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催化剂金属及载体促进木质素加氢研究进展

高洁^{1, 2, 3, 4}, 张译天^{1, 2, 3, 4}, 罗刚^{1, 2, 3, 4}, 曹阳^{5, *}, 张士成^{1, 2, 3, 4, *}

(1. 复旦大学环境科学与工程系, 上海 200438; 2. 上海市有机固废污染控制与资源化专业技术服务平台, 上海 200438; 3. 上海市大气颗粒物污染防治重点实验室, 上海 200438; 4. 上海污染控制与生态安全研究院, 上海 200438; 5. 香港理工大学土木与环境工程系, 香港 999077)

摘要: 发展木质素资源化利用技术以获得高附加值芳香族化学品, 不仅能提高木质素的经济价值, 还有助于实现“双碳”目标。近年来, 大量研究集中在木质素的加氢解聚。根据氢供体的不同, 木质素的加氢解聚可以分为外源氢供氢(包括氢气、醇溶剂或甲酸)和内源氢供氢(木质素自转移氢解)。木质素的加氢解聚具有高产率、组成简单等优势。然而, 苛刻的反应条件促使人们开发高效的加氢催化剂。提升加氢催化剂性能的研究重点在于金属活性位点和载体活性位点的调控。通过对大量木质素加氢催化剂的研究, 梳理了木质素加氢解聚的研究进展, 分析了催化剂金属活性位点的亲氧性和尺寸效应对木质素外源氢供氢解聚的产物分布和自转移氢解的影响规律, 归纳了催化剂载体活性位点的酸性和表面官能团、多孔和缺陷结构对催化剂性能和木质素多步转化的影响。最后, 展望了木质素加氢解聚制备高附加值芳香族化学品领域未来的研究重点和发展方向。

关键词: 木质素; 加氢解聚; 活性金属亲氧性; 活性金属尺寸效应; 载体酸性; 载体结构

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Advances in catalyst metals and supports for lignin hydrogenation

GAO Jie^{1, 2, 3, 4}, ZHANG Yitian^{1, 2, 3, 4}, LUO Gang^{1, 2, 3, 4}, CAO Yang^{5, *}, ZHANG Shicheng^{1, 2, 3, 4, *}

(1. Department of Environmental Science and Engineering, Fudan University, Shanghai 200438, China; 2. Shanghai Technical Service Platform for Pollution Control and Resource Utilization of Organic Wastes, Shanghai 200438, China; 3. Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention (LAP3), Shanghai 200438, China; 4. Shanghai Institute of Pollution Control and Ecological Security, Shanghai 200438, China; 5. Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, Hong Kong 999077, China)

Abstract: Developing technology for the utilization of lignin resources to obtain high-value aromatic chemicals will not only increase the economic value of lignin but also help achieve the "double carbon" goal. Considerable research efforts have been directed toward investigating lignin hydrogenation. Based on the different types of hydrogen donors, lignin hydrogenation can be divided into exogenous hydrogen (including molecular hydrogen, alcohol solvents, or formic acid) and endogenous hydrogen supply (lignin self-transfer hydrogenolysis). Lignin hydrogenation offers notable advantages, such as high

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作者简介: 高洁(1996—), 女, 江苏盐城人, 博士研究生, 主要研究方向为有机固废污染控制与资源化利用。E-mail: 19110740034@fudan.edu.cn

通讯作者: 张士成(1974—), 男, 山东蒙阴人, 教授, 主要研究方向为有机固废污染控制与资源化利用。E-mail: zhangsc@fudan.edu.cn

曹阳(1993—), 女, 山东菏泽人, 博士后, 主要研究方向为生物质催化转化、生物质碳基材料的设计构筑及环境应用。

E-mail: yang.cao@polyu.edu.hk

product yields and relatively simple product compositions. However, harsh reaction conditions have prompted the development of efficient hydrogenation catalysts. The focus of research is on regulating the active metal and support centers of hydrogenation catalysts to improve the activity. Through extensive studies of numerous lignin hydrogenation catalysts, advances in lignin hydrogenation depolymerization have been summarized. The influence of metal oxygen affinity, along with the different catalytic effects of various sizes of metal on the product distribution of lignin depolymerization through exogenous hydrogen supply and self-transfer hydrogenolysis, is analyzed. Additionally, the impacts of acidity, surface functional groups, and porous and defective structures of supports on catalytic performance are elucidated. Finally, the prospective outlook on the future of lignin resource utilization is presented.

