



生物乙醇制备航空煤油的研究进展

李攀 赵宇 吴兴国 张璐璐 胡俊豪 陈玮 白净 常春 方书起

Progress of research on aviation kerosene preparation using bioethanol

LI Pan, ZHAO Yu, WU Xingguo, ZHANG Lulu, HU Junhao, CHEN Wei, BAI Jing, CHANG Chun, FANG Shuqi

引用本文:

李攀, 赵宇, 吴兴国, 张璐璐, 胡俊豪, 陈玮, 白净, 常春, 方书起. 生物乙醇制备航空煤油的研究进展[J]. *北科大: 工程科学学报*, 2025, 47(3): 514–525. doi: 10.13374/j.issn2095–9389.2024.05.31.005

LI Pan, ZHAO Yu, WU Xingguo, ZHANG Lulu, HU Junhao, CHEN Wei, BAI Jing, CHANG Chun, FANG Shuqi. Progress of research on aviation kerosene preparation using bioethanol[J]. *Chinese Journal of Engineering*, 2025, 47(3): 514–525. doi: 10.13374/j.issn2095–9389.2024.05.31.005

在线阅读 View online: <https://doi.org/10.13374/j.issn2095–9389.2024.05.31.005>

您可能感兴趣的其他文章

Articles you may be interested in

用于木质素转化制备生物质燃料多功能催化剂的研究进展

Research advances in multifunctional catalysts for the conversion of lignin to biomass fuels

工程科学学报. 2022, 44(4): 664 <https://doi.org/10.13374/j.issn2095–9389.2021.09.28.003>

微波辅助炭基催化剂催化热解生物质的研究进展

Research progress on biomass catalytic pyrolysis via microwave effects combined with carbon-based catalysts

工程科学学报. 2023, 45(9): 1592 <https://doi.org/10.13374/j.issn2095–9389.2022.11.16.002>

异相类Fenton催化剂降解废水中抗生素研究进展及发展趋势

Research progress and development trends in heterogeneous Fenton-like catalysts for degradation of antibiotics in wastewater

工程科学学报. 2021, 43(4): 460 <https://doi.org/10.13374/j.issn2095–9389.2020.10.29.002>

直接甲醇燃料电池 (DMFC) 阳极过渡金属基催化剂的研究进展

Research progress in anode transition metal-based catalysts for direct methanol fuel cell

工程科学学报. 2022, 44(4): 625 <https://doi.org/10.13374/j.issn2095–9389.2021.09.30.005>

废催化剂中铂族金属回收现状与研究进展

Status and research progress on recovery of platinum group metals from spent catalysts

工程科学学报. 2020, 42(3): 257 <https://doi.org/10.13374/j.issn2095–9389.2019.11.26.001>

甲苯催化氧化研究进展

Current progress on catalytic oxidation of toluene: a review

工程科学学报. 2024, 46(7): 1286 <https://doi.org/10.13374/j.issn2095–9389.2023.11.17.003>

生物乙醇制备航空煤油的研究进展

李攀^{1,2,3,4}, 赵宇^{1,3,4}, 吴兴国^{1,3,4}, 张璐璐^{1,3,4}, 胡俊豪^{1,2,3,4}✉, 陈玮³,
白净^{1,2,3,4}, 常春^{2,3,4}, 方书起^{1,2,3,4}

1) 郑州大学机械与动力工程学院, 郑州 450001 2) 生物基运输燃料技术全国重点实验室, 郑州 450001 3) 河南省生物基化学品绿色制造
重点实验室, 濮阳 457000 4) 生物质炼制技术与装备河南省工程实验室, 郑州 450001

✉通信作者, E-mail: junhaohu_hust@163.com

摘要 生物基航空煤油是一种可持续、绿色环保的航空燃料, 能够有效降低航空业的碳排放, 具有巨大的应用前景。本文综述了以生物质为原料制备航空煤油的工艺方法, 重点关注我国生物乙醇产业的快速发展及其充足的产量。在此基础上, 详细阐述了生物乙醇制备航空煤油的主要工艺流程, 分析了生物乙醇制航油技术中的三个关键反应(乙醇脱水制乙烯、烯烃低聚反应以及加氢反应)的工艺条件和催化剂应用。此外, 介绍了乙醇碳碳偶联与加氢脱氧制备航空煤油的最新进展, 探讨了高碳醇制备反应的机理和催化剂, 以及加氢脱氧反应的研究动态。指出当前乙醇制备航空煤油面临成本较高和催化剂开发等挑战, 并对未来该技术的发展方向进行了展望, 为生物乙醇制备航空煤油的工业化提供了重要参考。

关键词 航空煤油; 生物乙醇; 催化剂; 高碳醇; 加氢脱氧

分类号 TK6

Progress of research on aviation kerosene preparation using bioethanol

LI Pan^{1,2,3,4}, ZHAO Yu^{1,3,4}, WU Xingguo^{1,3,4}, ZHANG Lulu^{1,3,4}, HU Junhao^{1,2,3,4}✉, CHEN Wei³, BAI Jing^{1,2,3,4}, CHANG Chun^{2,3,4},
FANG Shuqi^{1,2,3,4}

1) School of Mechanical and Power Engineering, Zhengzhou University, Zhengzhou 450001, China

2) State Key Laboratory of Biobased Transport Fuel Technology, Zhengzhou 450001, China

3) Henan Key Laboratory of Green Manufacturing of Biobased Chemicals, Puyang 457000, China

4) Engineering Laboratory of Henan Province for Biorefinery Technology and Equipment, Zhengzhou 450001, China

✉Corresponding author, E-mail: junhaohu_hust@163.com

ABSTRACT In recent years, the Chinese government has proposed the “dual carbon” goal of achieving a carbon peak by 2030 and carbon neutrality by 2060. In achieving this goal, the petrochemical industry is experiencing the urgent challenge regarding its development and transformation vis energy conservation and emission reduction. Biobased aviation kerosene is a sustainable and environmentally friendly alternative for reducing carbon emissions in the aviation industry, offering a notable promise for widespread adoption. This study comprehensively reviews the process for producing aviation kerosene from biomass. Vegetable oil, oil from inedible oil crops, pyrolysis oil, lignocellulosic residues, sugar, and starch biomass can be used as raw materials for the production of bioaviation kerosene. Biobased aviation kerosene can be classified into the following types according to its production technology: oil to jet (OTJ), gas to jet (GTJ), alcohol to jet (ATJ), and sugar to jet (STJ) fuels. With the rapid development of China’s bioethanol industry and abundant production, the energy supply-diversification strategy represented by ethanol and other alternative energy sources has become a guide for energy policies in various countries. The use of bioethanol as a raw material for preparing aviation kerosene is

收稿日期: 2024–05–31

基金项目: 国家自然科学基金资助项目(52006200); 河南省自然科学基金资助项目(242300421229); 河南省杰出外籍科学家工作室项目(GZS2022007); 河南省重点研发与推广专项(232102321036); 南阳市协同创新重大专项(22XTCX12007)

important for the environment, economy, and sustainability. This study focuses on the process of converting bioethanol into aviation fuel. It analyzes and summarizes the reaction conditions and catalysts involved in the three main reactions: ethanol dehydration to ethylene, olefin oligomerization, and hydrogenation. Currently, the ATJ process still suffers several disadvantages, such as long process flow and low conversion efficiency. The conversion route from ethanol to jet kerosene is complex and requires three different catalysts. We must develop a catalyst that can catalyze both the dehydration reaction and oligomerization hydrogenation reaction, increase the conversion efficiency, and reduce the production cost. This study introduces the carbon-carbon coupling of ethanol and hydrodeoxygenation for the production of aviation kerosene, including discussions on reaction mechanisms and catalysts for the preparation of high-carbon alcohol. The Guerbet condensation reaction of ethanol is hindered by the presence of water as a by-product. Therefore, a catalyst is proposed for carbon-carbon coupling reaction of aqueous ethanol to produce high-carbon alcohols. The catalyst, with its satisfactory water resistance, can retain its activity and selectivity for high-carbon alcohols even in the presence of water and effectively inhibit the interference of water molecules, thereby increasing the efficiency and stability of the catalytic reaction. Jet kerosene is obtained via hydrodeoxygenation of high-carbon alcohols, in which noble metal- and molybdenum-based catalysts exhibit satisfactory catalytic performance. Transition metals combined with Mo₂C catalysts can selectively break the C-O bonds in polyols and avoid C-C bond breakage. Research and development of efficient hydrodeoxygenation catalysts can facilitate the conversion of high-carbon alcohols into hydrocarbons, providing important support for the development of alternative aviation fuels. This study highlights the current challenges facing the production of ethanol-based jet fuel, such as the high production cost and the need for new catalysts. Furthermore, it proposes future development directions, offering valuable insights for the industrialization of bioethanol-based aviation kerosene production.

