轭结构与苯分子可产生更强的π-π相互作用, 骨架中的吸附位点可通过C–H···π和C–H···N作用力与苯分子产生更强的亲和力, 从而增强了TUS-88对苯的吸附和分离能力.

COFs骨架中引入缺电子中心与芳烃产生较强的相互作用也可实现芳香烃/环烷烃的分离. Mandal课题组[54]设计并合成了一种三嗪基苯并双咪唑桥联(triazine-based benzbis(imidazole)-bridged, TBI) TBICOF, 利用COF骨架中三嗪和苯并双咪唑基团缺π电子特性可通过π-π相互作用选择性吸附富电子的苯. 室温下TBICOF对苯的饱和吸附量高达641.9 $cm^3\ g^{-1}$, 远超其他多孔材料如Mn-MOF-74[55](210.1 $cm^3\ g^{-1}$)和共轭微

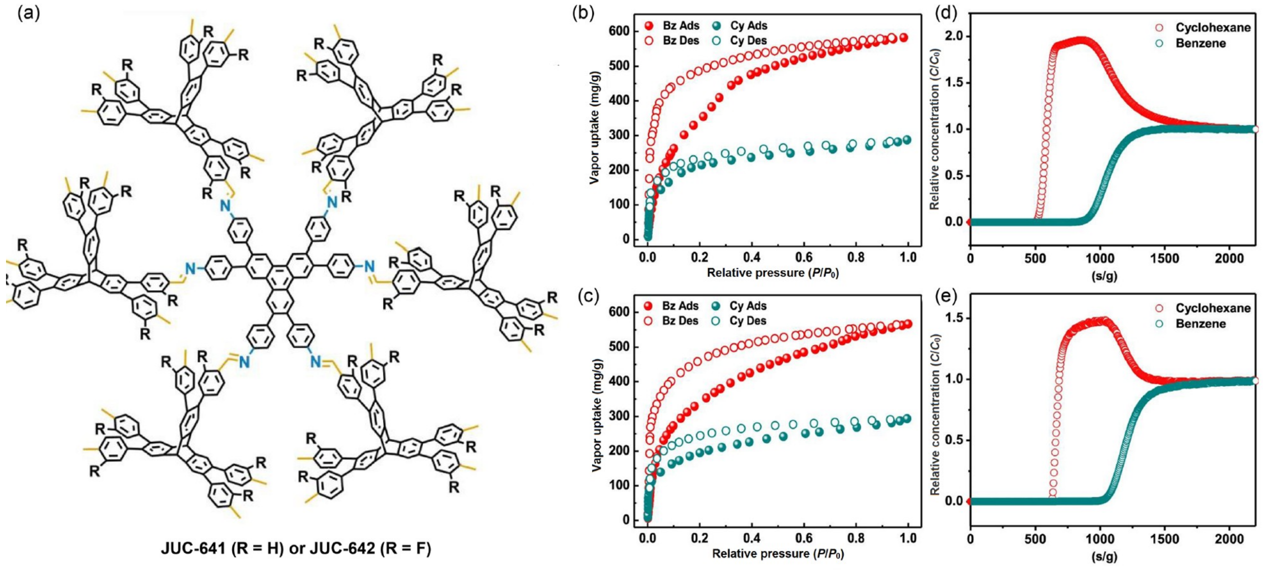

图 4 (网络版彩色)JUC-641与JUC-642的结构示意图和苯/环己烷分离性能[51]. (a) JUC-641与JUC-642的结构示意图; JUC-641(b)和JUC-642(c)在298 K下的苯与环己烷吸附曲线; JUC-641(d)和JUC-642(e)在298 K下的苯/环己烷穿透曲线

Figure 4 (Color online) Structure of JUC-641, JUC-642 and their corresponding benzene/cyclohexane separation performance[51]. (a) Structural representation of JUC-641 and JUC-642; vapor adsorption isotherms of benzene and cyclohexane of JUC-641 (b) and JUC-642 (c) at 298 K; breakthrough experiments of JUC-641 (d) and JUC-642 (e) with an mixture of benzene and cyclohexane at 298 K

孔聚合物(conjugated microporous polymers, CMPs) CMP-S-1[56](185.9 cm^3 g^{-1}), 而对环已烷饱和吸附量仅有186.2 cm^3 g^{-1}, 其理想吸附溶液理论选择性为44.