Keywords: Lignin; Hydrodepolymerization; Oxygen affinity of active metal; Size effect of active metal; Support acidity; Support structure

0 引 言

自 19 世纪以来,以煤、石油、天然气为代表的化石资源成为绝大多数能源、燃料和化学品的原料。石化工业的高速发展提高了人们的生活质量,但带来的环境污染问题也日益凸显。低碳经济的理念和可持续发展的战略促使人们聚焦于可再生能源。生物质年产量约 1 200~1 300 亿 t,是天然有机碳最丰富的可再生来源,其资源化利用具有重要意义^[1]。然而,我国每年产生的生物质大部分被废弃或直接燃烧,造成严重的能源浪费和环境污染^[1-4]。因此,充分利用生物质资源已成为本世纪最重要的挑战之一。生物质主要由半纤维素、纤维素和木质素组成^[5]。半纤维素和纤维素的高值化利用技术相对成熟,但木质素尚未得到高效开发利用,通常以废弃物形式丢弃^[6-8]。这是因为木质素的分子和聚集态结构复杂,理化性质不均一^[9]。

废弃木质素的资源化利用具有重要的经济价值和广阔的应用前景。从物质含量来看,木质素光合产量约为 2×10^{10} t/a,其重量占生物质的 15%~30%,其所含能量占生物质的 40% 左右^[10-11]。高效利用废弃木质素可以提高生物质利用过程的经济性。从化学结构来看,木质素是一种异质芳香性高聚物,由对羟苯基丙烷、愈创木基丙烷和紫丁香基丙烷结构单元通过 C—C 和 C—O 键相互键合而成^[12-13]。它具有苯环结构单元,在替代化石资源制备芳香族化合物方面具有很大潜力^[14]。因此,以废弃木质素为原料制备高附加值芳香族化学品,既可以有效利用废弃木质素资源,实现能源结构的转型,又能减少废弃木质素燃烧或排放所造成的环境污染。

将废弃木质素转化为高附加值芳香族化学品,涉及木质素结构单体间连接键的断裂^[15-16]。加氢转化是实现上述过程的重要途径^[2, 17],即在 100~350 °C 的范围内,在氢参与条件下对废弃木质素进行热还原以生产单体芳香族化合物,如苯酚、苯、甲苯和二甲苯,甚至烷烃燃料^[2]。开发新颖的加氢催化剂和反应体系策略受到越来越多关注。然而,木质素的低转化率和产物的低选择性、高温高压反应的危险性和高能耗、操作步骤的烦琐性和催化剂的短使用寿命等多方面因素限制了加氢反应在木质素增值过程中的应用^[18-20]。开发新颖高效的加氢催化剂已成为研究热点。针对木质素加氢解聚催化剂的研究尚缺乏最新总结。特别是在催化剂活性金属组分的亲氧性和尺寸效应、载体组分的酸性和结构特性等方面,已涌现大量研究,对这些研究进行全面综述具有迫切的必要性。基于木质素加氢解聚的重要意义,本文综述了废弃木质素加氢解聚研究现状与进展,重点分析了金属活性位点亲氧性和尺寸效应的催化作用以及载体活性位点酸性和结构特性对催化性能的影响。最后对木质素加氢解聚的发展方向进行展望,旨在为木质素加氢解聚研究提供参考。

1 废弃木质素资源化利用的环境效益与能源效益

木质素通常作为废物产自制浆造纸和生物燃料行业。在制浆造纸行业中,经强碱处理的木质素是造纸黑液的主要成分。全球每年仅纸浆和造纸业就可产生约 6×10^7 t 废弃木质素^[10-13],而在生物燃料领域,每生产 1 L 乙醇就会产生 0.5~1.5 kg 废弃木质素。美国计划到 2030 年使用生物质替代 30% 的化石燃料,这需要生产约 2.3×10^{11} L 生

物乙醇,预计产生约 2.3×10^8 t 废弃木质素^[21]。

然而,由于木质素具有刚性结构,其资源化利用面临巨大挑战。目前,木质素用作商业产品的占比不到 2%,通常作为添加剂掺入建筑材料,或生产大分子材料和高附加值产品。其余大部分木质素均作为低价值燃料燃烧发电或供热,或者作为废水废渣经处理后排放进入环境^[22]。大量废弃木质素直接焚烧释放出颗粒物、氮氧化物和硫氧化物,造成严重的大气污染^[23]。具有强碱性的造纸黑液若进入环境,会破坏水体或土壤的酸碱平衡和氧化还原平衡,进而扰乱生态系统的平衡。

将木质素转化为高附加值化学品是生物质资源化利用领域的关键。目前主要存在 2 种转化方式,一种是以木质素为原料合成各种功能聚合物,如聚氨酯、聚酯、环氧树脂或酚醛树脂^[24];另一种方式是选择性切割木质素大分子中的连接键,产生酚、环烷烃、芳烃和芳香酮/醛/酸等小分子化合

物^[13, 25]。近年来,由于一次能源石油的短缺和对芳香族化学品的迫切需求,木质素的第二种利用方式已成为研究热点。这种方式不仅能为下游工业供应可再生的芳香类碳氢资源,还能显著提高当前生物精炼产业链的经济效益^[26]。

2 木质素加氢解聚研究现状

木质素加氢解聚是生产高附加值化合物最流行的方法之一,通常发生在 $30 \sim 250$ °C^[27-28]。该方法通过破坏木质素分子中的连接键将木质素降解为小分子片段,并通过活性中间体与氢或小分子之间的反应稳定木质素片段,从而避免木质素的缩合^[29]。因此,木质素加氢解聚可以使产物混合物逐步加氢脱氧,从而降低产物复杂性,提高目标产物选择性,利于产品分离和下游产品升级。通常,木质素的加氢解聚需要加氢催化剂和氢供体的参与^[10]。木质素加氢解聚示意如图 1 所示。