KEY WORDS aviation kerosene; bioethanol; catalyst; high-carbon alcohol; hydrodeoxygenation

为了实现“2030年实现碳达峰、2060年实现碳中和的‘双碳’”目标,石化行业面临着转型发展、节能减排的迫切挑战^[1]。在碳中和目标的推动下,炼化企业需要以原料构成和加工技术为出发点,积极探索低碳、零碳原料的炼制技术,以实现低碳发展^[2]。航空业是高空温室气体排放的主要来源,其中航空煤油是飞机主要的动力来源。生物航油以生物质为原料,可替代部分传统航油,实现减排55%至92%,具有显著环保优势^[3-5]。生物航空煤油技术具有全生命周期温室气体排放降低的潜力,采用生物航空煤油能够有效减少航空业的碳排放,推动航空业可持续发展。

生物质能是一种可再生的优质能源,植物油、热解油等油类作物、木质纤维素、糖和淀粉生物质都可以作为生物航煤的原料^[6-7]。近年来,为解决化石能源的短缺的问题、减少碳排放,以生物质为原料制备航空煤油的工艺技术有了长足的发展^[8-9]。生物航空煤油的制备工艺技术主要有生物油制航煤技术、生物质经合成气制航煤技术、醇和糖制航煤技术。本文对近年来生物乙醇制备航空煤油工艺技术相关领域的文献进行了整理,重点介绍了以生物乙醇为原料制备航空煤油的发展现状,该技术包括醇脱水、烯烃低聚和烯烃加氢三个主要反应步骤,同时也涉及高碳醇加氢脱氧制备航空煤油的技术进展,并对生物基航空煤油领域的

发展前景进行一定的展望,为生物乙醇制备航空煤油的后续研究提供了重要参考和理论依据。

1 生物基航空煤油概述

航空煤油的主要成分通常包括C₈到C₁₆之间的烃类,成分包含烷烃和异构烷烃、环烷烃,以及少量的烯烃和芳香烃^[10]。生物基航空煤油是指直接或间接利用生物质合成的航空煤油,其含硫量较低,尾气排放污染小,还有良好的低温流动性和热稳定性^[11]。此外,生物基航煤与传统航空煤油在技术上基本兼容,不需要对飞机或基础设施进行显著改动,这也有助于减少对化石燃料的依赖,同时促进可再生资源的利用。生物基航空煤油生产所涉及的生物质来源可以分为可食用植物作物、非食用油料作物、木质纤维素生物质以及藻类等^[6,12-13]。将不同类型的原料转化为生物航空煤油的生产工艺路线众多,各路线的简要流程如图1所示^[5]。

Wang和Tao^[14]按照生物航油生产技术的不同原料来源分为生物油制航油(OTJ)、合成气制航油(GTJ)、乙醇制航油(ATJ)以及糖制航油(STJ)等四类,如表1所示是制备航空煤油的主要途径比较。在技术成熟度方面,油制航油技术目前领先于其他技术,但仍面临诸如原料可得性较差、温室气体排放和缺乏芳烃等问题需要解决。合成气制备航油生产工艺已有示范工厂运营,但高资本成本仍

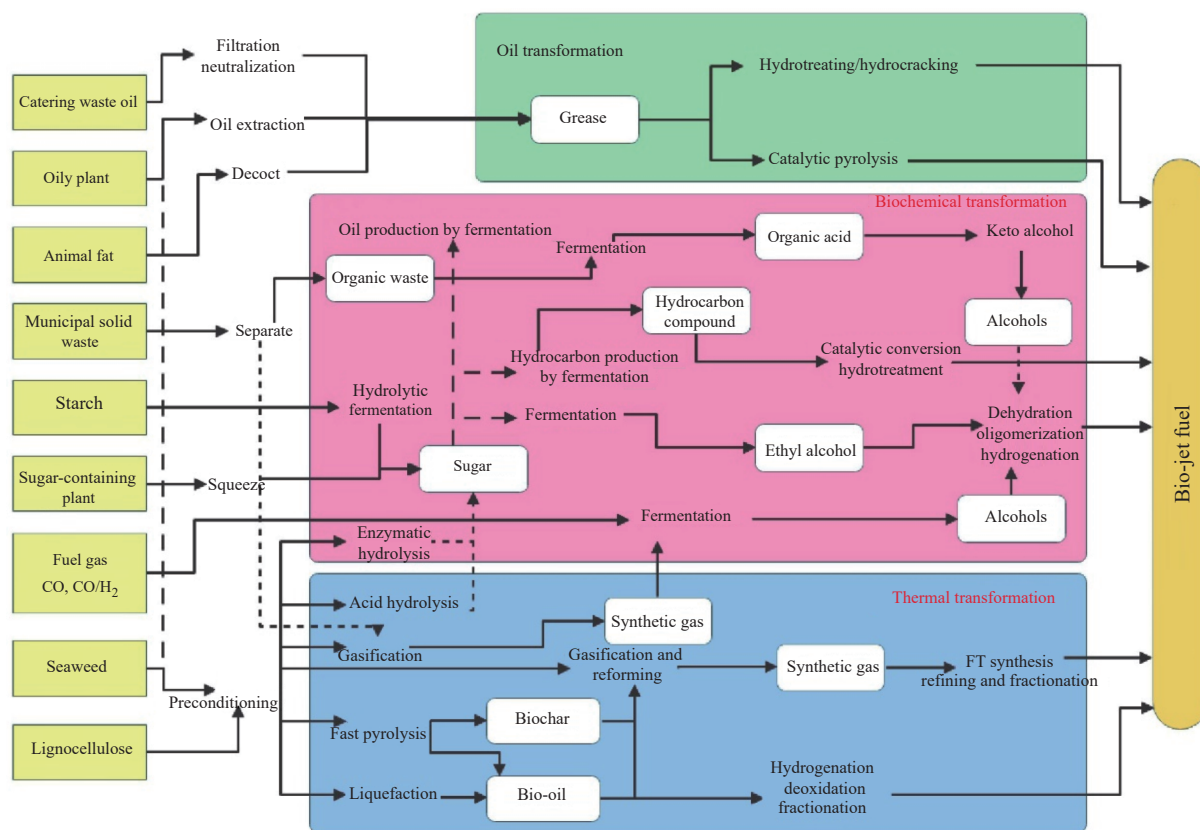


图 1 生物航煤主要制备技术^[5]

Fig.1 Main preparation technologies for biological aviation kerosene^[5]

表 1 生物质制备航空煤油的主要途径^[16]

Table 1 Main methods of preparing aviation kerosene from biomass^[16]

Category	Ingredients	Reaction step	Catalyst	Minimum selling price/\$	Greenhouse gas emission/ (10 ⁶ g·J ⁻¹)	Aromatic-containing aviation coal	ASTM-approved fuel
OTJ	Vegetable oil	1. Hydrotreating 2. Fractionation	It is mainly alumina-supported metal sulfide	4.4–5.1	13–141	NO	Yes, mixed with fossil jet fuel up to 50%
GTJ	Lignocellulosic, urban, and agricultural residues	1. Gasification 2. Fischer–Tropsch synthesis 3. Fractionation	Fe base- and Co base-supported catalysts	3.9–4.3	2–10	YES	Yes, mixed with fossil jet fuel up to 50%
ATJ	Biomass-derived alcohol	1. Dehydration 2. Oligomerization 3. Hydrogenation 4. Fractionation	Heterogeneous and homogeneous acid catalysts			YES	Yes, mixed with fossil jet fuel up to 50%
STJ	Sugar, furan	1. Deoxygenate 2. C–C coupling 3. Hydrogenation 4. Fractionation	Heterogeneous catalyst	>3.5	15–49	YES	ASTM test phase

是其商业化的主要障碍. ATJ 工艺是将生物质制取醇转化为航空煤油, 可通过工艺强化和研发新型催化剂等方法来改进工艺的高耗能, 以补偿醇生产的高成本和低产率^[15]. ATJ 工艺显示出将生物醇转化为航空燃料的潜力, 但需要解决催化升级步

骤与醇生产的整合挑战. 此外, 糖转化为液态烃燃料的水相催化转化在实验室和中试阶段展示出了潜力, 但需要进一步改进以提高其经济前景. 生物航空煤油生产工艺受到了广泛关注, 在航空燃料市场中占据着重要地位, 尽管目前存在一些挑战, 但