2.5 C$_8$芳烃分离

C$_8$芳烃包括对二甲苯、邻二甲苯、间二甲苯和乙苯, 由于分子大小和沸点相近, 难以通过传统的分离方法如蒸馏来分离, C$_8$芳烃分离被视为化工领域七大具有挑战性的分离体系之一[29]. 崔勇课题组[57]设计并合成了一系列具有不同孔道环境的三维水杨醛基(salen) COFs(图5(a)), 可作为高效液相色谱的固定相填料用于分离二甲苯异构体和乙苯(图5(b)). 研究发现未经金属修饰的COF-1和COF-2孔道内存在大量裸露的极性水杨醛基团可与C$_8$烷基苯的烷基发生特异性吸附从而高效分离C$_8$异构体, C$_8$烷基苯在色谱柱中的保留时间顺序为乙苯<对二甲苯<间二甲苯<邻二甲苯. 对于水杨醛基团与Zn^{2+}配位后形成的COF-1-Zn和COF-2-Zn, 由于引入的金属离子会对所有C$_8$异构体产生强吸附, 反而不利于C$_8$烷基苯的分离. 严秀平课题组[58]制备了一系列具有不同官能团结构的COFs填料色谱柱并系统探究了COFs官能团对C$_8$异构体的分离性能的影响. 结果表明COFs骨架中引入羟基可提供氢键位点, 引入三氟甲基则会增强偶极力相互作用和空间位阻效应, 因此同时具备羟基和三氟甲基的TpTFMB COF(TFMB = 2,2′-*bis*-(trifluoromethyl)benzidine, 2,2′-双(三氟甲基)联苯胺)作为色谱柱固定相具有最佳的C$_8$异构体的分离能力. 尽管目前COFs在C$_8$芳烃色谱分离中取得了显著的进展, 但与其他多孔材料如分子筛和金属有机框架相比, 依然缺少C$_8$芳烃的静态与动态穿透吸附数据, 并且对动力学控制分离机制的研究有所欠缺.

3 总结与展望

综上所述, 本文系统地总结了COFs材料在碳烃分离领域的研究进展, 介绍了孔尺寸调控、引入不同的酸碱位点或金属离子提供吸附中心、增加极性官能团提高其骨架与客体分子间的相互作用等实现碳烃高效分离的方法. 由丰富多样的有机单体构筑的共价有机框架材料由于具备高度可控的孔隙结构、可定制化设计和功能多样性的特点使其成为研究碳烃分离的绝佳平台. 然而, COFs材料在碳烃分离领域的研究仍处于起步阶段, 在可实际应用之前仍然存在一些问题和挑战亟待解决: (1) 高质量COFs材料制备技术. COFs在制备过程中不可避免地会存在部分杂质和缺陷, 这些位于孔道内的杂质或缺陷位点可能会与客体分子间形成

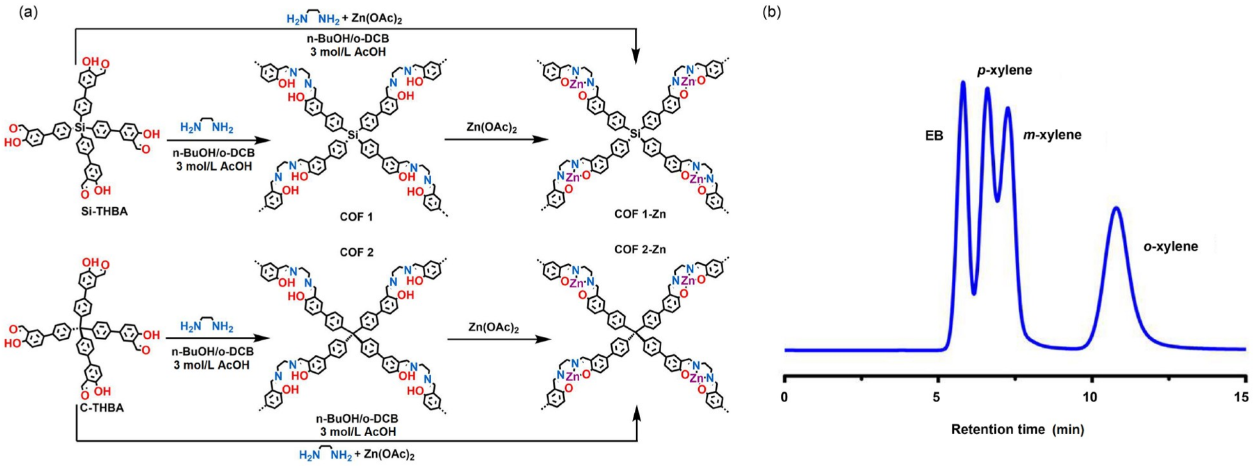

图 5 (网络版彩色)3D水杨醛基和Zn(水杨醛基) COF的合成和C_8芳烃分离[57]. (a) 两类3D水杨醛基和Zn(水杨醛基) COF的结构与合成路线图; (b) C_8异构体经过COF 1-Zn填充柱的高效液相色谱图

Figure 5 (Color online) Illustration of the formation and C_8 isomers separation of 3D salen- and Zn(salen)-based COFs[57]. (a) Structures and synthesis of two pairs of 3D salen- and Zn(salen)-based COFs; (b) HPLC chromatograms of C_8 isomers on the COF 1-Zn packed column

强烈的相互作用, 使COFs的分离性能偏离真实情况, 不利于研究者系统总结COFs的构效关系. 因此, 优化和改善COFs材料制备技术来获取高纯度低缺陷的COFs材料至关重要. (2) COFs材料的规模化制备技术. 常见的溶剂热法造成COFs合成依赖于大量有机溶液的使用, 过程繁琐且纯化困难, 不可避免地提高了其生产成本和导致了环境压力. 目前绝大部分COFs仍处于实验室制备阶段, 开发绿色、低成本和可大规模生产的合成路线仍是COFs材料在工业应用中需要克服的难关. (3) COFs材料成型技术研究. 由于碳烃混合物通过吸附柱时的质量损失和压降问题, 粉末吸附材料在工业应用中无法满足高效、稳定和经济的要求. 目前工业常用的高压机械造粒或黏合剂辅助成型, 会造成COFs骨架部分坍塌或阻塞孔道, 从而削弱其分离性能. 开发满足工况条件需求的高机械强度和稳定性COFs成型造粒工艺十分必要.