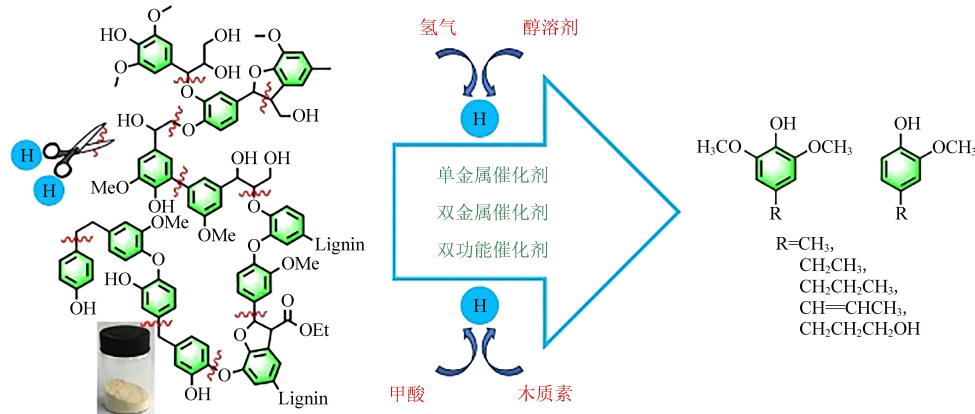


图 1 木质素加氢解聚的示意图

Fig. 1 Schematic illustration of reductive depolymerization of lignin

非均相催化剂因其可回收、易分离的特点而被广泛使用。非均相催化剂包含活性金属和载体。活性金属包括 Pd、Pt、Ru、Rh 等贵金属和 Fe、Co、Ni、Cu 等非贵金属。载体包括金属氧化物、金属磷酸盐、生物炭等。LIU 等^[30]使用 Ru/C 催化剂对桦木锯末进行加氢解聚,获得了产率为 41.4% 的单酚类化合物。HE 等^[31]利用 Ni/SiO₂ 催化剂选择性裂解芳基 C—O 键,将木质素降解为单体或低聚体化合物。此外,由于侧链 C=C 键的氢化,4-丙基愈创木酚和 4-丙基丁香酚的选择性高达 82.8%。与单金属相比,添加第二种金属能够进一步提高催化剂活性。ZHANG 等^[32]证明木质素在 130 °C、 1 MPa H₂ 的条件下反应 1 h, Ni 单金属催化剂可获得 36% 的原料转化率和 70% 的单体选择性。Ru 单金属催化剂可获得 100% 的原料转

化率和 8% 的单体选择性。相比之下, NiRu 双金属催化剂获得了 100% 的原料转化率和 58% 的单体产率。同时该研究证明,双金属 NiRu 的协同效应来自表面原子比例的增加(与 Ni 相比)、H₂ 和底物活化的增强(与 Ni 相比)以及苯环加氢的抑制(与 Ru 相比)。近年来,催化剂载体的酸性调控受到广泛关注,含有金属和酸性位点的双功能催化剂逐渐受到重视。ZHU 等^[33]证明与单一功能的 Pt/SiO₂ 催化剂相比,双功能 Pt/HBeta 催化剂的活性有较大提高,能够有效保留反应底物的苯环结构,减少体系的氢气消耗,同时催化剂失活率和结焦率也有效降低。XIA 等^[34]使用多功能 Pt/NbOPO₄ 催化剂促进原木的直接加氢脱氧,该催化剂可以将锯末中的纤维素、半纤维素及木质素分别同时转化为己烷、戊烷和烷基环己烷,获得液体

烷烃的总收率高达 28.1%。同时通过分子机制的研究证明了 Pt、NbO_x 物种和酸性位点之间的协同作用。

木质素加氢所需要的氢来自氢气、体系中的醇溶剂及其他供氢剂(如甲酸)或木质素本身含有的氢(木质素自供氢)^[35]。当体系中存在高压氢气时,由于其扩散迅速并且活性较高,是反应体系的主要氢源。高压氢气能够与反应底物和催化剂充分接触,从而获得高产率的芳香族化合物^[11]。然而,氢气通常通过煤、天然气和石油等化石燃料的蒸汽重整法产生,该工艺步骤复杂且需要消耗大量能量。与绿氢相比,这种方法产生的氢气被称为灰氢。使用灰氢会增加碳足迹,使木质素的增值转化不可持续且成本高昂。此外,氢气解离产生的活性氢在高温高压(220~450 °C, 5~25 MPa)下容易导致芳香族产物的过度加氢生成环己烷,导致芳香族化学品的选择性降低^[27, 36]。因此,减少氢气生产的碳足迹和提高产品选择性是提高木质素衍生单体整体原子效率和能源效率的迫切需要。在这种背景下,催化转移加氢(Catalytic Transfer Hydrogenation, CTH)作为一种化学高效、环境可持续的替代传统加氢处理工艺而得到了发展。该工艺已被证明是各种生物质转化反应的一种替代方法。醇溶剂(包括甲醇、乙醇、异丙醇等)和甲酸通常作为木质素加氢的供氢体和反应介质。使用醇溶剂作为木质素加氢解聚体系的次要氢源,不仅可以减少对高压氢气的依赖,而且可以促进底物的溶解及其与催化剂活性位点的接触,此外还可以抑制苯环加氢^[37]。采用甲酸作为氢源也是目前的研究热点。一方面,甲酸容易从纤维素生物质中获得(产率>90%),而储存在甲酸中的氢可以通过催化脱氢反应释放^[38];另一方面,在同一反应器中,氢原位产生、原位消耗可以增加反应的安全性。NING 等^[39]提出,甲酸在木质素及其衍生物的加氢脱氧(Hydrodeoxygenation, HDO)反应中发挥了多种作用:氢供体,酸性添加剂,脱羰和环氧化抑制剂,形成甲酸酯前体。因此,以甲酸为氢供体选择性催化升级木质素及其衍生物具有重要意义。然而,反应过程中大量溶剂分子脱氢后与原料缩合形成中间体,使最终产物的分离和纯化更加困难^[40]。近年来,木质素的自转移氢解反应引起了研究者的极大关注。它是指在没有外源 H₂ 的情况下利用木质素中丰富的脂肪族羟基(包括 C_nH—OH 和 C_yH₂—