从长远来看,生物航空煤油有望逐渐减少对传统石油航空煤油的依赖,并直接作为航空燃料使用。

随着国际石油需求的进一步增加和国际油价的上涨,以乙醇等替代能源为代表的能源供应多元化战略已成为各国能源政策的一个方向.生物乙醇是世界上应用最广泛的可再生能源,许多国家和地区正在积极推动生物乙醇产业的发展^[17-18].全球生物乙醇产业正处于从以粮食为主的一代产业向以非粮原料(如秸秆、木薯、枯草)为主的二代产业转变,甚至向以藻类等为原料的第三代产业转变的时期.近年来,全球燃料乙醇产量发展快速,美国和巴西的乙醇产量分别约占全球产量的54%和30%.中国的生物乙醇产业以粮食为原材料的第一代工艺为主,产能占比超过70%,主要使用玉米和小麦等作物,是第三大乙醇生产国,约占全球的4%^[19-21].生物乙醇产业在面对人口众多和粮食需求增加的背景下,选择非粮原料作为生产乙醇的原料显得尤为重要,这有助于避免与粮食资源的竞争,并促进生物乙醇产业的可持续发展.但面临多重挑战,高昂的生产成本、非粮原料供应的可持续性和有效的环境保护措施也是亟待解决的关键问题。

因此,用生物乙醇作为制备航空煤油的原料,对环境、经济和可持续性都有重要作用.开发乙醇的高值高端利用技术不仅能够与现行乙醇产业接轨,保障其发展,还有助于我国能源结构的多元化,进而保障国家的能源安全。

2 乙醇制备航空煤油工艺技术

ATJ工艺流程如图2所示,涉及三个主要步骤:①乙醇脱水生成相应的烯烃;②烯烃低聚成新的低聚烯烃;③低聚烯烃氢化成饱和烃产物.通过ATJ工艺生产的生物航空煤油可以与化石喷气燃料混合使用,其中生物航空煤油的体积百分比高达50%^[22-23].ATJ整个工艺流程的所有工艺步骤都已在商业相关规模上得到证明,最大限度地降低了扩大生产规模的风险.下面将从乙醇脱水、烯烃

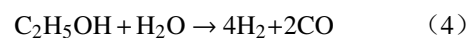
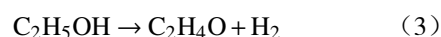
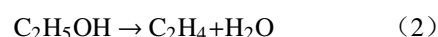
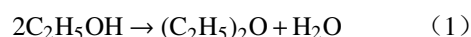
低聚和加氢三个反应对ATJ工艺进行综述。

2.1 乙醇脱水制烯烃

目前,乙醇脱水制乙烯技术比较成熟,已成为调整能源结构、减少环境污染、促进国民经济和社会可持续发展的重要途径之一.该技术具有产物纯度高、易于提纯、生产工艺简单等优点.当前,针对生物质乙醇脱水制乙烯的研究主要集中在催化剂的开发和工艺优化上,被广泛研究的催化剂包括活性氧化铝、沸石、磷酸和磷酸盐等,工业上常用的催化剂有HZSM-5催化剂、活性炭负载型催化剂和活性氧化铝.然而,生物乙醇主要通过农作物和有机废料的发酵过程获得,经过分离和提纯后,乙醇的含量通常在13%至26%之间.目前使用的催化剂对乙醇浓度要求较高,对于低浓度乙醇的应用研究较少,存在催化剂活性不足和稳定性问题,限制了技术的进一步发展。

2.1.1 工艺反应条件的影响

Cheng等^[24]指出乙醇脱水有两种可能的反应机制,分别是有利于乙烯形成的分子内脱水吸热反应和产生乙醚的分子间脱水放热反应.反应温度是影响乙醇催化脱水制备乙烯的重要因素之一,当反应温度在150~300℃时,主要进行反应(1),乙醇脱水生成乙醚,而当反应温度在300~500℃时,发生反应(2),生成乙烯.反应温度超过500℃时,则会发生反应(3),乙醇脱氢生成乙醛,同时,水的生成会导致乙醇的蒸汽重整,发生反应(4)。



乙醇的浓度也会对乙醇脱水反应造成影响,乙醇在不同浓度下的反应转化率和选择性会有差异^[25].祝阳^[26]通过实验研究了分子筛作为催化剂在反应中的表现.实验结果表明,乙烯转化率对乙醇浓度变化的敏感性较低,而选择性却随着乙醇浓度的变化出现了显著变化.这种选择性变化可

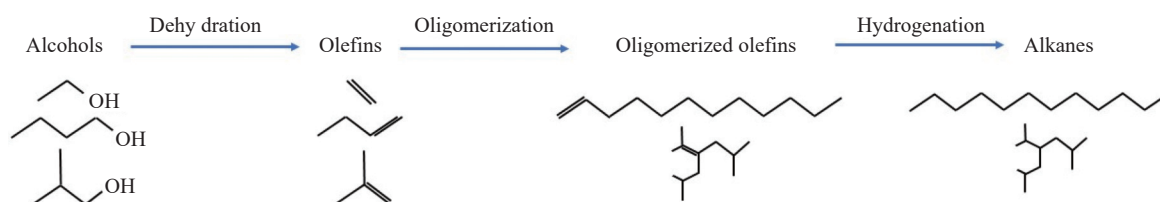


图2 醇制航油流程图

Fig.2 Flow chart of alcohol jet fuel production

能与催化剂表面酸性的不同有关. 在乙醇浓度较低的情况下, 水分作为加热载体, 有助于维持反应温度的稳定, 并能与烯烃的中间产物竞争吸附, 进而抑制乙烯的进一步反应, 这样一来, 不仅有效防止了催化剂积炭失活, 还提高了乙烯的选择性.

乙醇质量空速是影响反应进程以及乙烯产量的重要指标. 王菊等^[27]通过对乙醇脱水制乙烯工艺的实验研究发现, 乙醇的转化率随空速的降低而逐渐增加直至平衡. 在催化剂量一定的情况下, 活性位点的数量是有限的. 当空速较高时, 催化剂无法有效容纳大量的乙醇和水, 导致乙烯的收率下降^[24]. 同时, 当空速增加时, 乙醇分子在催化剂床层的停留时间变短, 少部分乙醇还来不及反应即被带出催化剂床层, 从而导致转化率降低.

2.1.2 催化剂的影响

乙醇脱水生成乙烯是一个酸催化反应^[28], 常见酸性催化剂包括金属氧化物催化剂、磷酸催化剂、分子筛催化剂和杂多酸催化剂, 表 2 是乙醇脱水催化剂性能的比较. Al_2O_3 是最常见的氧化物催化剂, 也是酸碱双功能催化剂^[29-30], 为提高催化剂的表面积和孔结构, 在 Al_2O_3 的基础上, 又研发出二元氧化物和多元氧化物催化剂, 如 $\gamma\text{-Al}_2\text{O}_3$ 、 $\text{MgO-Al}_2\text{O}_3$ 等. 酸碱双功能催化剂具备较长的使用寿命, 稳定性高, 能够持续保持其催化活性和选择性, 提高反应效率.

目前研究较多的分子筛催化剂是 ZSM-5 分子筛催化剂, ZSM-5 分子筛比表面积高, 传质孔道规整并且具备较高的酸性, 对于乙醇脱水有高活性. Ouayloul 等^[36]通过对 ZSM-5 分子筛进行酸性改性, 调节催化剂表面酸性, 使得乙醇在低温下选择性地脱水生成乙烯. Zhan 等^[37]对 HZSM-5、磷改性 HZSM-5 和镧磷改性 HZSM-5 催化乙醇脱水制

乙烯的反应进行了研究, 结果表明, 镧磷改性 HZSM-5 的催化性能和抗结焦能力最强, 其中 HZSM-5 分子筛催化剂负载镧质量分数为 0.5% 和磷质量分数为 2% 的催化剂 (0.5%La-2%PHZSM-5) 的抗结焦能力最强, 图 3 为 H-ZSM-5 分子筛催化乙醇脱水反应机理图, 其中 TS 表示过渡态 (Transition State), 是化学反应路径中的中间状态. 分子筛催化剂研究和应用的关键是要实现在醇脱水反应中提高稳定性, 分子筛催化剂能够长时间保持催化活性而不发生结构变化或失效, 减缓催化剂积碳而导致的失活. 杂多酸催化剂是含有氧桥的多核配位物的催化剂, 用于乙醇脱水制乙烯的杂多酸催化剂具有反应温度低等优点, 但杂多酸催化剂在使用时通常需要负载在载体上, 存在损耗严重、制备成本高的问题^[38-39]. 催化剂在乙醇脱水制乙烯过程中起着重要作用, 制备高效且稳定性好的催化剂是下一步进行的主要工作.

2.2 乙烯低聚反应

烯烃聚合是指通过化学反应将烯烃单体聚合成高分子量的聚合物, 广泛应用于塑料、橡胶等行业. 烯烃聚合技术涵盖了从聚乙烯、聚丙烯到特种聚烯烃等多种聚合物的生产. 近年来, 烯烃聚合技术取得了显著进展, 主要集中在优化催化剂、推广环保技术和开发新型聚合物三个方面. 优化催化剂目标在于提高反应效率和产品质量, 环保技术则致力于减少环境负担, 使用更环保的反应条件和材料. 同时, 开发具有特殊功能或性能的新型聚合物, 如高性能塑料和功能性聚合物, 以满足市场对高附加值产品的需求. 尽管烯烃聚合技术已有重大进展, 仍需解决一些技术挑战, 特别是在催化剂固载和替代昂贵助催化剂方面的研究, 以进一步推动该领域的发展.

