

天然糖类模板辅助合成多级孔 ZSM-5 分子筛研究进展

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摘 要:天然糖类作为绿色模板在多级孔 ZSM-5 分子筛合成中,不但能发挥结构导向作用,还可调控晶粒尺寸与酸中心分布,因此成为研究热点。本文综述了以天然糖类及其衍生物为模板辅助合成多级孔 ZSM-5 的研究进展,重点讨论了糖类模板的作用原理及其对分子筛结构、性质及催化性能的影响。研究表明:糖类模板的类型直接影响分子筛的孔径、酸性及形貌。葡萄糖和蔗糖模板倾向于形成较小介孔的 ZSM-5,而淀粉、纤维素及其衍生物有助于构建较大介孔甚至微-介-大孔 ZSM-5 分子筛。此外,不同糖类模板可诱导特殊形貌的形成,如葡萄糖和淀粉可促进 *b* 轴方向生长,淀粉与蔗糖模板倾向于形成链状结构,纤维素衍生物则有助于构建中空球形结构。最后,指出未来研究应聚焦于开发新型合成方法、深入探索糖类模板与多级孔结构的构效关系、以及优化模板剂用量以实现孔结构和酸位点的精准调控。

关键词:糖类; 生物质; 多级孔; ZSM-5 分子筛; 合成

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多级孔 ZSM-5 分子筛因其独特的微-介孔、微-大孔和微-介-大孔分级结构^[1],在保留传统 ZSM-5 分子筛优异催化活性和分子择形性的同时,显著提升了传质效率和活性位点的可达性^[2-3]。目前,多级孔 ZSM-5 分子筛的合成主要采用碳纳米管、碳纤维等硬模板和表面活性剂类软模板^[4-6],虽然由这类模板合成的多级孔 ZSM-5 分子筛具有较大的比表面积、较高的结晶度和优异的催化性能,但仍存在合成成本高、工艺复杂和污染环境等问题。相比之下,生物质模板特别是葡萄糖、淀粉和纤维素等天然糖类模板,凭借其绿色环保、来源广泛、官能团丰富等优势,以及出色的结构导向性和可调控性成为当前研究热点^[7-9]。

Liu 等^[10]综述了生物质模板(糖类、氨基酸)用于合成多级孔沸石(ZSM-5 分子筛、Beta 分子筛、TS-1 分子筛等)的研究进展。Li 等^[11]针对木质素催化转化生成生物油和芳香烃的反应,综述了生物质模板对多级孔 ZSM-5 分子筛孔道结构、酸性及催化性能的调控机制。尽管二者均涉及生物质模板在多级孔 ZSM-5 分子筛中的应用,但前者关注多类型多级孔沸石的普适性合成策略,后者侧重特定催化反应中

多级孔 ZSM-5 分子筛的性能。为了弥补现有报道中关于天然糖类模板对 ZSM-5 分子筛多级孔结构精准调控机制的系统性研究的不足,本文针对不同的天然糖类模板,从多级孔 ZSM-5 分子筛的合成方法及条件,所得分子筛的结构、酸性及应用角度展开论述,为多级孔 ZSM-5 分子筛的优化设计提供理论指导,展望未来的发展方向。

1 葡萄糖模板

1.1 葡萄糖本体模板

葡萄糖($C_6H_{12}O_6$)作为单糖,具有丰富的羟基($-OH$)官能团。合成的多级孔 ZSM-5 分子筛具有均匀的孔道,主要形成晶间介孔,且聚集的葡萄糖分子发挥类似中性表面活性剂的胶束化作用,有效调节中间相的形成^[12]。

葡萄糖为模板合成多级孔 ZSM-5 分子筛的方法有水热法、两步结晶法、水蒸气辅助法(SAC)和种子结晶法等^[12-16],不同的合成方法对分子筛的结构、性质有显著影响。例如, Ma 等^[12]采用水热法制备多级孔 ZSM-5 分子筛,经 7 d 的水热处理仍

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保持多孔结构,具有优异的水热稳定性。Feng 等^[15]采用两步结晶法提高了结晶效率,克服了传统水热法中低葡萄糖含量对结晶度的限制。SAC 法利用水蒸气与干凝胶界面反应诱导硅铝酸盐有序组装,从而形成均匀有序的多级孔道^[14]。种子结晶法通过引入晶种加速成核过程,提高分子筛的结晶度^[17]。此外,晶种的引入为铝原子提供更多的成核位点,抑制了非骨架铝的形成^[13]。

葡萄糖作为多级孔分子筛合成的多功能助剂,不

仅能调控孔道结构,还可诱导特殊形貌的形成^[18]。其多羟基结构通过氢键和静电相互作用优先吸附在 ZSM-5 的(010)晶面,选择性抑制该晶面的生长速率,从而改变分子筛沿三维方向的生长动力学,最终获得 *b* 轴取向的 ZSM-5 分子筛^[19-21]。如图 1 所示,在甲醇制丙烯(MTP)反应中,*b* 轴取向的直通孔道结构为反应物和产物提供了更优的扩散路径,使得丙烯选择性由 42.89% 提高到 50.98%,催化剂的使用寿命延长了 2.1 倍(24 h)^[21]。