OH)和甲氧基(—OCH₃)作为内部氢供体以进行加氢解聚^[27]。该法具有能量输入少、操作安全性高、氢解能力强、碳排放少和避免过度加氢等优点,使木质素的增值转化更加安全、廉价和可持续,为木质素加氢解聚提供了一种较有前景的策略^[41]。

3 金属催化剂催化木质素加氢解聚研究

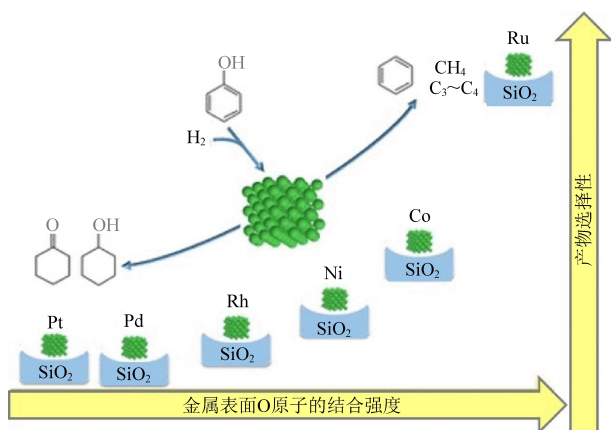
木质素加氢涉及加氢、加氢烷基化、氢解和 HDO 等技术^[42]。其中, HDO 工艺可以断裂 C—C 或 C—O 键,去除产物中的氧元素,因此得到广泛的研究和使用^[43-44]。此外,木质素水热解聚后获得的生物油热值低、黏度高、热稳定性差、酸性强、含水量高。为了解决这些问题,需要使用 HDO 工艺对生物油进行化学升级,从而降低产物复杂性并保留芳环结构^[45]。HDO 工艺需要使用催化剂,非均相加氢催化剂的不同活性位点具有不同的催化功能,包括金属活性位点(亲氧性和颗粒尺寸)和载体活性位点(酸性位点和结构性质)。

3.1 金属活性位点对催化性能的影响

3.1.1 金属的亲氧性

金属亲氧性被认为是影响负载型金属催化剂脱氧和加氢能力的重要因素。随着 d 带中心的位置更接近费米能级,金属和氧杂化产生的反键轨道离费米能级更远,电子占有率更低,金属变得更亲氧,因此形成更强的金属—O 键^[46]。图 2 展示了使用惰性载体二氧化硅负载的催化剂用于苯酚 HDO 反应,催化剂金属中心包括 Ni、Pd、Ru、Pt、Rh 和 Co^[47]。研究表明,Pt、Pd 和 Rh 对芳环的氢化表现出高活性,产生环己醇和环己酮,而 Ru、Co 和 Ni 更亲氧,能促进 C—O 键的氢解,产生苯作为主要产物。

TAN 等^[48]证明在外源氢作氢供体的情况下,二氧化硅负载的 Pt、Ru 和 Fe 在苯甲醚 HDO 中表现出不同的催化性能。在 Pt/SiO₂ 催化剂上,苯氧基产物被氢化为苯酚。随着反应时间的延长,苯酚脱氧生成苯。更亲氧的 Fe/SiO₂ 催化剂可以有效催化苯氧基中间体中 C—O 键的断裂,直接生成苯。这项研究说明更亲氧的金属组分有利于脱氧反应。ZHANG 等^[49]总结了催化剂 HDO 活性与金属亲氧性之间的关系。根据亲氧性将活性金属分为 3 类:低亲氧金属(Pd、Pt、Ni、Rh 和 Au)、中亲氧金属(Ru、Co、Fe、Re 和 Mo)和高亲氧金属(W、Al、Zr、Nb、Ce 和 Ti)。高亲氧金属降低了直

图2 金属亲氧性对苯酚加氢的影响^[47]Fig. 2 Influence of metal oxygen affinity on phenol hydrogenation^[47]