表 2 乙醇脱水催化剂的性能的比较

Table 2 Comparison of performances of catalysts for ethanol dehydration

Catalyst	Catalyst preparation method	Reaction temperature/°C	Ethylene yield/%	Reference
Cu-SSZ-13 zeolite	Cu-tetraethylenepentamine complex was synthesized <i>via</i> the one-pot method	212	>99	[31]
$\text{WO}_3/\text{MCF-Si}$	WO_3 was impregnated on MCF-Si carrier <i>via</i> the initial wet immersion method	400	98.3	[32]
W/Pd/ TiO_2	TiO_2 negative support was prepared <i>via</i> the solvothermal method; Pd was impregnated first, and W was impregnated <i>via</i> the equal volume impregnation method	400	68.1	[33]
Ni/Sr-ZSM-5	H-ZSM-5 with Si/Al molar ratio of 25-30 was converted into Sr-ZSM-5 <i>via</i> ion exchange, and then Ni was loaded onto Sr-ZSM-5 <i>via</i> the impregnation method	250	95	[34]
HT- $\gamma\text{-Al}_2\text{O}_3$	HT- $\gamma\text{-Al}_2\text{O}_3$ was synthesized <i>via</i> solvent protection and hydrothermal treatment	450	98	[29]
HPW/T1b	HPW/T1b was prepared from phosphotungstic acid hydrate and 1.5mm diameter silicon trilobes	210	96	[35]

Notes: MCF-Si is mesocellular form silica; HT- $\gamma\text{-Al}_2\text{O}_3$ is high-energy plane (111)-exposed gamma alumina; HPW is phosphotungstic acid hydrate.

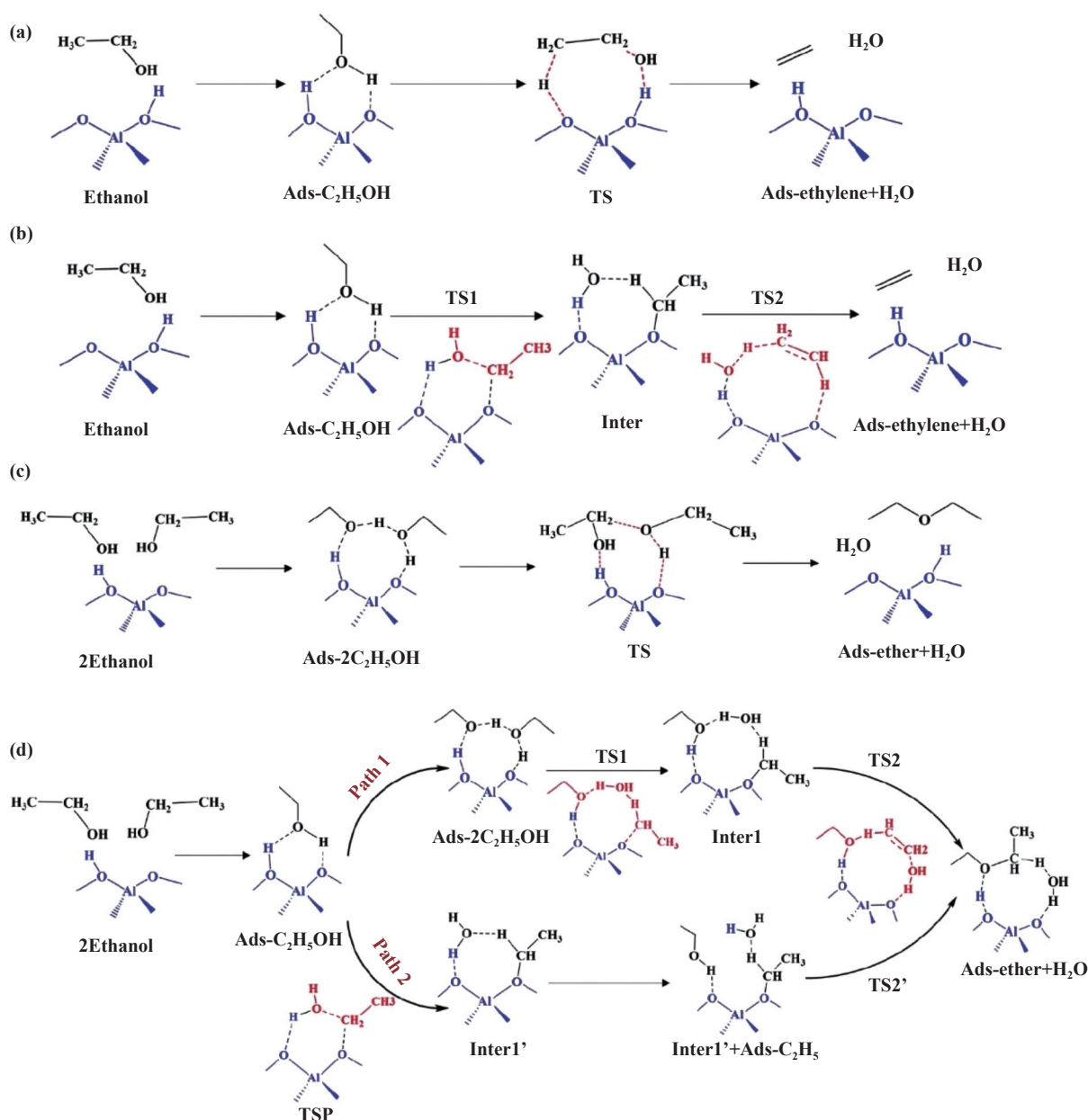


图3 H-ZSM-5分子筛催化乙醇脱水反应机理图^[40]。(a)生成乙烯的协同反应机理; (b)生成乙烯的分步反应机理; (c)生成乙醚的协同反应机理; (d)生成乙醚的分步反应机理

Fig.3 Mechanism of ethanol dehydration catalyzed using H-ZSM-5 molecular sieve^[40]: (a) synergistic reaction mechanism of ethylene production; (b) step-by-step reaction mechanism of ethylene generation; (c) synergistic reaction mechanism for ether formation; (d) step reaction mechanism for ether production

2.2.1 工艺反应条件的影响

反应条件(如温度、压力和空速以及催化性能等)对乙烯低聚反应均有影响. Attanatho等^[41]通过实验制备了片状Ni-Al-SBA-15(含镍和铝的SBA-15介孔分子筛)催化剂,并在空速($0.56 \sim 4.5 \text{ h}^{-1}$)、温度($150 \sim 350 \text{ }^{\circ}\text{C}$)和压力($0.1 \sim 2 \text{ MPa}$)的不同组合条件下,在连续流动固定床反应器中进行乙烯低聚实验,得出最佳反应条件为:反应温度为 $275 \sim 300 \text{ }^{\circ}\text{C}$,反应压力为 2 MPa ,空速为 0.56 h^{-1} .在最佳反应条件下,乙烯摩尔转化率可达 $98\% \sim 99\%$.由

此可得,在高温、高压和低空速条件下有利于 C_{8+} 碳氢化合物的生成.

2.2.2 催化剂的影响

乙醇转化为生物航空燃料需要制备高活性、高稳定性的乙烯低聚催化剂.乙烯低聚催化剂可以分为均相和非均相两种类型.在均相催化剂中,常见的是有机过渡金属配合物,由含有过渡金属的化合物与含有配位能力的有机配体组成^[42].乙烯在催化剂的过渡金属活性位点上发生链增长反应,但这类配合物需要通过助催化剂适当比例

地激活, 才能实现高催化活性和选择性^[43]. Bekmukhamedov 等^[44]考察了镍基催化剂在乙烯低聚反应中的应用, 以及镍中心的电子态和配位态对催化性能的影响. 镍基催化剂优点是高活性, 产物中不存在聚合物, 通过在较低的温度(25~30 ℃)和乙烯压力(1~2 MPa)下反应, 可以降低低聚反应的能量成本. Panpian 等^[45]制备负载有镍和铝的多孔硅(NiAlKIT-6)催化剂, 通过实验测得乙烯转化率>95%, C₈+选择性高达 55%, 催化剂表现出良好的稳定性. 但是, 均相催化剂存在回收困难、需大量的助催化剂活化、链长难以控制等缺点.

虽然均相催化体系在乙烯低聚反应中处于中心地位, 但是为解决均相催化剂存在的问题, 非均相催化剂开始被提出并研发^[42-43]. 常见的非均相催化剂载体有硅胶、分子筛和碳纳米管等. 轻质烯烃也可以通过 ZSM-5 分子筛催化低聚反应转化为长链烯烃, 为生产航空煤油系列产品开辟了一条可持续发展的途径^[46-48]. 多相催化体系可以减少使用有机溶剂, 易于分离反应介质和催化剂回收, 但价格一般比较昂贵.