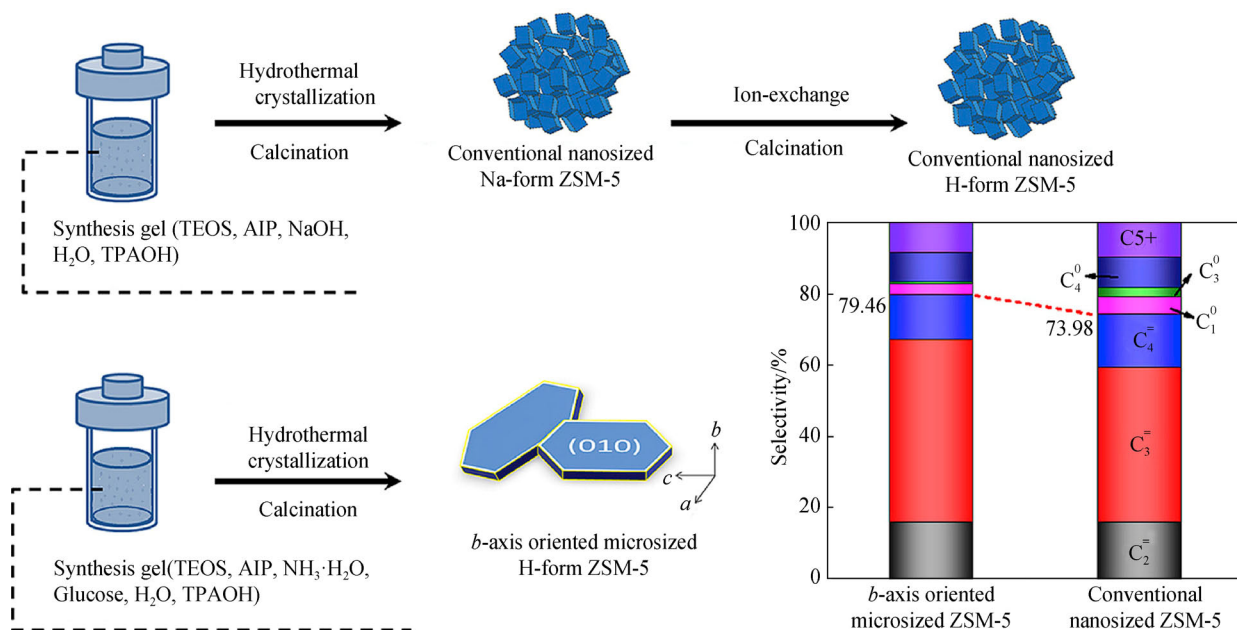


图 1 *b* 轴取向 ZSM-5 分子筛合成^[21]

Fig. 1 Synthesis of *b*-axis oriented ZSM-5 zeolite^[21]

葡萄糖的添加量会对分子筛的孔道结构和酸性产生显著影响。Nandan 等^[14]发现,随葡萄糖浓度的增加, ZSM-5 分子筛的结晶度呈下降趋势,孔径分布由微孔主导逐渐向介孔转变,介孔比表面积和孔容显著提高。在酸性调控方面,适量添加葡萄糖可有效降低总酸量和减少强酸位点数量,同时增加弱酸位点比例^[15]。这种酸性调控在 MTP 反应中表现出明显优势,较弱的酸强度和适中的酸密度有利于丙烯的形成^[22]。然而,添加过量葡萄糖会导致凝胶体系黏度增大,减弱模板与 SiO₂ 前驱体的相互作用,增加结晶阻力并引入晶格缺陷,进而降低酸度并削弱催化性能^[23]。这一研究为通过精确调控葡萄糖添加量来优化分子筛催化性能提供了重要依据。

1.2 葡萄糖衍生物模板

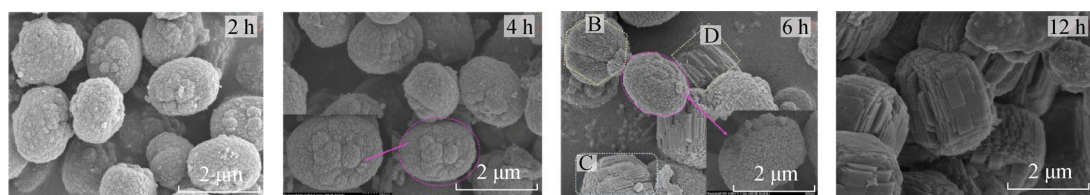
1.2.1 多糖苷模板 烷基多糖苷 1214 (APG1214) 作为葡萄糖衍生物,由糖基和烷基链组成,相比于葡萄糖单一的亲水性, APG1214 表现出较好的亲水-

疏水双亲性^[24-25],在多级孔 ZSM-5 的合成中, APG1214 中的疏水官能团可以沿分子筛的 *b* 轴方向精准地填充孔道,提高分子筛的结晶度和产率。如图 2 所示, Sang 等^[26]使用水热法以 2.5 Al₂O₃: 50 SiO₂: 2 Na₂O: 8 TPAOH: 3000 H₂O: 25 APG1214 的原料配比合成了 30~100 nm 的棺材状多级孔 ZSM-5 分子筛。APG1214 通过亲水糖苷与硅铝酸盐的相互作用及自身的定向排列促进纳米颗粒定向生长形成 2D 纳米片^[27]。相比常规 ZSM-5 分子筛,该分子筛独特的 2D 纳米片结构显著缩短扩散路径。在 MTP 反应中,丙烯选择性提高 10%,催化剂寿命延长 1.5 倍^[26]。

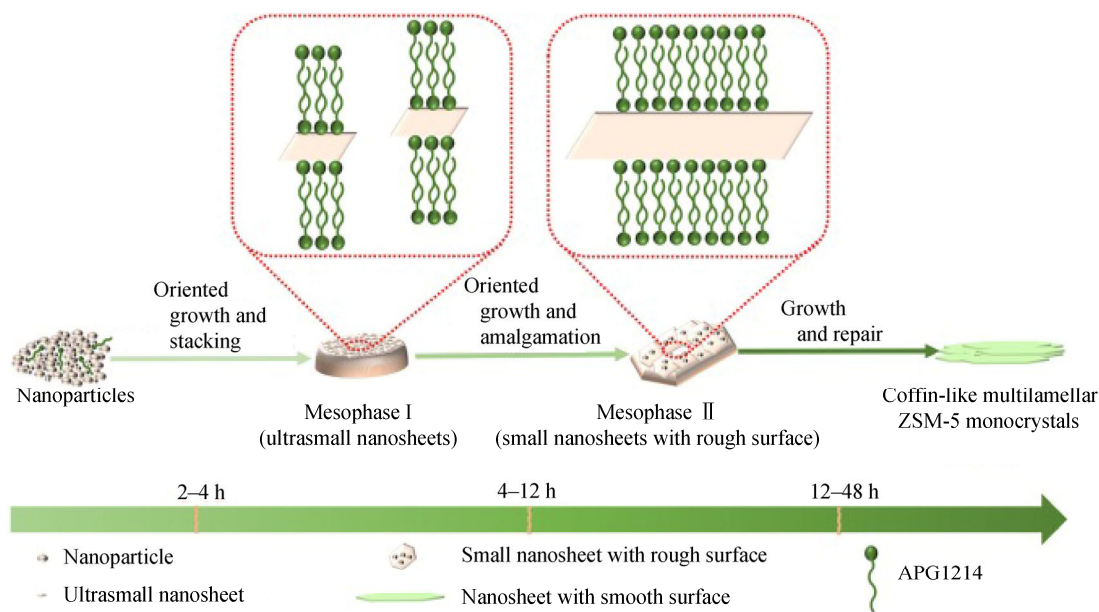
1.2.2 氮掺杂碳质模板(NDC) NDC 由葡萄糖和卵清蛋白水热炭化得到^[28],相比于传统碳基模板, NDC 具有结构可调性,可通过改变溶剂体积、反应时间等参数调控 NDC 模板的分支尺寸,进而控制多级孔 ZSM-5 分子筛的介孔尺寸。此外,其独特的氮掺杂表面化学特性有助于与硅铝酸盐相互作用,有效控制