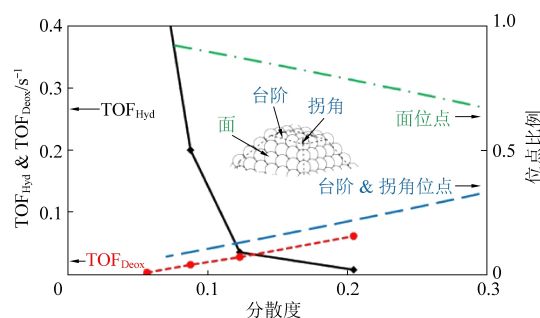
接断裂 C—O 键的能垒,但增强了氢化的能垒。低亲氧金属在氢化反应中具有高催化活性。将低亲氧金属的氢化能力与高亲氧金属的脱氧能力结合的双金属催化剂对 HDO 反应表现出更高的活性和选择性。在这种双金属催化剂中,低亲氧金属提供了表面吸附的氢原子,高亲氧金属与反应物中的氧原子结合,氢原子强大的还原能力促进吸附反应物中 C—O 键的断裂^[50]。HSU 等^[51]系统比较了不同亲氧程度的金属氧化物 (FeO_x 、 MoO_x 和 WO_x) 对甲酚转化的催化行为。研究发现 NiMo (MoO_x 具有中等亲氧性) 将对甲酚更多地转化为甲苯(直接脱氧产物),而 NiW (WO_x 具有最高亲氧性) 更快地将对甲酚转化为甲基环己烷(甲苯氢化产物)。

金属位点的不同性质也会影响木质素的自转移氢解。木质素分子中的 $\text{C}_\alpha\text{—OH}$ 基团可被氧化为 $\text{C}_\alpha\text{=O}$,从而为 C—O 键的氢解提供氢源,同时还可以降低 C—O 键的键解离能^[52]。已有大量研究证明 Ru 和 Rh 基均相催化剂、Pd 基非均相催化剂、 ZnIn_2S_4 和 Ni/CdS 半导体光催化剂催化木质素模型化合物的自转移氢解中均获得较高的产率和选择性^[53-57]。相比之下,天然木质素在溶剂中难以溶解,其与催化剂活性位点间的接触受限,导致天然木质素的氢解效率较低。天然木质素的苯环结构中还有丰富的 —OCH_3 基团。 —OCH_3 基团中大量 C—H 键的断裂可以实现自供氢。此外, —OCH_3 基团从木质素中去除后生成甲醇,甲醇可以通过随后的甲醇蒸汽重整反应供氢^[58]。然而,Ru、Pt、Pd 等加氢能力较强的金属在惰性气氛下不能催化苯环上 —OCH_3 基团的裂解。将 W 引入催化剂时,苯甲醚可以通过自转移氢解,利用甲氧

基作为氢源选择性转化为苯。SHEN 等^[27] 利用 RuW/SiO_2 催化苯甲醚的自转移氢解,发现芳烃的选择性 >99.9%,其中苯的产率高达 97%。机理研究表明催化剂中相邻的 Ru 和 W 具有协同作用,可以从 $\text{C}_{Ar}\text{—H}$ 中提取氢,并通过氢解有效地裂解 $\text{C}_{Ar}\text{—O}$ 键。此外, RuW/SiO_2 催化剂还可以高效促进木质素转化为丙苯,收率达到 8.5%。总的来说,选用合适金属或利用不同金属之间的协同作用,可以调控产物分布,还可以实现底物分子的自转移氢解。

3.1.2 金属的尺寸效应

活性金属的颗粒尺寸也对催化剂的活性和选择性产生极大影响。如图 3 所示,MORTENSEH 等^[59] 在 275 °C 和 10 MPa H_2 的条件下使用 Ni/SiO_2 催化苯酚 HDO 反应,发现当 Ni 颗粒尺寸大于 10 nm 时,主要产物是环己醇。当颗粒尺寸减小时,环己醇会进一步转化为环己烷。机理研究表明,C—O 键的解离更可能发生在台阶/拐角位点,因此小尺寸 Ni 颗粒(台阶/拐角位点的 Ni 更多)的脱氧率更高。



注: TOF_{Hyd} 为加氢周转频率; TOF_{Dcox} 为脱氧周转频率。

图3 Ni 颗粒尺寸对苯酚 HDO 反应的影响^[59]Fig. 3 Influence of Ni particle size on phenol hydrogenation^[59]

此外,有研究认为不同金属尺寸之间存在协同作用。LU 等^[60] 合成了在 SAPO-31 载体上同时存在的钯单原子和钯团簇的 $\text{Pd}_{\text{SA+C}}/\text{SAPO-31}$ 催化剂,该催化剂在温和条件下(0.1 MPa、80 °C、30 min)对香兰素的 HDO 反应具有优异的催化活性(周转频率值达 $3\,000\text{ h}^{-1}$,产率 >99%)。研究认为这归因于钯单原子和钯团簇的协同效应:香兰素中 C=O 基团的有效活化主要发生在钯单原子上,而钯团簇更能促进氢气的解离产生活性氢,活性氢迁移到与 C=O 基团结合的 Pd 单原子位点上以完成 C=O 基团的 HDO 反应(图 4)。在酮/醛选择性还原制醇反应和喹啉加氢反应中同样被证明存在单原子和纳米颗粒的协同作用^[61-62]。