尽管存在诸多潜在的挑战, 但我们相信基于现有的COFs数据, 通过融合人工智能和高通量自动化制备技术, 对COFs材料的吸附能力、选择性和稳定性等性能进行预测与评估, 可提升实验效率和加速COFs材料开发进程. 此外, 得益于近年来COFs单晶制备和原位表征技术的突破, 通过原位技术研究有望可以揭示客体分子在COFs孔道中的扩散行为与明确吸附位点, 指导研究人员深入理解COFs材料构效关系, 从而设计具有特定分离性能的COFs材料. 总之, COFs优异的可调控性使其在碳烃分离领域展现出巨大的潜力, 虽然目前还面临一些挑战, 但随着研究的深入和技术的不断发展, 相信未来COFs分离材料将利于简化碳烃分离过程与降低分离能耗, 可实现化工行业可持续发展.

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Summary for “用于碳烃分离的共价有机框架”

Covalent organic frameworks for hydrocarbons separation

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The efficient separation and purification of hydrocarbon mixtures poses critical challenges in the petrochemical industry owing to their structural and physicochemical similarities. Traditional separation technologies, such as distillation and extraction, have long been used. However, these methods are increasingly viewed as unsustainable given their high energy consumption and substantial capital investment requirements. Consequently, adsorptive separation technology based on porous materials is being developed to meet the demands of creating an economical and sustainable petrochemical industry. Covalent organic frameworks (COFs) is a novel and highly promising class of porous materials that have garnered substantial attention owing to their structural flexibility and functional diversity and have distinct advantages over conventional materials such as zeolites and carbon-based adsorbents. The unique combination of periodic porosity, abundant surface chemistry, and high chemical stability of COFs enables them to achieve superior adsorption capacities and selectivities for hydrocarbon separation processes.

This review begins by outlining the key attributes of COFs that are particularly advantageous for hydrocarbon separation, including the pore size, surface polarity, and stability. These features can be precisely engineered using strategies such as structural predesign and post-synthetic modifications. By carefully selecting and assembling monomers and functional groups, researchers can optimize the pore architecture and surface characteristics of COFs to enhance their separation efficiency. Furthermore, the stability of COFs can be significantly improved by constructing more robust covalent bonds or incorporating hydrogen bonds to further increase their practical utility in demanding industrial applications where durability is essential. In addition, the optimization of the delicate balance between periodicity, surface chemistry, and stability by precisely controlling the experimental parameters to maximize the separation performance is discussed.

Next, the application of COFs in the separation of various hydrocarbon mixtures, including olefins/alkenes, alkenes/alkynes, hexane isomers, aromatics/cycloalkanes, and C_8 alkylaromatics, is comprehensively discussed. This review provides a detailed analysis of the adsorptive capacity and selectivity of COFs for each hydrocarbon system, elucidating the underlying separation mechanisms and molecular interactions that drive these processes. The key separation mechanisms, including the enhancement of molecular sieving effects through the downsizing of pores to the sub-nanometer range, are thoroughly examined. This enhancement is achieved through techniques such as pore partitioning, topological structure design, and interlayer stacking adjustments. The thermodynamic aspects of separation are enhanced by modulating the chemical environments within COFs, such as by incorporating metal or Lewis base sites, and strengthening host–guest interactions, including $C–H\cdots\pi$, $C–H\cdots N$, or $\pi\cdots\pi$ interactions. Additionally, this review highlights the unique gate-opening effect that arises from the intrinsic structural flexibility of COFs, emphasizing their potential for the stimuli-responsive capture of target molecules under varying conditions.

The conclusion highlights the tunable pore structures, modular characteristics, and functional versatility of COFs that make them outstanding platforms for advancing hydrocarbon separation technologies. However, despite their potential, further technological advancements are necessary to fully realize their industrial applicability. Improvements in the high-quality synthesis, scaled-up production, and material shaping are required to bridge the gap between laboratory research and industrial implementation. Emerging technologies like *in-situ*/operando characterization techniques, artificial intelligence, and high-throughput experimentation can play a pivotal role in elucidating the structure-property relationships of COFs. These advances are expected to accelerate the development and application of COFs in the petrochemical industry, ultimately driving innovation, efficiency, and sustainability.

covalent organic frameworks, hydrocarbons, adsorption, separation

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