ZSM-5 分子筛的结晶度和介孔率。White 等^[29]通过 NDC 得到具有高结晶度、晶内介孔为 12~16 nm 的多

级孔 ZSM-5 分子筛, 相比于传统 ZSM-5 分子筛, 碳化 NDC 的引入导致晶粒尺寸更小, BET 比表面积更大。



(a) SEM images of ZSM-5



(b) Formation mechanism

图 2 棺材状多级孔 ZSM-5 分子筛形成过程^[26]

Fig. 2 Formation process of hierarchical ZSM-5 zeolite with coffin-shaped^[26]

2 蔗糖模板

蔗糖是由葡萄糖与果糖链接而成的二糖, 相比于其它天然糖类, 廉价易得。蔗糖模板合成的多级孔 ZSM-5 分子筛表现出介孔体积略微增加, 可有效促进均匀孔道的形成, 生成较小且规则的微-介孔结构, 适用于小分子反应或对孔道均匀性要求高的催化反应^[30]。

目前, 水热法、干凝胶法、预结晶法与 SAC 法在以蔗糖为模板合成多级孔 ZSM-5 分子筛方面均有报道^[31–33], 这些方法各具特色, 如水热法过程中蔗糖会发生部分炭化, 兼具软硬模板的双重作用, 进一步优化分子筛的孔道结构^[31]; 预结晶法相比于干凝胶法表现出更好的结晶效果^[32]; SAC 法适用于低硅铝比, 强酸性多级孔 ZSM-5 分子筛的合成^[33]。这些不同的合成方法使所得分子筛表现出差异性结构特性, 为多级孔 ZSM-5 分子筛的制备提供多种技

术选择。

蔗糖作为多羟基极性有机物, 通过氢键与铝硅酸盐相互作用促进晶粒自堆积形成链状结构^[34]。Jin 等^[31]采用蔗糖模板合成了具有 7 nm 介孔分布的链状多级孔 ZSM-5, 随蔗糖用量增加其链状结构更加显著。在 2-甲基萘(2-MN)转化反应中, 当蔗糖/SiO₂ 达到 2 时, 链状 ZSM-5 分子筛具有较高的介孔比表面积和孔体积, 2, 6-二甲基萘(2, 6-DMN)的产率由 3.8%提升至 7%。此外, 增加蔗糖用量会显著增大分子筛的介孔比表面积和孔容, 降低微孔参数^[32]。但蔗糖的引入增加了非骨架铝的比例, 降低了分子筛的总酸量^[31]。

3 淀粉模板

3.1 淀粉本体模板

淀粉由 α -D-葡萄糖单元通过糖苷键连接形成的多糖, 其较大的分子量与优异的水溶性有利于较大

介孔分子筛的形成。与葡萄糖促进介孔数量增加不同,淀粉主要促进介孔孔径的增大,孔径分布较宽(0~30 nm)^[35]。此外,淀粉模板合成的分子筛多表现为无序不规则性,包括晶内与晶间介孔,这些介孔主要来源于晶内空隙和晶体内部缺陷^[36-37]。

淀粉模板与结构导向剂协同作用,在铝硅酸凝胶(含 Si—O—Si 和 Si—O—Al 键)形成后包裹凝胶,诱导分层多孔结构形成。Sabarish 等^[38]使用淀粉模板在 175 °C 水热 6 h 后经 550 °C 煅烧 5 h 制得孔径范围在 5~15 nm 的分层多级孔 ZSM-5 分子筛,相比于常规多级孔 ZSM-5 分子筛具有更大的比表面积和更高的热稳定性。同时在乙酸与苄醇的酯化反应中,苄醇转化率和苄基乙酸酯选择性分别达到 76%与 93%。此外,

有研究者对淀粉模板制备的 ZSM-5 分子筛中引入磺酸基团^[39],成功拓展其应用至油酸酯化和将劣质油转化为生物柴油领域,展现出优异的催化性能^[40]。

淀粉可分为直链淀粉(螺旋结构)和支链淀粉(高度分支结构)^[41]。支链淀粉的分支结构能限制分子筛晶粒的生长方向,促使其进行链状组装^[42]。如图 3 所示,Liu 等^[43]通过淀粉与 ZSM-5 分子筛晶体中羟基间的强脱水反应,合成链状多级孔 ZSM-5 分子筛,通过调节淀粉/二氧化硅的摩尔比(达 6.4×10^{-4} 时)可获得 3 μm 链长结构,其晶体单元间强化化学键合赋予了该结构优异的稳定性^[44]。在间二甲苯异构化反应中,该链状结构的 *b* 轴直孔道促进对二甲苯扩散,同时介孔提高间二甲苯转化率^[42, 44]。

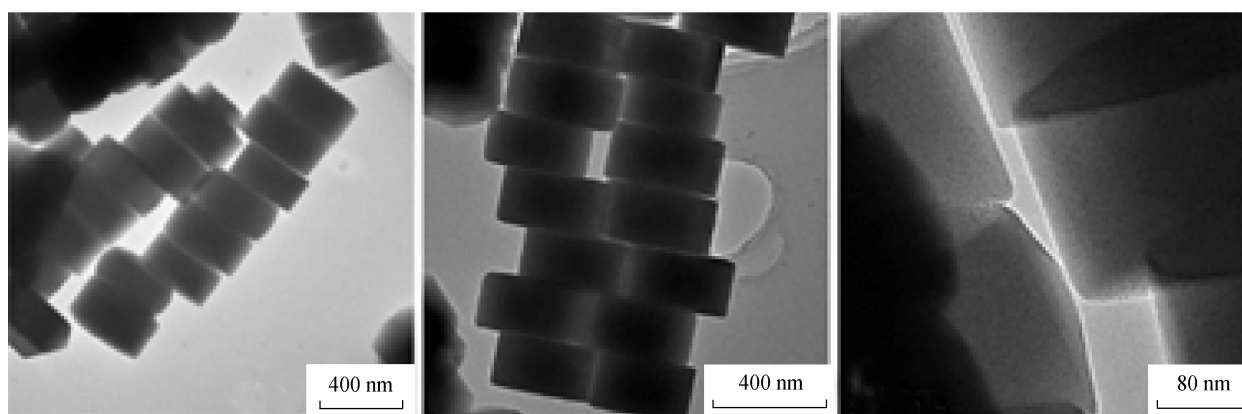


图 3 淀粉与二氧化硅摩尔比为 6.4×10^{-4} 合成的 ZSM-5 分子筛 TEM 照片^[43]