2.3 烯烃氢化制烷烃

烯烃低聚物首先经过蒸馏过程分离出柴油、航空煤油和轻质烯烃. 在石油化工工业中, 加氢饱和是一种常见工艺, 用于完成烯烃的氢化反应, 氢化过程在固体催化剂上进行, 该催化控制反应可在相对高压(>2 MPa)和高温(200~350 ℃)条件下完成^[49-50]. 通过蒸馏分离的轻质烯烃(C₄~C₈)再循环回到低聚步骤, 低聚产物在 370 ℃和空速 3 h⁻¹下加氢, 加氢的条件是活性炭上含有质量分数为 5% 的钨或铂^[14, 51], 由氢化步骤产生的 C₈~C₁₆ 烷烃适用于可再生航空燃料. 过量的氢气被引入反应器中, 烯烃经过氢化反应, 使双键被饱和, 从而确保所有的烯烃都转化为链烷烃. 这对于确保燃料的低反应性至关重要, 因为饱和的产物通常比

烯烃更加稳定, 有助于提高燃料的质量和性能.

3 乙醇碳碳偶联和加氢脱氧制备航空煤油工艺技术

3.1 制备高碳醇

3.1.1 Guerbet 反应机理及其催化剂

以生物乙醇作为原料, 通过 Guerbet 反应将低碳醇乙醇转化为高碳醇. 乙醇 Guerbet 反应有直接缩合和间接缩合两种反应机理, Guerbet 直接缩合反应是通过活化乙醇 β 位 C—H 键, 与另一分子乙醇羟基脱水生成正丁醇; 间接缩合反应是通过乙醇脱氢成乙醛, 然后羟醛缩合成丁烯醛, 最后氢化为饱和醇^[52-53], 图 4 是乙醇间接缩合反应原理图.

生物航空煤油的制备过程中, 首先需要制取 C₈~16 醇. 然而, 实现长链高碳醇的高选择性和高选择性, 尤其是 C₈ 以上的醇类合成, 仍然是一个巨大的挑战^[55]. Guerbet 偶联反应可以提高 C₈+ 高级醇的产率, 促进二次改质以延长碳链, 对于该反应选择一种同时具有水热稳定性和碱性位点的催化剂是关键. 生物乙醇制备高碳醇的催化剂包括金属氧化物催化剂、羟基磷灰石(HAP)和负载型金属催化剂, 其中负载型金属催化剂对反应催化有较好的性能^[56], 表 3 是制备高碳醇所使用的催化剂比较结果. 负载型过渡金属催化剂如: Pb、Cu、Ni 基催化剂等, 可显著促进乙醇的偶联反应、和提高高碳醇的选择性, 通过调整酸碱性, 促进乙醇脱氢和乙醛的羟醛缩合^[57-59]. 对于非负载型催化剂, 反应条件相对严格, 而且高碳醇选择性不高, 即使温度升高, 提高高碳醇选择性的效果也十分有限, 而且可能导致大量气体副产物的生成. 因此, 为了改善催化效果和提升催化剂活性, 通常以过渡金属负载在载体上, 作为乙醇转化为高碳醇的催化剂.

3.1.2 水对 Guerbet 反应的影响

在乙醇的 Guerbet 缩合反应中, 副产物水的存

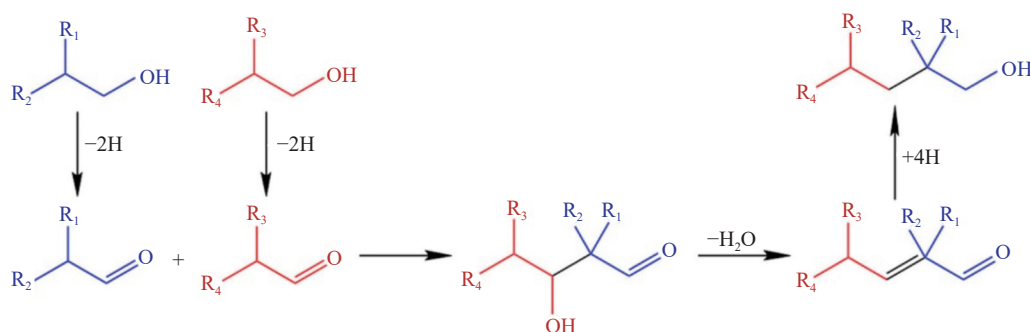


图 4 乙醇间接缩合反应原理图^[54]

Fig.4 Indirect condensation reaction of ethanol^[54]

表3 制备高碳醇催化剂的比较

Table 3 Comparison of catalysts for preparation of high-carbon alcohols

Catalyst type	Catalyst	Catalyst application characteristics	Reference
Unsupported catalyst	Hydroxyapatite	Various preparation methods of HAP (ultrasonic, microwave, and autoclave) can affect the catalytic activity of ethanol conversion. The number and strength of alkaline sites on the surface of hydroxyapatite are mainly affected by the use of ultrasonic waves and microwaves. In this catalytic system, the conversion rate and product selectivity can be adjusted by changing the surface distribution of acidic and alkaline sites, and the difference in Ca/P ratio on the surface of hydroxyapatite solids results in different catalytic activities of hydroxyapatite in ethanol conversion.	[60]
	Hydrotalcite	MgO mixed oxide exhibits higher catalytic activity than a single MgO catalyst. MgO only has a strong basic site and cannot generate n-butanol and C ₄₊ products, resulting in extremely low activity for ethanol dehydrogenation. Lewis acidic sites are required to stabilize acetaldehyde intermediates generated during the reaction. The adjacent Lewis acid–base sites on Mg–Al mixed oxide catalysts can facilitate the synthesis of C ₄₊ compounds.	[61–62]
	CaC ₂	Calcium carbide (CaC ₂) exhibits remarkable catalytic activity in the formation of C ₄ –C ₉ alcohols via ethanol condensation at 275–300 °C. The alkyne group in CaC ₂ is important in the catalytic pathway and has a strong hydrogen-absorption capacity.	[63]
Supported catalyst	Single-metal-supported catalyst	Ni-, Cu-, Ag-, and Pd-based catalysts, i.e., single-metal-supported catalysts, can decrease the reaction temperature and increase the selectivity for high-carbon alcohols owing to their dehydrogenation performance and adjustable distribution of active sites. Metals are responsible for ethanol dehydrogenation and hydrogenation of unsaturated aldehydes, while the adjacent Lewis acid–base provides the active center for acetaldehyde condensation and subsequent dehydration.	[56, 64]
	Multimetal-supported catalyst	The introduction of Ni–Co bimetallic catalysts, Sn–Ni/CS catalysts, and other polymetallic catalysts considerably increased the dehydrogenation efficiency of ethanol, although some limitations were observed in the catalytic process. An increase in metal loading can enhance the conversion of ethanol, but it is also accompanied by the formation of a large number of by-products, such as gas and alkane. In contrast, decreasing the loading is beneficial to increasing the selectivity for high-carbon alcohols, but this may affect the conversion rate.	[65]

在会对反应的进行造成阻碍. 此外, 水还会对催化剂表面的酸碱位点产生影响, 导致催化剂的催化性能降低^[54, 66]. Hanspal 等^[67]通过乙醇 Guerbet 缩合反应进行研究, 当进料加入水后对丁醇的产生有明显的抑制作用; 而从反应器的进料中去除水后, 丁醇和乙醛的产生速率恢复到原始稳态值的 70% 以上, 表明水与催化剂 HAP 表面之间存在可逆的相互作用. 水的存在改变了丁醇形成的平衡, 竞争性吸附在催化活性位点上. 水与 HAP 表面上的磷酸根基团的相互作用以及水对丁醇形成的抑制作用表明, 磷酸根基团可能影响到 C—C 键形成的活性位点.

生物乙醇通常以水溶液形式存在, 所以在水中直接转化生物醇将具有很大优势^[68–69]. Liao 等^[70]通过集成生物乙醇碳碳偶联和重质醇加氢脱氧催化工艺, 制备了生物航空煤油碳氢化合物. 以 Na/Ni@C 为催化剂, 在水溶液中直接完成了生物乙醇的碳碳偶联反应, C₈ ~ C₁₆ 产物的选择性达到 67.1%. 刘文平^[71]制备了非贵金属 Sn 改性的 Ni 基催化剂, 在 250 °C 的水相环境下, Ni 和 Sn 的摩尔比为 20 的 NiSnH 催化剂催化乙醇水相碳碳偶联反应生成混合高碳醇, C₄₊ 高碳醇在液相产物中选择性高达 91.6%. 生物乙醇碳碳偶联反应中, 具有良好耐水性的催化剂能够在水存在的环境下保持其活性和

选择性, 有效地抑制水分子的干扰, 从而提高催化反应的效率和稳定性.