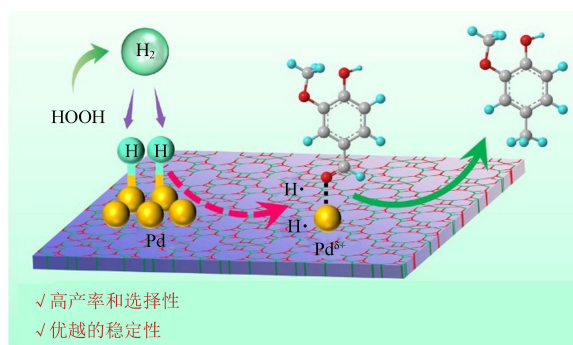


图 4 钯单原子和钯团簇协同催化香兰素加氢^[60]

Fig. 4 Pd single atoms and Pd clusters synergistically catalyze vanillin hydrogenation^[60]

颗粒尺寸受催化剂的制备方式影响较大。以加氢反应中最常用的 Pd/碳基材料催化剂为例,通常其制备及催化过程是先将 Pd 前体物质混合炭载体,通过液相还原法或氢气还原法还原,随后再将催化剂引入底物的转化过程。通常液相还原法制备过程烦琐,制得的 Pd 颗粒较大,一定程度上阻碍了大颗粒内部 Pd⁰ 发挥作用。XU 等^[63]通过 NaBH₄液相还原制得 Pd 平均尺寸为 4.9 nm 的 Pd/介孔 N 掺杂炭催化剂,在温和条件下(90 °C、1 MPa H₂)反应 1 h,可获得 65% 的香兰素转化率和选择性为 44.8% 的 2-甲氧基-4-甲基苯酚。相反,氢气还原法制得的 Pd⁰ 颗粒尺寸较小。LU 等^[55]使用氢气还原法制得平均尺寸 2.16 nm 的 Pd⁰ 颗粒,在 200 °C 下反应 6 h,考察其对 2-苯氧基-1-苯乙酮中 β-O-4 键断裂的影响,得到 62.4% 的转化率,苯乙酮选择性达 34.1%,苯酚选择性达 36.8%。然而该法需要在高温(200~450 °C)下使用氢气,危险性大^[64];且在催化剂转移到反应体系的过程中液相还原和氢气还原均不可避免地接触空气,造成 Pd 活性位点的损失^[65]。因此,探索新颖的催化剂制备方法、简化催化剂制备及应用的步骤,并合理利用活性金属的尺寸效应,是具有重要价值的研究方向。

3.2 载体活性位点对催化性能的影响

3.2.1 载体的酸性和表面官能团

HDO 反应中,载体组分通常优先催化脱水反应^[66-70]。载体的 Lewis 酸位点(Lewis Acid Sites, LAS)和 Brønsted 酸位点(Brønsted Acid Sites, BAS)对底物 HDO 反应的选择性有较大影响^[71-73]。ZHAO 等^[74]报告了固体酸 HZSM-5 作为酸性添加剂在 Pd/C 催化酚类单体 HDO 中的应用。在 200 °C 的水中, HZSM-5 可以促进苯酚在 Pd/C 上完全转化为环烷烃;而使用其他含有 LAS

的添加剂(如无定形二氧化硅-氧化铝、氧化铝和二氧化硅)取代 HZSM-5 时,环烷烃的选择性小于 3%^[75]。研究认为水分子的竞争吸附可能发生在 LAS 上,导致有效酸位点数量减少。因此,足够数量的酸性位点用于反应物种的吸附和活化对于 C—O 裂解至关重要。此外,研究发现含有大量 BAS 的材料,如 Nafion/SiO₂ 和硫酸化氧化锆,也表现出理想的脱氧性能^[74, 76]。然而,在 HZSM-5、Nafion/SiO₂ 和硫酸化氧化锆上,环己醇的脱水速率存在较大差异,分别约为 41.0、11.0 和 0.3 mol · mol⁻¹_{BAS} · h⁻¹。原位红外光谱证明, HZSM-5 可以吸附大量的环己醇,而 Nafion/SiO₂ 和硫酸化氧化锆上几乎没有检测到环己醇的吸附峰^[74]。因此, BAS 主要通过影响底物的吸附控制反应的进行。

金属磷酸盐(Metal Phosphides, MP)因其环境友好、成本低廉、合成路线简便且易于修饰以实现所需的化学转化而引起了广泛关注^[78]。MP 中的 BAS 来自 P—OH 基团,而 LAS 源于缺电子的 M^{x+} 位点(x 代表金属的价态)^[79]。通过调控 MP 中的 LAS,可获得 BAS 与 LAS 之间最佳的协同作用。此外,MP 中不同的金属具有不同的亲氧性,因此对底物的激活能力不同。已经证明磷酸钛(TiP)^[80-81]、磷酸锆(ZrP)^[80-84]、磷酸镧(LaP)^[83, 85]和磷酸铈(CeP)的良好催化脱水活性^[83, 85-87]。GAO 等^[77]合成了一系列 Ni 基金属磷酸盐催化剂,在 220 °C、0.5 MPa H₂ 的条件下使用 Ni/ZrP 催化香兰素转化 30 min,可获得 97.08% 的香兰素转化率,2-甲氧基-4-甲基苯酚产率达到 88.39%,并提出 Ni、BAS 和 LAS 在香兰素转化中的协同催化作用(图 5)。