Fig. 3 TEM images of ZSM-5 sample synthesized using molar ratio of starch to silica of 6.4×10^{-4} ^[43]

生物质模板合成多级孔分子筛作为一种特殊的晶体聚集机制^[45],添加适量的模板可显著提升分子筛的催化性能。研究表明,以 10%淀粉模板合成的多级孔 ZSM-5 分子筛具有较高强酸含量,在生物质催化热解(CFP)反应中表现出较大的潜力,BTX(苯、甲苯和二甲苯)的产率由 62.32 mg/g 提高到 91.84 mg/g^[30]。此外,在 CFP 反应中,强酸位点可促进含氧物种转化为烃类,高介孔体积可减少副反应对反应物传输效率的影响^[46]。但过量淀粉模板虽能增大介孔体积,却会减少酸性位点数量,导致产率提升并不明显^[30],因此需精确控制淀粉用量。

3.2 淀粉衍生物模板

3.2.1 包覆硅球模板 为进一步增加分子筛的介孔体积,改善孔隙扩散限制。如图 4 所示,Rani 等^[47]采用淀粉包覆二氧化硅纳米球(SSS)成功合成比表面积为 596 m^2/g 、总孔体积为 0.64 cm^3/g 的三模态(微-介-大孔)分子筛。在酯化反应中,Nano-SSS-ZSM-5

因其扩散路径较短和酸性活性位点较高,催化活性较商业 ZSM-5 显著提升。

3.2.2 面包模板 Wang 等^[48]以淀粉基面包为模板制备多级孔 ZSM-5 分子筛,该面包模板作为 $((\text{C}_6\text{H}_{10}\text{O}_5)_n)$ 聚合物基质,具有亲水多孔特性,其丰富的羟基可与 ZSM-5 前驱体相互用,促进形成含有 10~40 nm 晶内介孔的多级孔结构,且分子筛表面粗糙度随模板量增加而提高。在 1,3,5-三异丙苯裂解和氢吸附实验中,1,3,5-三异丙苯在 80 h 的转化率由 42.1%提升至 75.5%,储氢性能提升 13%^[48]。

3.2.3 碳基硬模板 Zhang 等^[49]采用淀粉炭化法制备碳基硬模板,成功合成了具有高热稳定性的多级孔 ZSM-5 分子筛。该方法通过煅烧碳基硬模板形成微孔-介孔-大孔贯通的晶内介孔结构。研究表明,随着淀粉含量增加,炭化颗粒增大,导致介孔孔径扩大,且碳基硬模板被包裹在 ZSM-5 分子筛中间体中,可有效抑制晶体聚集过程。

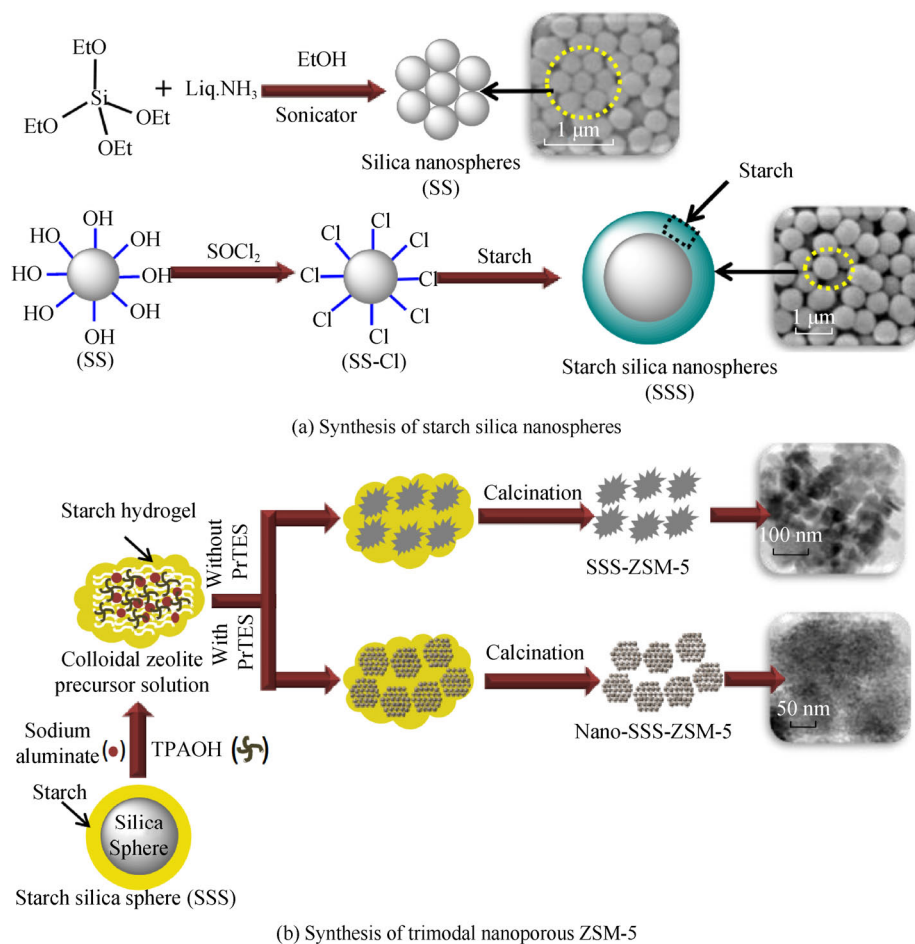


图4 球形多级孔 ZSM-5 分子筛形成过程^[47]
Fig. 4 Formation process of hierarchical ZSM-5 zeolite^[47]

4 纤维素模板

纤维素由 β -D-葡萄糖通过 β -1, 4 糖苷键连接形成的高分子多糖, 其较强的结晶性与有序结构有助于形成稳定、均匀的微-介多级孔结构^[50–51]。同时, 纤维素的交联效应增强了 ZSM-5 分子筛的结构稳定性。

4.1 纤维素本体模板

天然甘蔗渣中富含纤维素, 可作为纤维素本体模板用于多级孔 ZSM-5 分子筛的合成。在合成过程中, 纤维素的羟基基团与铝硅酸盐及模板阳离子的相互作用, 为晶体的成核与生长提供基本条件^[52–53]。Pereira 等^[54]研究发现甘蔗渣水解后产生的衍生物 (BSST)^[55]优先与铝酸盐螯合, 在合成低 Si/Al 比(8)的多级孔 ZSM-5 分子筛的过程中, 提高了多级分子筛中 Al 含量, 形成高酸度分子筛。此外, 甘蔗渣经碱性水解后, 还可有效指导高 Si/Al 比(25~120)多级孔 ZSM-5 分子筛的合成^[56]。