3.2 高碳醇加氢脱氧反应

与生物乙醇相比, 高碳醇具有更高的十六烷值、更高的能量密度、更好的共混稳定性和压缩点火质量等, 这归因于高碳醇分子的碳链更长, 高碳醇无论物理性质还是燃烧性能都与运输燃料更相容, 更适合作为航空燃料使用, 能够提供更高的航程和能量输出^[72–74]. 高碳醇可以通过加氢脱氧反应得到烃类航空煤油, 加氢脱氧反应的关键是选择性地断裂多元醇中的 C—O 键并避免 C—C 键断裂^[75]. 贵金属和钼基催化剂因其出色的加氢脱氧 (HDO) 活性而备受关注.

其中 Mo₂C 表面具有高的氧结合能, 在高碳醇加氢脱氧反应中有良好的催化性能, 并具有水稳定性和抗焦炭性能. 此外, 金属和 Mo₂C 之间的强金属和负载相互作用也可以调节加氢活性和特定选择性^[76–77], 用过渡金属对 Mo₂C 表面进行部分修饰可以产生不同的活性位点来控制 HDO 反应途径, 即选择性 C—O 键断裂, 但 Ru、Pt、Pd 在高碳醇的加氢脱氧反应中具有较强的 C—C 键断裂活性, 不利于高碳烃的生成.

钟全旺^[78]对 2-乙基-1-己醇进行加氢脱氧反应, 使用引入过渡金属 Co 的 Mo₂C 催化剂, 与未掺

杂的 Mo_2C 相比, 添加质量分数为 2% 的 Co 后, 虽然转化率降至 80.9%, 但 3-甲基庚烷的选择性提高至 94.3%。如图 5 所示, X_{CSR} 代表碳骨架保留能力, 选取了不同分子结构类型的典型高碳醇作为原料进行加氢脱氧实验, 碳骨架保留率超过了 87%, 因此上述实验结果表明, 掺杂了质量分数为 2% 的 Co 的 Mo_2C (2%Co- Mo_2C) 对不同碳链分子构型

的高碳醇都具有良好的加氢脱氧活性和碳骨架保留能力。加氢脱氧反应的催化剂对于高碳醇转化至烃类是非常重要的, 在工艺中可以维持高碳醇的支化碳骨架, 并且能够实现选择性地断裂 C—O 键。研究和发高效的加氢脱氧催化剂可以推动高碳醇向烃类的转化, 并为替代航空燃料的开发提供重要支持。

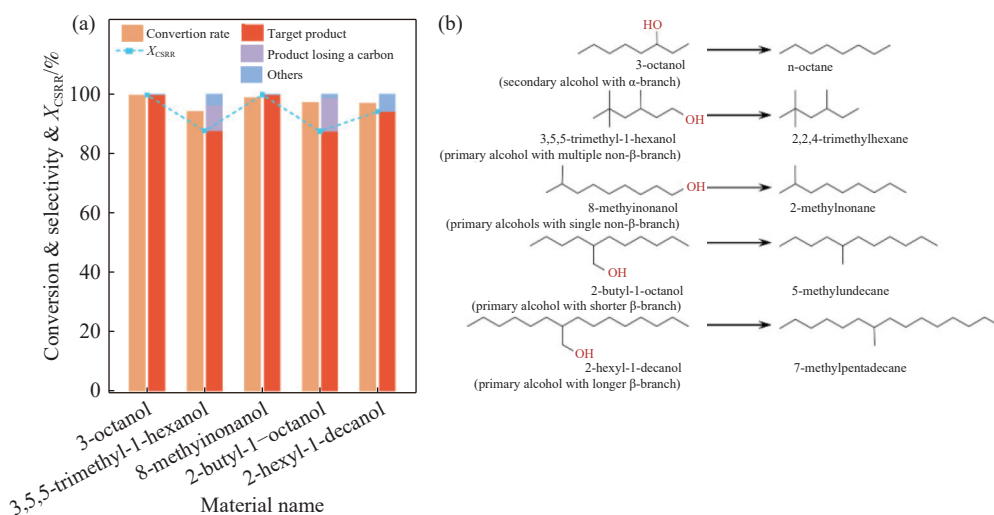


图 5 不同碳链骨架的单组分高碳醇在 2%Co- Mo_2C 上的催化性能。(a) 不同分子构型的高碳醇在 2%Co- Mo_2C 催化剂上的加氢脱氧反应活性;(b) 碳骨架保留的加氢脱氧反应示意图^[78]

Fig.5 Catalytic performance of one-component high-carbon alcohols with different carbon chain frameworks on 2%Co- Mo_2C : (a) hydrodeoxygenation activity of high-carbon alcohols with various molecular configurations on 2%Co- Mo_2C catalyst; (b) hydrodeoxygenation reaction with carbon skeleton retention^[78]

4 结语

本文介绍了以生物乙醇为原料制备航空煤油的两种工艺技术, 乙醇制备航空煤油(ATJ)技术和高碳醇加氢脱氧工艺技术。可持续航空燃料现在已经成为航空业减少碳排放、减少航空业整体环境影响的重要措施, 尽管替代航空生物燃料的需求正在迅速增长, 但在替代化石航空燃料之前, 仍有许多挑战需要克服, 根据本文的综述内容, 提出几点建议与展望。

(1) 当前研究重点在于将生物质转化为生物航空煤油, 以生产可再生的航空煤油。关注的重点主要包括可再生资源的利用、温室气体排放的降低、可持续性以及成本的可承受性。生物航油制备成本高昂, 如何降低其成本、解决制备难题, 并提高其经济性仍然是研究的重点, 尤其是通过生物乙醇制备生物航空煤油的工艺流程, 虽然生产的航空煤油已经用于商业飞行, 但成本较高且大规模生产还有一定的困难。

(2) ATJ 工艺分离过程中每个步骤的产物使得

该过程非常复杂和昂贵, 还存在产品异构体比例难以控制、工艺流程长、转化效率低等缺点。醇到航空煤油的工艺流程复杂, 需要三种不同的催化剂, 需要我们开发出一种既能催化脱水反应又能催化低聚加氢反应的催化剂, 探索新型催化剂结构和生物质预处理方式来提高产率。

(3) 生物乙醇发酵液中含有大量的水分, 直接对含水乙醇进行提质可以简化昂贵的分离过程。催化生物乙醇升级为高碳醇越来越受到广泛关注, 研究一种兼具脱氢、氢化以及羟醛缩合作用的多功能非贵金属催化剂, 在保持优异脱氢能力的同时, 减弱对 C—C 键的断裂能力, 增强催化剂自身促进羟醛缩合的能力, 从而提高高碳醇的选择性, 这对未来产业化生产高碳醇有十分重要的意义。

参 考 文 献

- [1] Wang C Z, Zhao T L. Discussion on the development of rotary equipment in petrochemical industry under the dual carbon Strategy. *Compress Technol*, 2023(6): 1

(王存智, 赵天雷. 双碳战略下的石化行业转动设备发展探讨.