将活性金属组分锚定在载体上,可制备同时具有金属和酸性位点的双功能催化剂。ZHAO 等^[88]考察了酸载体对苯酚 HDO 的影响。在中性水中, Pd/C 可催化苯酚转化为环己醇,其转化率达到 100%,选择性可达 98%。相反,在主要含有 LAS 的负载型钯催化剂上,如 Pd/Al₂O₃ 和 Pd/ASA(无定形二氧化硅-氧化铝),在 90% 的苯酚转化率下可获得 30% 的环己酮。这表明 LAS 可能稳定环己酮中间体,抑制其进一步转化为环己醇。还有研究证明,酸位点浓度或数量与催化活性线性相关。SONG 等^[89]认为对于 Ni/HZSM-5 催化剂上苯酚的 HDO,周转频率与 200 °C 下酸性位点的浓度(每单位质量载体的酸摩尔量)密切相关。

此外,在愈创木酚的 HDO 中, Ni/Beta 和 Pt/HY 催化剂的脱氧活性与酸位点数之间也存在线性关系^[90-91]。然而,在 300 °C 的较高温度下,高浓度的 BAS 可能导致产物缩合和焦炭沉积,从而导致催化剂失活^[92-93]。因此,酸性位点对反应的促进效果取决于目标产物的实际需求以及 HDO 反应的条件。载体的表面官能团(如氨基、羟基和羧基

等)可以调节催化剂的电子结构,从而促进反应底物的电子转移^[39, 94]。NING 等^[39]成功使用甲酸(FA)-Pd/HPC-NH₂催化体系实现香兰素的加氢。在 30 °C 下可实现>99%的对甲酚选择性和香兰素的完全转化。在该体系中,氨基作为稳定剂来锚定 Pd NPs 并防止其聚集,并作为助催化物质加速 H⁺/Pd-H⁻物质的形成。

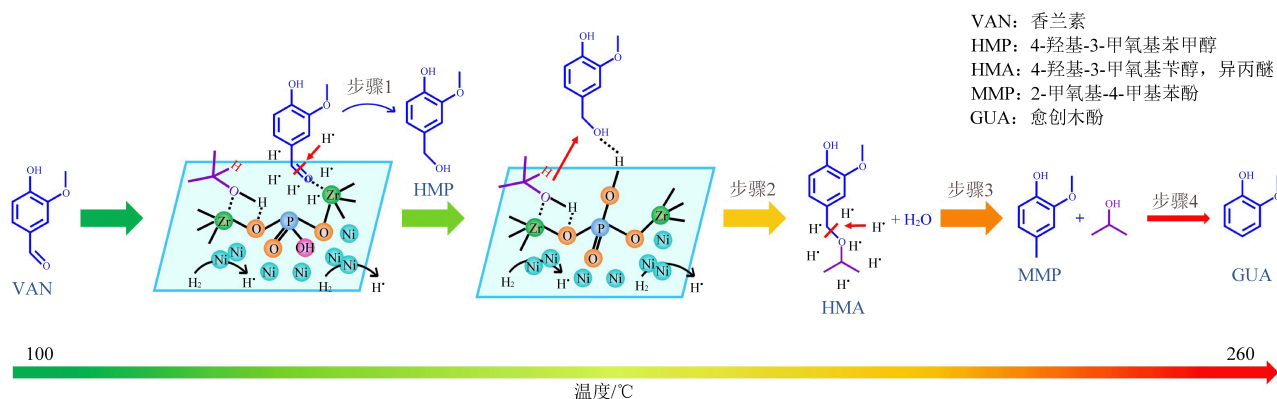


图 5 Ni/ZrP 催化香兰素 HDO 反应机理^[77]

Fig. 5 Reaction mechanism for the HDO of vanillin over Ni/ZrP^[77]

3.2.2 载体的多孔和缺陷结构

催化剂载体的多孔和表面缺陷结构被认为是影响催化活性关键因素^[95-98]。载体的多孔结构使载体具有高比表面积和适宜的孔径分布,利于加氢金属的分散,从而增加活性位点数量,微孔和中孔结构还可以增加木质素分子的接触几率,提高原料转化率和选择性^[99-102]。多种具有多孔结构的载体大量应用于木质素的转化中,如活性炭、石墨烯、二氧化硅、氧化铝和沸石等^[103]。其中,活性炭优良的孔隙率和较大的表面积促进了其作为催化载体的应用。BISWAS 等^[104]使用活性炭为载体合成双金属 Ni-Co/AC 催化剂促进碱木质素解聚产生 72.0%(质量分数)的生物油。AMBURSA 等^[105]使用负载在 Ti-MCM-41(比表面积 705 m²/g)的双金属 Cu-Ni 催化剂,可促进愈创木酚加氢脱氧制环己烷。在 10 MPa, 260 °C 下反应 6 h,愈创木酚转化率达到 90.2%,环己烷选择性达到 51.7%。石墨烯也具有多孔结构(比表面积达 2 600 m²/g,理论值),其高导电性还可以促进反应物与催化剂之间的电子传递^[106-107]。近年来,使用新兴的闪光焦耳加热(Flash Joule Heating, FJH)技术能够以废弃生物质为来源的生物炭(Biochar, BC)为原料制备石墨烯,成本低廉、稳定性好^[101, 108-114]。与传统技术不同, FJH 技术采用电流直接通过样品的方式,在急速升温(ms, 约