以纤维素本体为模板合成多级孔 ZSM-5 分子筛

的过程中, 模板的添加量对分子筛的结晶度产生显著影响。适量纤维素模板可促进更多的 Al 原子进入 ZSM-5 分子筛骨架, 增加强酸位点的数量。但当纤维素添加过量时, 其结晶度将大幅下降, 这是由于纤维素在水解过程中不断释放酸性物质, 抑制了 ZSM-5 分子筛的结晶速率^[57]。实验表明, 当纤维素添加量达到 10% 时, 分子筛的结晶度最高, 此时多级孔 ZSM-5 分子筛的介孔比例与酸度在纤维素与低密度聚乙烯(LDPE)热解反应中有利于 BTX 的形成(26.1%)。

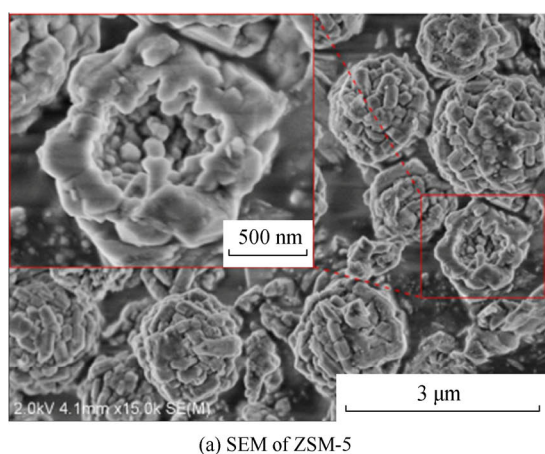
纳米纤维素(NCC)作为模板具有胶体稳定性、高比表面积和丰富羟基等特性, 可有效扩宽孔径并抑制团聚现象^[58–60]。在木质素的催化裂解反应中, 用 NCC 模板制备的多级孔 ZSM-5 分子筛具有较高的介孔体积可促进反应物向酸性位点的快速扩散, 显著提升了含氧化合物向芳烃的转化效率, 相比于常规或碱处理的 ZSM-5 分子筛, 单环芳烃的选择性提高了 40%^[61]。此外, 通过改变 NCC 的添加量可实现对多级孔 ZSM-5 分子筛孔结构与酸性的调节^[62]。

4.2 纤维素衍生物模板

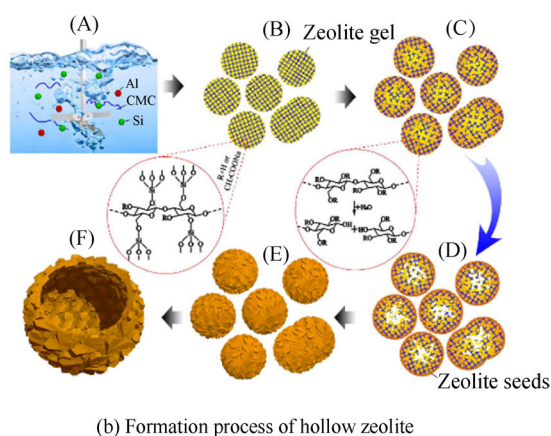
羟乙基甲基纤维素(HEMC)、羟丙基甲基纤维素(HPMC)和羧甲基纤维素(CMC)等衍生物在多级孔 ZSM-5 分子筛合成中也被广泛应用。研究表明,HEMC 和 HPMC 凭借其丰富的羟基特性,能够在 SiO_2 体系中稳定分散并增强界面相互作用,同时通过与 $\text{Si}-\text{OH}$ 形成强氢键作用促进沸石结构重结晶^[63]。此外,HEMC 和 HPMC 作为两亲性共聚物,能够增加分子筛的无定形度并促进大孔形成^[11,64]。例如,Hoang 等^[65]以 HEMC 和 HPMC 为模板成功合成具有优良中大孔的多级孔 ZSM-5 分子筛,显著提高烷基化反应催化效率,其中 HPMC 在相同摩尔

量下比 HEMC 产生更高的介孔率。

羧甲基纤维素(CMC)由纤维素进行亲水官能团化得到,改善了纤维素的亲水性。如图 5 所示,CMC 长链中丰富的羟基和羧基^[66]与沸石凝胶中的硅羟基发生相互作用,调控晶体生长,使其遵循“由表及里”的生长过程,最终形成空心微球特殊形貌的多级孔 ZSM-5 分子筛^[67]。此外,以 CMC 为模板制备的多级孔 ZSM-5 在缩醛反应中展现出独特优势,避免腐蚀性酸的侵蚀,同时介孔结构的引入提高了分子筛表面的可接触性,有效降低反应物的扩散阻力,促进大分子与 H^+ 之间的相互作用^[68]。



(a) SEM of ZSM-5



(b) Formation process of hollow zeolite

图 5 空心微球 ZSM-5 分子筛形成过程^[67]

Fig. 5 Formation process of hollow microsphere ZSM-5 zeolite^[67]

除上述糖类模板外,Khamkeaw 等^[69]以细菌纤维素衍生的碳基模板(BC-AC500)合成多级孔 ZSM-5 分子筛,合成的分子筛对甲醛吸附速率优于传统 ZSM-5 分子筛,且在经历 4 次循环后仍具有良好的吸附性能。

5 其它糖类模板

壳聚糖、海藻酸钠、果糖等糖类模板虽应用范围相对有限,但其独特的化学结构和作用机制使其成为构建多级孔结构的重要原料^[70-71]。如 Fu 等^[72]以壳聚糖为模板对经过碱处理的 HZSM-5 分子筛进行原位重组,壳聚糖通过重组硅酸铝碎片修复部分坍塌的微孔结构,同时提高 L 酸活性位点(LAS)的含量,成功引入新的微-介孔结构和路易斯酸位点^[73],从而促进了生物质(玉米秸秆)与高密度聚乙烯(HDPE)发生共热解反应,生成单环芳烃(MAHs)(36.9%),同时抑制了多环芳烃(PAHs)和焦炭的产生。此外,溶解在碱溶液中的 SiO_2 碎片在壳聚糖上

重组后渗透到晶体内部或表面^[74],这一过程有效提高了分子筛的结晶度。

海藻酸钠(SA)为模板合成多级孔 ZSM-5 分子筛时,其主链上的羟基和羧基阴离子($-\text{COO}^-$)与硅物种相互作用形成三维网络结构^[75],促进形成小尺寸晶体。然而,SA 添加过量时,分子间氢键作用增强^[76],导致纳米晶体因表面吸附 SA 而卷曲团聚,形成蒲公英状颗粒^[77]。同时,SA 中的 $-\text{COO}^-$ 与 Al 配位,阻碍 Al 进入骨架,导致非骨架 Al 增加和酸性位点减少。此外,SA 的添加顺序对 ZSM-5 分子筛的晶体尺寸和酸性具有重要影响,当在正硅酸乙酯(TEOS)前添加 SA,其羟基优先于原本与 Si 结合的 Al 进行配位^[78],导致 SA 形成的网络结构孔径增加,晶粒尺寸增大,并阻碍 Al 进入骨架减少酸性位点数量^[77]。