- 压缩机技术, 2023(6): 1)
- [2] Han W, Han H W, Cheng W, et al. Research progress of biomass fuels technology driven by carbon neutrality. *Chem Ind Eng Prog*, 2024, 43(5): 2463
(韩伟, 韩恒文, 程薇, 等. 碳中和目标驱动下生物质燃料技术研究进展. *化工进展*, 2024, 43(5): 2463)
- [3] Zhou J D, Zhang K. Development status and countermeasures of bio-aviation kerosene. *Chem Eng Equip*, 2023(10): 175
(周建东, 张凯. 生物航空煤油发展现状及对策. *化学工程与装备*, 2023(10): 175)
- [4] Chen J H, Wang F F, Zhang N L, et al. Preparation and application of bio-jet fuel. *Energy Res Util*, 2021(4): 21
(陈佳慧, 王斐斐, 张乃丽, 等. 生物航油的制备与应用发展前景. *能源研究与利用*, 2021(4): 21)
- [5] Li X T, Wang S L, Li H, et al. Prospects for bio-jet fuel under dual-carbon policy. *Green Petrol Petrochem*, 2022, 7(3): 6
(李晓彤, 王树雷, 李辉, 等. 双碳政策下生物喷气燃料的发展展望. *石油石化绿色低碳*, 2022, 7(3): 6)
- [6] Guo H, Han L, Zhang C K, et al. Research on the hydrothermal conversion of cellulose catalyzed by homogeneous acid. *Energy Eng*, 2022, 42(6): 22
(郭会, 韩龙, 张诚琨, 等. 均相酸催化纤维素水热转化制备乙酰丙酸研究. *能源工程*, 2022, 42(6): 22)
- [7] Yu Y M, Fang M X, Tian J L, et al. Influence of catalyst on rice husks steam gasification. *Energy Eng*, 2021(4): 8
(余一鸣, 方梦祥, 田江磊, 等. 催化剂对稻壳水蒸气气化特性和焦油转化的影响. *能源工程*, 2021(4): 8)
- [8] Liu Q, Qiu J X, Peng F, et al. Research progress of biological aviation kerosene. *Recycl Resour Circ Econ*, 2018, 11(5): 20
(刘强, 邱敬贤, 彭芬, 等. 生物航空煤油的研究进展. *再生资源与循环经济*, 2018, 11(5): 20)
- [9] Akdeniz H Y, Balli O, Caliskan H. Energy, exergy, thermoecologic, environmental, enviroeconomic and sustainability analyses and assessments of the aircraft engine fueled with biofuel and jet fuel. *J Therm Anal Calorim*, 2023, 148(9): 3585
- [10] Peters M A, Alves C T, Onwudili J A. A review of current and emerging production technologies for biomass-derived sustainable aviation fuels. *Energies*, 2023, 16(16): 6100
- [11] Liu W Z. *Life Cycle Evaluation and Economic Analysis of Aviation Kerosene Produced by Fischer-Tropsch Synthesis of Biomass Gasification* [Dissertation]. Wuhan: Huazhong University of Science and Technology, 2018
(刘文质. 生物质气化费托合成生产航空煤油的生命周期评价及经济性分析[学位论文]. 武汉: 华中科技大学, 2018)
- [12] Wei H J, Liu W Z, Chen X Y, et al. Renewable bio-jet fuel production for aviation: A review. *Fuel*, 2019, 254: 115599
- [13] Ahmed M, Alam M N, Abdullah A, et al. Bio-jet fuel: An overview of various feedstock and production routes // *Advances in Fracture and Damage Mechanics XX*. Malaga, 2023: 030007
- [14] Wang W C, Tao L. Bio-jet fuel conversion technologies. *Renew Sustain Energy Rev*, 2016, 53: 801
- [15] Contreras-Zarazúa G, Sánchez-Ramírez E, Hernández-Vargas E A, et al. Process intensification in bio-jet fuel production: Design and control of a catalytic reactive distillation column for oligomerization. *Chem Eng Process Intensif*, 2023, 193: 109548
- [16] Díaz-Pérez M A, Serrano-Ruiz J C. Catalytic production of jet fuels from biomass. *Molecules*, 2020, 25(4): 802
- [17] Sur S, Dave V, Prakesh A, et al. Expansion and scale up of technology for ethanol production based on the concept of biorefinery. *J Food Process Eng*, 2021, 44(2): e13582
- [18] Verma D, Paul J S, Tiwari S, et al. A review on role of nanomaterials in bioconversion of sustainable fuel bioethanol. *Waste Biomass Valorization*, 2022, 13(12): 4651
- [19] Wu B, Wang Y W, Dai Y H, et al. Current status and future prospective of bio-ethanol industry in China. *Renew Sustain Energy Rev*, 2021, 145: 111079
- [20] Manochio C, Andrade B R, Rodriguez R P, et al. Ethanol from biomass: A comparative overview. *Renew Sustain Energy Rev*, 2017, 80: 743
- [21] Phillips S D, Jones S B, Meyer P A, et al. Techno-economic analysis of cellulosic ethanol conversion to fuel and chemicals. *Biofuels Bioprod Bioref*, 2022, 16(3): 640
- [22] Romero-Izquierdo A G, Gómez-Castro F I, Gutiérrez-Antonio C, et al. Intensification of the alcohol-to-jet process to produce renewable aviation fuel. *Chem Eng Process Intensif*, 2021, 160: 108270
- [23] Park H, Chae H J, Suh Y W, et al. Techno-economic analysis and CO₂ emissions of the bioethanol-to-jet fuel process. *ACS Sustainable Chem Eng*, 2022, 10(36): 12016
- [24] Cheng Y W, Chong C C, Cheng C K, et al. Ethylene production from ethanol dehydration over mesoporous SBA-15 catalyst derived from palm oil clinker waste. *J Clean Prod*, 2020, 249: 119323
- [25] Krutpjit C, Tochaeng P, Jongsonjit B. Temperature and ethanol concentration effects on catalytic ethanol dehydration behaviors over alumina-spherical silica particle composite catalysts. *Catal Commun*, 2020, 145: 106102
- [26] Zhu Y. Dehydration of low concentration to ethylene over 4A zeolite catalyst. *Chem Eng Oil Gas*, 2009, 38(6): 487
(祝阳. 4A 分子筛催化稀乙醇制备乙烯. *石油与天然气化工*, 2009, 38(6): 487)
- [27] Wang J, Zhong S Q, Zhang C F, et al. Process of dehydration of ethanol to bioethylene. *Chem Eng*, 2015, 43(11): 72
(王菊, 钟思青, 张成芳, 等. 乙醇脱水制生物基乙烯工艺研究. *化学工程*, 2015, 43(11): 72)
- [28] Phung T K, Busca G. Diethyl ether cracking and ethanol dehydration: Acid catalysis and reaction paths. *Chem Eng J*, 2015, 272: 92
- [29] Lv J G, Wang D, Peng L M, et al. Ethanol dehydration to ethylene over high-energy facets exposed gamma alumina. *Catalysts*, 2023, 13(6): 994
- [30] Liang N. *Study on Preparation and Application of Catalyst for*

- Ethanol to Ethylene* [Dissertation]. Nanning: Guangxi University, 2018
(梁娜. 乙醇制乙烯催化剂制备与应用研究[学位论文]. 南宁: 广西大学, 2018)
- [31] Wu Z Y, Zhang J, Su Z, et al. Low-temperature dehydration of ethanol to ethylene over Cu-zeolite catalysts synthesized from Cu-tetraethylenepentamine. *Ind Eng Chem Res*, 2020, 59(39): 17300
- [32] Trongjitraksa P, Klinthongchai Y, Praserttham P, et al. Elucidation on supporting effect of WO₃ over MCF-Si and SBA-15 catalysts toward ethanol dehydration. *J Inst Chem Eng*, 2023, 152: 105168
- [33] Tresatayawed A, Glinrun P, Autthanit C, et al. Pd modification and supporting effects on catalytic dehydration of ethanol to ethylene and diethyl ether over W/TiO₂ catalysts. *J Oleo Sci*, 2020, 69(5): 503
- [34] Saini S, Verma A, Sharma B, et al. Ni and Sr modified ZSM-5 catalyst with enhanced catalytic activity for selective dehydration of bio-derived ethanol to ethylene. *Mol Catal*, 2023, 551: 113587
- [35] Peinado C, Campos-Martin J M, Rojas S. Phosphotungstic acid catalysed bioethylene synthesis under industrially relevant conditions. *React Chem Eng*, 2023, 8(4): 815
- [36] Ouayloul L, Agirrezabal-Telleria I, Arias P L, et al. Tuning the acid nature of the ZSM-5 surface for selective production of ethylene from ethanol at low temperatures. *Energy Fuels*, 2024, 38(5): 4492
- [37] Zhan N N, Hu Y, Li H, et al. Lanthanum-phosphorous modified HZSM-5 catalysts in dehydration of ethanol to ethylene: A comparative analysis. *Catal Commun*, 2010, 11(7): 633
- [38] Liu Y K. *Study on Preparation and Performance of Catalyst for Dehydration of Bioethanol to Ethylene* [Dissertation]. Beijing: China University of Petroleum (Beijing), 2020
(刘亿魁. 生物乙醇脱水制乙烯催化剂的制备与性能研究[学位论文]. 北京: 中国石油大学(北京), 2020)
- [39] Zhang M H, Yu Y Z. Dehydration of ethanol to ethylene. *Ind Eng Chem Res*, 2013, 52(28): 9505
- [40] Nie X W, Yang W C, Guo X W. A computational chemistry experiment on the reaction mechanisms of intra-and intermolecular ethanol dehydration. *Univ Chem*, 2023, 38(9): 179
(聂小娃, 杨文超, 郭新闻. 乙醇分子内及分子间脱水反应机理的计算化学实验研究. 大学化学, 2023, 38(9): 179)
- [41] Attanatho L, Lao-ubol S, Suemanotham A, et al. Jet fuel range hydrocarbon synthesis through ethylene oligomerization over platelet Ni-AISBA-15 catalyst. *SN Appl Sci*, 2020, 2(5): 971
- [42] Li D. *Construction of Nickel Catalysts Supported on Schiff-base Covalent Organic Frameworks and its Catalytic Performance for Ethylene Oligomerization* [Dissertation]. Daqing: Northeast Petroleum University, 2023
(李丹. Schiff 碱基 COFs 负载镍催化剂的构筑及催化乙烯齐聚性能研究[学位论文]. 大庆: 东北石油大学, 2023)
- [43] Lu Q, Xiao L J, Liu G G, et al. Research progress of olefin oligomerization catalyst. *Contemp Chem Ind*, 2020, 49(11): 2602
(卢琪, 肖林久, 刘蝓蝓, 等. 烯烃齐聚催化剂的研究进展. 当代化工, 2020, 49(11): 2602)
- [44] Bekmukhamedov G E, Sukhov A V, Kuchkaev A M, et al. Ni-based complexes in selective ethylene oligomerization processes. *Catalysts*, 2020, 10(5): 498
- [45] Panpian P, Tran T T V, Kongparakul S, et al. Production of bio-jet fuel through ethylene oligomerization using NiAlKIT-6 as a highly efficient catalyst. *Fuel*, 2021, 287: 119831
- [46] Mohamed H O, Parsapur R K, Hita I, et al. Stable and reusable hierarchical ZSM-5 zeolite with superior performance for olefin oligomerization when partially coked. *Appl Catal B Environ*, 2022, 316: 121582
- [47] Mohamed H O, Abed O, Zambrano N, et al. A zeolite-based cascade system to produce jet fuel from ethylene oligomerization. *Ind Eng Chem Res*, 2022, 61(43): 15880
- [48] Jin F, Zhang P, Wu G Y. Fundamental kinetics model of acidity-activity relation for ethylene oligomerization and aromatization over ZSM-5 zeolites. *Chem Eng Sci*, 2021, 229: 116144
- [49] Neuling U, Kaltschmitt M. Techno-economic and environmental analysis of aviation biofuels. *Fuel Process Technol*, 2018, 171: 54
- [50] Atsonios K, Kougioumtzis M A, Panopoulos K D, et al. Alternative thermochemical routes for aviation biofuels via alcohols synthesis: Process modeling, techno-economic assessment and comparison. *Appl Energy*, 2015, 138: 346
- [51] Villareal-Hernández A C, Ramírez-Mendiola M D, Quiroz-Ramírez J J, et al. Intensification of the oligomerization and hydrogenation stage for biojet fuel production: Preliminary outlines. *Ind Eng Chem Res*, 2023, 62(22): 8820
- [52] Li S Q. *Study on the Catalytic Performance of Ni-Cu/TiO₂ for Guerbet Reaction of Ethanol* [Dissertation]. Tianjin: Hebei University of Technology, 2021
(李帅琦. Ni-Cu/TiO₂ 催化乙醇 Guerbet 反应性能研究[学位论文]. 天津: 河北工业大学, 2021)
- [53] Li S Q, Zhu X H, An H L, et al. Ethanol guerbet condensation to n-butanol or C₄-C₈ alcohols over Ni/TiO₂ catalyst. *ChemistrySelect*, 2020, 5(28): 8669
- [54] Cui Y Y, Li S Q, An H L, et al. Improvement of ethanol guerbet condensation by acetal hydrolysis. *Ind Eng Chem Res*, 2022, 61(34): 12392
- [55] Liao J W, Liu Z H, Ling Y J, et al. Electronic and surface engineering of Mo doped Ni@C nanocomposite boosting catalytic upgrading of aqueous bio-ethanol to bio-jet fuel precursors. *Chem Eng J*, 2023, 461: 141888
- [56] Wang W W, Lu Y Y, Li Z Y, et al. Research progress in catalysts for producing higher alcohols from bioethanol. *J Fuel Chem*: 2024, 52(4): 461
(王文文, 逯焯焯, 李治宇, 等. 生物乙醇制高级醇催化剂研究进展[J]. 燃料化学学报(中英文), 2024, 52(4): 461)
- [57] Yuan B W, Zhang J, An Z, et al. Atomic Ru catalysis for ethanol coupling to C⁴⁺ alcohols. *Appl Catal B Environ*, 2022, 309: 121271
- [58] Cuello-Penalosa P A, Dastidar R G, Wang S C, et al. Ethanol to