3 000 K)和急速冷却(约 10⁵ K/s)过程中,利用电场效应剥离出石墨结构。这是一种无溶剂消耗的制备方法,且该方法可调节石墨烯的结构性质与化学性质^[110]。GAO 等^[115]使用 FJH 技术制备多孔石墨烯为载体,在 30 °C, 0.5 MPa H₂的温和条件下,获得 99%的香兰素转化率和>95%的 2-甲氧基-4-甲基苯酚产率。

载体的表面缺陷也会对木质素的转化和产物选择性产生较大影响,能够增强金属与载体之间的相互作用,对金属颗粒产生限域效应^[98, 116-119]。杂原子掺杂能够在材料高温挥发过程中留下丰富的孔道和缺陷。此外,该方法能够调整催化剂的电子结构和表面活性位点,并引入新的催化活性中心^[120]。N 元素是最常用的掺杂元素之一,因其可以与活性金属形成金属-氮配位结构。这种结构提供了额外的金属负载位点,有效防止金属的团聚^[68, 115, 121-124]。NIE 等^[68]使用吡咯在炭黑(CB)中掺杂 N 元素合成 Ni/NCB-900 催化剂,证明与无 N 元素掺杂的 Ni/CB 催化剂相比,香兰素转化率从 37.8%提高到 74.4%,2-甲氧基-4-甲基苯酚产率从 50.6%提高到 64.6%(图 6)。

总而言之,载体的多孔结构和表面缺陷在木质素加氢过程中起着关键作用。通过优化载体的比表面积和孔径分布、引入表面缺陷位点,可以显著提高木质素加氢的反应效率和选择性。

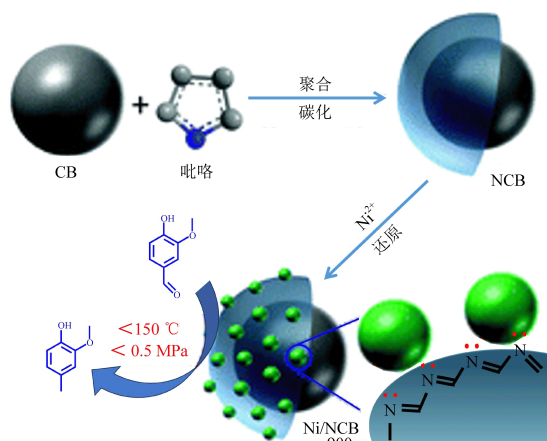


图6 Ni负载的N掺杂炭黑促进木质素衍生物香兰素的加氢脱氧^[68]

Fig. 6 Hydrodeoxygenation of vanillin over porous nitrogen-doped carbon black supported nickel nanoparticles^[68]

4 结论与展望

木质素是一种颇具应用前景的可再生原料,可生产高附加值芳香族化学品。随着化石资源的不断开发利用,木质素的资源化利用是未来研究的重点。目前,通过加氢解聚将木质素转化为高附加值芳香族化学品是一种高效、绿色、可持续的方法,本文对木质素的结构特性和加氢解聚工艺进行了综述,并在此基础上提出未来可能的研究方向,以促进木质素增值转化的发展。

(1)木质素结构是加氢解聚工艺的一个关键影响因素。不同来源和提取方法得到的木质素具有多样的结构特征,包括不同的侧链、分支和聚合度。这种结构差异影响加氢解聚的效率和产物的选择性。因此,深入研究木质素的结构-性能关系,探索不同结构木质素的加氢解聚途径,将有助于优化工艺,提高芳香族化学品的产率。

(2)在木质素的加氢解聚过程中,催化剂的选择和设计是另一个关键因素。催化剂活性直接影响产物的分布和选择性。通过设计新型催化剂,可以实现更高的反应活性和选择性。同时,寻找更环保、经济的催化剂可以提高木质素增值转化过程的可持续性。

(3)木质素加氢解聚过程的工艺优化也是重要的研究方向。调控温度、气氛、压力、溶剂等反应条件对于加氢解聚的效果至关重要。绿色溶剂的开发是木质素增值领域的重要研究部分。提高木质素在绿色溶剂中的溶解度,有利于降低木质素的固体颗粒效应,从而增加其与催化剂活性位

点间的接触。因此,木质素加氢解聚过程的工艺优化在工业应用领域有巨大的研究价值。

(4)在木质素的增值转化中,产物的后续利用也是一个亟待解决的问题。开发解聚产物的下游应用,探索木质素衍生物在医药、材料等领域的潜在用途,将有助于形成一个可持续的木质素利用链条,最大程度地发挥木质素的资源价值。

(5)木质素自转移氢解是一种较有前景的木质素增值转化策略。供氢基团的反应性以及其与催化剂之间的作用机理仍需进行更多的研究。

总体而言,尽管木质素的加氢解聚面临诸多挑战,但是随着对木质素本征结构和加氢解聚工艺的深入理解,木质素的资源化利用有望在未来取得更为显著的进展。

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