糖类模板合成的多级 ZSM-5 分子筛在催化、环境保护、生物医药等领域存在非凡的应用价值^[79-81]。研究表明,采用甲壳素为模板时,通过自组装和煅烧造孔过程成功将 ZSM-5 分子筛从单一微孔结构转变为

多级孔体系，显著提升了对大分子吸附能力。如图 6 所示，在结晶紫(CV)染料吸附实验中，用甲壳素模板法合成的多级孔 ZSM-5 分子筛表现出显著优势，其多级孔结构的形成和晶体有序生长的抑制产生了更多无定形区域，从而大幅增加了表面活性位点^[82]，使最

大吸附容量从传统 ZSM-5 分子筛的 141.76 mg/g 提升至 1217.34 mg/g，吸附性能提高了近 1 个数量级^[83]。
为系统比较不同糖类模板的造孔特性，将具有优异多孔结构的 ZSM-5 分子筛所对应的各类糖类模板进行归纳总结并列于表 1 和表 2。

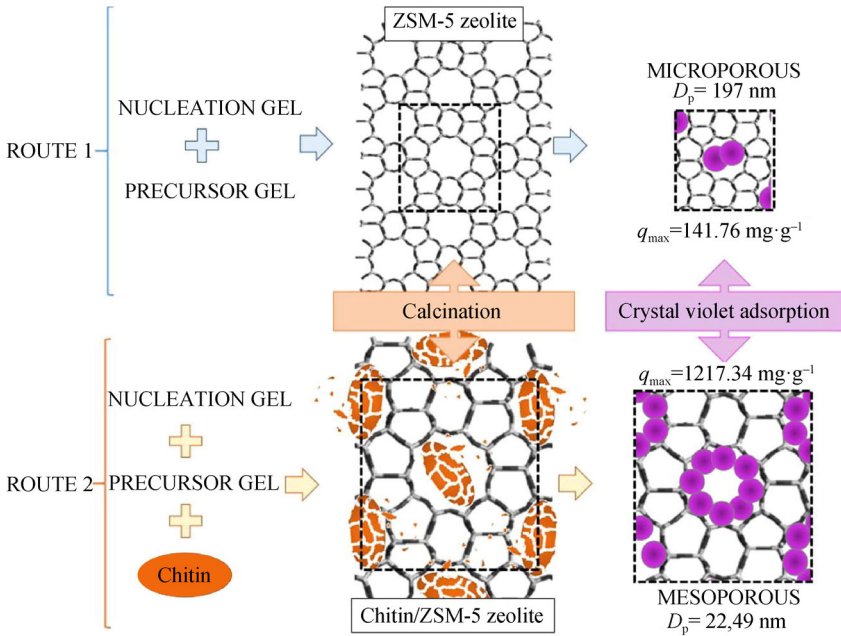


图 6 甲壳素合成多级孔 ZSM-5 分子筛^[83]
Fig. 6 Multi-stage pore for chitin synthesis ZSM-5 zeolite^[83]

表 1 不同糖类模板制备多级孔 ZSM-5 分子筛的合成方法与条件

Table 1 Synthesis methods and conditions for the preparation of multi-stage pore ZSM-5 zeolite synthesis from different sugars templates					
Template	Synthesis method	Synthesis compositions	Synthesis condition		Reference
			Temperature/°C	Time/h	
Glucose	SAC	1 TPABr : 5.2 TEOS : 0.215 AlNO ₃ : 60 H ₂ O : 2.4 glucose	Hydrothermal (80)	2	[14]
			Crystallize (170)	144	
			Calcine (650)	10	
	Two-stage crystallization	1 Al ₂ O ₃ : 50 SiO ₂ : 2 Na ₂ O : 8 TPAOH : 3000 H ₂ O : <i>n</i> glucose(<i>n</i> =0, 10, 15, 20, 25)	Crystallize (110)	24	[15]
			Recrystallize (170)	48	
			Calcine (550)	4	
	Two-stage crystallization	1 Al ₂ O ₃ : 50 SiO ₂ : 2 Na ₂ O : 8 TPAOH : 3000 H ₂ O : <i>n</i> glucose(<i>n</i> =0, 6, 12)	Crystallize (110)	24	[84]
			Recrystallize (170)	48	
			Calcine (550)	4	
Sucrose	Hydrothermal method				[13]
	Hydrothermal method	1 Al ₂ O ₃ : 50 SiO ₂ : 2 Na ₂ O : 3000 H ₂ O : <i>n</i> sucrose (<i>n</i> =0, 0.5 ,1.0, 1.5, 2.0)	Hydrothermal (180)	6	[57]
			Calcine (550)	6	
	Hydrothermal method	1 SiO ₂ : 0.011 Al ₂ O ₃ : 0.25 TPAOH : 30 H ₂ O : <i>n</i> sucrose (<i>n</i> =0–2)	Hydrothermal (170)	72	[31]
			Calcine (550)	10	
	Dry gel conversion method				[32]
Starch	Hydrothermal method	1 SiO ₂ : 0.02 Al ₂ O ₃ : 0.25 TPAOH : 33 H ₂ O : <i>n</i> starch (<i>n</i> =0.37, 0.56)	Carbonize (170)	24	[49]
			Hydrothermal (170)	120	
			Calcine (550)	6	
	Hydrothermal method	1 SiO ₂ : 0.02 Al ₂ O ₃ : 0.08 starch	Hydrothermal (135)	48	[35]
			Calcine (550)	5	
	Hydrothermal method		Crystallize (180)	48	[85]
			Calcine (600)	10	

(to be Continued)

(Continued Table 1)