- distillate-range molecules using Cu/Mg_xAlO_y catalysts with low Cu loadings. *Appl Catal B Environ*, 2022, 304: 120984
- [59] Nezam I, Zak J, Miller D J. Condensed-phase ethanol conversion to higher alcohols over bimetallic catalysts. *Ind Eng Chem Res*, 2020, 59(31): 13906
- [60] Brasil H, Bittencourt A F B, Yokoo K C E S, et al. Synthesis modification of hydroxyapatite surface for ethanol conversion: The role of the acidic/basic sites ratio. *J Catal*, 2021, 404: 802
- [61] Ramasamy K K, Gray M, Job H, et al. Tunable catalytic properties of bi-functional mixed oxides in ethanol conversion to high value compounds. *Catal Today*, 2016, 269: 82
- [62] Benito P, Vaccari A, Antonetti C, et al. Tunable copper-hydroxalite derived mixed oxides for sustainable ethanol condensation to *n*-butanol in liquid phase. *J Clean Prod*, 2019, 209: 1614
- [63] Wang D, Liu Z Y, Liu Q Y. Efficient conversion of ethanol to 1-butanol and C₅-C₉ alcohols over calcium carbide. *RSC Adv*, 2019, 9(33): 18941
- [64] Xue M C, Yang B L, Xia C G, et al. Progress in heterogeneous catalyst for ethanol upgrading to higher (C₆₊) alcohols. *Chem Ind Prog*, 2023, 42(1): 194
(薛马晨, 杨伯伦, 夏春谷, 等. 乙醇缩合制高碳醇(C₆₊醇)多相催化剂研究进展. *化工进展*, 2023, 42(1): 194)
- [65] Chen B, Zheng X Q, Gu J W, et al. Engineering Sn doping Ni/chitosan to boost higher alcohols synthesis from direct coupling of aqueous ethanol: Modifying adsorption of aldehyde intermediates for C—C bond cleavage suppressing. *Appl Catal B Environ*, 2023, 321: 122048
- [66] Han X X, Li S Q, An H L, et al. Improvement of *n*-butanol Guerbet condensation: A reaction integration of *n*-butanol Guerbet condensation and 1, 1-dibutoxybutane hydrolysis. *React Chem Eng*, 2021, 6(10): 1845
- [67] Hanspal S, Young Z D, Prillaman J T, et al. Influence of surface acid and base sites on the Guerbet coupling of ethanol to butanol over metal phosphate catalysts. *J Catal*, 2017, 352: 182
- [68] Xu G Q, Lammens T, Liu Q, et al. Direct self-condensation of bio-alcohols in the aqueous phase. *Green Chem*, 2014, 16(8): 3971
- [69] Xie S Q, Li Z X, Luo S J, et al. Bioethanol to jet fuel: Current status, challenges, and perspectives. *Renew Sustain Energy Rev*, 2024, 192: 114240
- [70] Liao J W, Zhong Q W, Gu J W, et al. New approach for bio-jet fuels production by hydrodeoxygenation of higher alcohols derived from C—C coupling of bio-ethanol. *Appl Energy*, 2022, 324: 119843
- [71] Liu W P. *Aqueous C—C Coupling of Bio-ethanol to Higher Alcohol Fuel Chemicals* [Dissertation]. Guangzhou: Guangdong University of Technology, 2021
(刘文平. 水相催化生物乙醇 C—C 偶联合成高级醇燃料化学品研究[学位论文]. 广州: 广东工业大学, 2022)
- [72] Yesilyurt M K. A detailed investigation on the performance, combustion, and exhaust emission characteristics of a diesel engine running on the blend of diesel fuel, biodiesel and 1-heptanol (C7 alcohol) as a next-generation higher alcohol. *Fuel*, 2020, 275: 117893
- [73] Jung J K, Lee Y S, Choi J W, et al. Production of high-energy-density fuels by catalytic β -pinene dimerization: Effects of the catalyst surface acidity and pore width on selective dimer production. *Energy Convers Manag*, 2016, 116: 72
- [74] Fei X, Xu Q Z, Xue L J, et al. Aqueous phase catalytic conversion of ethanol to higher alcohols over NiSn bimetallic catalysts encapsulated in nitrogen-doped biorefinery lignin-based carbon. *Ind Eng Chem Res*, 2021, 60(49): 17959
- [75] Wan W M, Ammal S C, Lin Z X, et al. Controlling reaction pathways of selective C—O bond cleavage of glycerol. *Nat Commun*, 2018, 9(1): 4612
- [76] Chen X, Zheng Y N, Zhang Q, et al. Controlling transformation of sorbitol into 1-hexanol over Ru-MoO₃/Mo₂C catalyst via aqueous-phase hydrodeoxygenation. *ACS Sustainable Chem Eng*, 2021, 9(27): 9033
- [77] He L L, Qin Y, Lou H, et al. Highly dispersed molybdenum carbide nanoparticles supported on activated carbon as an efficient catalyst for the hydrodeoxygenation of vanillin. *RSC Adv*, 2015, 5(54): 43141
- [78] Zhong Q W. *Preparation of Bio-aviation Fuel by Selective Hydrogenation of C—O Bond from High-carbon Alcohols Derived from Bioethanol* [Dissertation]. Guangzhou: Guangdong University of Technology, 2022
(钟全旺. 生物乙醇衍生高碳醇选择性氢解 C—O 键制备生物航空燃料[学位论文]. 广州: 广东工业大学, 2023)