Template	Synthesis method	Synthesis compositions	Synthesis condition		Reference
			Temperature/°C	Time/h	
Starch	Hydrothermal method	1 API : 47.69 TPAOH : 123.08 TEOS : 3000 H ₂ O : 4.62 starch	Hydrothermal (80)	24	[38]
			Crystallize (175)	6	
			Calcine (550)	5	
		2.5 Al ₂ O ₃ : 90 SiO ₂ : 3.3 Na ₂ O : 25 TPAOH : 15 H ₂ O : 10 PrTES	Crystallize (120)	144	[47]
Cellulose	Hydrothermal method		Calcine (550)	6	[45]
			Desilication (75)	1	
			Reassembly (160)	72	
			Calcine (660)	6	
CMC	Hydrothermal method	200 SiO ₂ : 7.4 Al ₂ O ₃ : 35 NaOH : 10T PABr : 15 H ₂ SO ₄ : 2445 H ₂ O : 0.00494 MCC	Crystallize (180)	48	[86]
			Calcine (550)	6	
	Hydrothermal method		Crystallize (80)	12	[87]
			Calcine (550)	5	
Chitosan	Hydrothermal method	60 SiO ₂ : 1 Al ₂ O ₃ : 6 NaOH : 12 TPAOH : 7200 H ₂ O : 21 CMC	Hydrothermal (80)	4	[88]
			Crystallize (180)	72	
			Calcine (550)	5	
			Hydrothermal (100)	48	[89]
Chitin	Crystalline seed method	1 Al(iPro) ₂ : 18 TPAOH : 50 TEOS : 1570 H ₂ O	Crystallize (150)	18	
			Calcine (650)	10	
			Hydrothermal (170)	24	[83]
			Calcine (600)	5	
Sodium alginate	Hydrothermal method	1 TPAOH : 2.82 TEOS : 0.091NaAlO ₂ : 120.89 H ₂ O : 9.18×10 ⁻⁴ SA	Crystallize (180)	48	[90]
			Calcine (550)	3	
NCC	Hydrothermal method		Hydrothermal (160)	48	[61]
			Calcine (550)	5	
JR-400	Hydrothermal method	3 NMP : 1 SiO ₂ : 0.023 Al ₂ O ₃ : 0.048 Na ₂ O : 0.636 TPAOH : 15.6 H ₂ O : 0.05 JR400	Crystallize 160	72	[91]
			Calcine 400	3	
HPMC	Dry gel conversion method	1 NaAlO ₂ : 34 TPAOH : 5 KOH : 0.0148 HPMC : 48 TEOS	Hydrothermal 80	12	[64]
			Calcine 550	5	
APG1214	Hydrothermal method	2.5 Al ₂ O ₃ : 50 SiO ₂ : 2 Na ₂ O : 8 TPAOH : 3000 H ₂ O : 25 APG1214	Crystallize 170	48	[26]
			Calcine 550	6	

表 2 不同糖类模板制备多级孔 ZSM-5 分子筛的结构特点和应用

Table 2 Structural characteristics and applications of multi-stage pore ZSM-5 zeolite synthesis from different sugars templates

Template	Morphology	Proe distribution/nm	V _{Total} /(cm ³ ·g)	V _{Meso} /(cm ³ ·g ⁻¹)	Application	Reference
Glucose		Intracrystal mesopores (2.3–7.2)	0.23	0.22	Tertiary butylation of phenol	[14]
	Prismatic	Intercrystal mesopores (2–25)	0.239	0.148	Mtp	[15]
	Hexagon	Intercrystal mesopores (5–50)	0.299	0.239	Mtp	[84]
	Hexagon	Intercrystal mesopores (2.5–5.0)	0.25	0.15	Catalytic pyrolysis of cellulose to aromatics	[13]
Sucrose	Octahedral		0.433	0.313	Catalytic co-cracking of cellulose and LDPE	[57]
	Chainlike	Intercrystal mesopores (7)	0.36	0.26	Methylation of 2-methylnaphthalene	[31]
		Intracrystal mesopores (10)	0.302	0.183	Catalytic pyrolysis of cellulose to aromatics	[32]
Starch	Spherical	Intracrystal mesopores(10)	0.24	0.21		[49]
		5.67	0.514	0.375	Catalytic pyrolysis of biomass to aromatics	[35]
	Prismatic		0.23	0.16	Acetalization of cyclohexanone	[85]
		Intracrystal mesopores (5–15)			Esterification reaction	[38]
	Spherical	Intercrystal mesopores (3.9–10.9)	0.64	0.52	Esterification reaction	[47]
Cellulose		Intracrystal mesopores (5–50)	0.206	0.095	Catalytic co-cracking of softwood biomass and LDPE	[45]

(to be Continued)

(Continued Table 2)

Template	Morphology	Proe distribution/nm	$V_{\text{Total}}/(\text{cm}^3 \cdot \text{g})$	$V_{\text{Meso}}/(\text{cm}^3 \cdot \text{g}^{-1})$	Application	Reference
CMC		3–30			Methyl orange ddsorption	[87]
	Coffin-like		0.39	0.28	MTP	[88]
Chitosan	Spherical	Intracrystal mesopores (5–20)	0.42	0.34	Esterification reaction	[89]
Chitin	Prismatic		0.197	0.142	CV adsorption	[83]
Sodium alginate	Spherical	Intracrystal mesopores (3–4)	0.211	0.062	Esterification of acetic acid with n-butyl alcohol	[90]
NCC		Intracrystal mesopores (4–40)		0.159	Catalytic pyrolysis of biomass to aromatics	[61]
JR-400	Hollow spherical	Intracrystal mesopores(20–80)	0.23	0.1	Benzene alkylation with the ethanol	[91]
HPMC	Layered		0.31	0.25	Alkylation reaction	[64]
APG1214	Coffin-like	Intracrystal mesopores (10–30)	0.169	0.067	MTP	[26]

6 结论与展望

天然糖类作为模板在多级孔 ZSM-5 分子筛合成中展现出独特优势,其绿色环保、经济高效、孔径可调、模板去除条件温和等特点为传统模板法提供了极具前景的替代方案。此外,不同糖类模板分子结构之间的差异在多级孔 ZSM-5 分子筛的合成中表现出独特的调控特性。具体而言,葡萄糖和蔗糖采用水热法或两步结晶法,通过羟基配位作用诱导纳米晶线性堆积,从而形成均匀的晶间介孔结构,可有效提升负载金属的分散性,但其对孔道的调控能力较弱,需复配其它模板剂协同调控孔道结构,常用于 MTO 等小分子反应;纤维素和淀粉等多糖模板具有支链结构,基于水热法或种子结晶法可构建微-介-大孔多级孔道结构,实现晶间介孔与晶内介孔的协同分布,凭借优异的水热稳定性常用于生物质催化热解等大分子反应。壳聚糖和海藻酸钠作为功能糖类,分别通过静电吸附和羧基($-\text{COO}^-$) Al^{3+} 螯合作用以促进均匀介孔与枝状介孔的形成,并提升表面酸性位点(Lewis)密度、调节分子筛形貌,以适配高酸性的油酸酯化、大分子扩散主导的吸附与生物质转化等高附加值场景。糖类模板通过提升传质效率与酸性位点可及性,显著增强生物质转化性能,推动实现生物质从“废弃物”向“碳中和核心载体”转型,为“双碳”目标提供可持续的解决方案。

虽然天然糖类模板在多级孔 ZSM-5 分子筛中以取得显著的进展,然而该领域研究仍面临诸多挑战。首先,部分糖类模板在合成多级孔 ZSM-5 分子筛时仍存在预处理复杂、介孔尺寸分布宽泛、高介孔体积导致结晶度下降等问题。其次,现有合成技术主要局限于水热法,其它方法如凝胶转换法和两步结晶法因工艺复杂和成本因素导致工业化进程

受阻;最后,分子筛的孔道结构与酸性位点难以实现精确调控,且模板利用量与材料性能的构效关系尚未完全明确。因此,探索多糖可控解聚与多模板复配策略突破结晶度与介孔均匀性瓶颈、开发普适性更强的合成方法、探索孔道-酸性协同调控机制以及深入解析模板的作用机理是未来研究的主要方向。

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Advances in the Template-Assisted Synthesis of Hierarchical ZSM-5 Zeolite from Natural Sugars

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Extended Abstract

Hierarchical ZSM-5 zeolite show significant advantages in the fields of catalysis, adsorption and separation due to their unique micro- or meso-macroporous hierarchical structure, but the traditional templating method suffers from the problems of high cost, process complexity and environmental burden. As green template agents, natural sugars (glucose, starch, cellulose, etc.) have the advantages of wide source, environmental friendliness and rich functional groups, which can not only regulate the grain size, pore structure and acidic distribution of molecular sieves through hydrogen bonding and electrostatic interactions, but also induce the formation of molecular sieves with special morphology, which provides a new strategy for the precise design of high-performance catalysts.

Recent studies have focused on the mechanism of action and performance optimization of different sugar templates, and the morphology, particle size and properties of natural sugar templates are closely related to the structural properties of hierarchical ZSM-5 zeolite. For example, glucose selectively binds to the molecular sieve crystal surface through hydroxyl groups and promotes b-axis orientation to enhance propylene selectivity, and the amphiphilic nature of its derivatives (e.g., alkyl polyglucosides) can precisely regulate mesopore distribution; sucrose templates enhance mesopore connectivity to optimize the diffusion of small molecules by inducing chain assembly; starch forms a wide pore size distribution by virtue of its large molecular weight, and enhances thermal stability and acidic strength by inducing chain assembly through branched chain structure; and the templates are also used in the study of the molecular sieve structure. Cellulose and its derivatives (e.g., carboxymethyl cellulose) enhance the structural stability through cross-linking effect, and the abundant hydroxyl and carboxyl groups in the long chains interact with the silica hydroxyl groups in the zeolite gel to build a hollow spherical multistage pore system. In addition, starch-coated silica nanorods and cellulose carbonized templates further expanded the pore types (trimodal pore structure), which showed excellent catalytic activity in esterification and cracking reactions. It was also shown that the amount of sugar templates directly affects the crystallinity, the number of acid sites and the pore volume, which needs to be optimized experimentally to balance the performance parameters,

and when the acid content is sufficiently high, the content of mesopore and the pore size become the key factors to improve the catalytic efficiency of the molecular sieves.

Finally, the optimization of different synthetic methods and the development of templates for sugar derivatives have further expanded their applications. However, the existing studies still need to break through the industrialization bottleneck of the synthesis process, clarify the constitutive relationship between the dosage and performance of sugar templating agents, and explore the pore-acid synergistic regulation mechanism. Future research should focus on the innovation of green and efficient synthesis technology to promote the large-scale application of hierarchical ZSM-5 zeolite in the fields of energy conversion, environmental protection, and fine chemicals.

Summary and prospects Natural sugars as templating agents show unique advantages in the synthesis of hierarchical ZSM-5 zeolite, which provide a promising alternative to the traditional templating method due to their green, cost-effective, pore-size-adjustable, and mild template-removal conditions. In addition, the differences between the molecular structures of different sugar templates exhibit unique regulatory properties in the synthesis of hierarchical ZSM-5 zeolite. Specifically, glucose and sucrose induce linear stacking of nanocrystals through hydroxyl coordination, and form a uniform intergranular mesoporous structure by combining with hydrothermal or two-step crystallization, which can effectively enhance the dispersion of loaded metals. But their ability to regulate the pore channels is weak. Other templating agents are needed to synergistically regulate pore structure. For example, polysaccharide templates, such as cellulose and starch, have branched chain structure. By using hydrothermal method or seed crystallization method, they can construct micro-medium-macroporous multilevel pore structure, and realize synergistic distribution of inter-crystalline mesopores and intra-crystalline mesopores. Polysaccharides and sodium alginate, serving as functional sugars, promote the formation of uniform and dendritic mesopores through electrostatic adsorption and carboxyl ($-\text{COO}-$) Al^{3+} chelation, respectively. They also enhance the density of acidic sites (Lewis) on the surface and regulate the morphology of molecular sieves. These modifications tailor the material for high-value-added applications, such as esterification of oleic acid with high acidity, the diffusion-controlled adsorption of macromolecules, and biomass conversion. By improving mass transfer efficiency and accessibility of acidic sites, the sugar templates can significantly enhance the performance of biomass conversion, promote the transformation of biomass from “waste” to “carbon neutral core carrier”, and provide a sustainable solution to the goal of “dual carbon”.

Although the natural sugar templates in hierarchical ZSM-5 zeolite to make significant progress, the field of research is still facing numerous challenges. Firstly, some of the sugar templates still suffer from complex pretreatment, wide mesopore size distribution, and high mesopore volume, leading to the decrease of crystallinity for synthesis of hierarchical ZSM-5 zeolite. Secondly, the existing synthesis techniques are mainly limited to hydrothermal methods, and other methods such as dry gel conversion and two-step crystallization are hindered in industrialization due to the complexity of the process and cost factors; finally, it is difficult to precisely regulate the pore structure and acidic sites of the molecular sieves, and the constitutive relationship between the templating agent dosage and the material properties has not been fully clarified. Therefore, exploring the controlled depolymerization of polysaccharides and multi-template compounding strategy to break through the bottleneck of crystallinity and mesopore homogeneity, developing more universal synthesis methods, exploring the mechanism of pore-acid synergistic regulation, and in-depth analysis of the mechanism of templating agents are the main directions of the future research, so that we can push forward the practical application of sugar templating method in the large-scale preparation of hierarchical zeolite.

Key words saccharide; biomass; hierarchical; ZSM-5 zeolite; synthesize