2018 年度陈嘉庚科学奖专辑

陈嘉庚青年科学奖——化学科学奖获奖人

黄正

1979 年生于浙江东阳, 2001 年和 2004 年获南开大学化学系学士和硕士学位, 2009 年获北卡罗莱纳大学化学博士学位, 2011 年入选中组部“青年千人计划”, 现任中国科学院上海有机化学研究所研究员, 从事金属有机化学和催化研究.

相关成果名称: 过渡金属催化的烷烃转化

烷烃是由碳与氢原子构成的饱和烃类化合物, 是最简单的有机化合物. 作为石油和天然气的主要成分, 烷烃价廉量大, 然而其在现代合成化学中的应用价值十分有限(通常仅作为溶剂被使用). 烷烃由高键能、低极性碳碳单键和碳氢键组成, 化学转化往往具有反应苛刻、产率低、区域选择性难以控制等特点. 因此, 将烷烃通过温和、简洁和绿色的方式转化为高值化学品具有重要的理论意义和实用价值, 但同时富有挑战性. 黄正课题组针对烷烃惰性化学键选择性活化内在本质规律, 发展了一系列高效的金属有机烷烃脱氢催化剂, 并利用双金属串联催化策略, 实现了烷烃至直链烷基硅、直链醛、直链胺等高值化学品的高效、高选择性转化; 采用交叉烷烃复分解催化策略, 利用低碳烷烃作为试剂和溶剂, 首次实现了各类聚乙烯在较温和条件下(175℃)选择性降解生成清洁柴油或高品质聚乙烯蜡, 该催化体系进一步被证实适用于日常生活所产生的聚乙烯废塑料可控降解. 这些工作推动了金属有机催化学科与能源和环境领域的交叉与融合, 丰富和促进了饱和烃类资源的高值化利用.

过渡金属分子催化的烷烃转化进展

汤铨铨, 黄正*

中国科学院上海有机化学研究所, 分子合成科学卓越创新中心, 金属有机化学国家重点实验室, 上海 200032

* 联系人, E-mail: huangzh@sioc.ac.cn

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摘要 烷烃价廉量大, 发展催化方法将其转化成高附加值的化学品具有重大的意义. 然而简单烷烃分子中无导向或活化基团, 仅含低极性、高键能 $C(sp^3)-H$ 键和 $C(sp^3)-C(sp^3)$ 键, 因此对烷烃分子化学键的活化, 尤其是众多类似化学键中某一特定化学键的选择性转化具有高度挑战性. 本文主要介绍金属配合物分子催化的烷烃脱氢反应, 以及基于该类反应发展起来的相关的烷烃转化, 包括: (1) 螯型过渡金属配合物催化的烷烃脱氢反应; (2) 基于烷烃脱氢的烷烃芳构化和烷/烯烃偶合反应和烷烃端位 $C-H$ 键官能团化反应; (3) 烷烃(交叉)复分解和基于烷烃交叉复分解的聚乙烯温和可控降解反应.

关键词 烷烃脱氢, 双金属催化, 螯型铈配合物, 烷烃端位官能团化, 聚乙烯降解

烷烃是由碳和氢原子组成的饱和烃类化合物, 作为石油和天然气等石化资源的主要成分, 目前主要作为燃料使用, 在合成化学上利用率极低. 近年来随着大量页岩气的发现, 烷烃的高值利用也越来越受到化学家的关注. 烷烃分子中仅含低极性、高键能的惰性 $C(sp^3)-H$ 键和 $C(sp^3)-C(sp^3)$ 键, 其活化存在困难^[1-5]. 另外, 烷烃分子中各级 $C-H$ 键的键解离能差别小, 如何区域选择性对某一特定 $C-H$ 键进行官能团化是另一个挑战. 目前一些非均相催化饱和烃转化过程在工业上已经得到广泛应用, 但整体而言非均相催化体系存在能耗高、产物选择性低等局限. 因此, 发展反应条件温和、选择性高的均相金属催化体系, 将价廉量大烷烃资源转化成高附加值的化学品具有重大科学意义和应用价值.

1 热条件下过渡金属分子催化的烷烃脱氢反应

烷烃是化学工业中重要的合成原料和中间体.

将烷烃通过脱氢方式直接转化为烯烃是清洁、原子经济性高的化学转化. 目前工业上一般使用非均相催化体系将饱和烃转化为烯烃, 但反应条件苛刻, 产物选择性差^[6-9]. 在过去数十年来, 均相过渡金属分子催化的烷烃脱氢反应取得了较大的进展. 该类反应按照反应条件可分为光照体系下烷烃脱氢反应^[10-13]和热条件下的烷烃脱氢反应. 而以螯型(pincer)铈配合物催化反应为代表的热条件下的烷烃脱氢反应得到金属有机化学家极大的关注, 大大促进了该领域的进步^[14-16]. 由于篇幅限制, 本文将集中于热条件下的分子催化烷烃脱氢反应.

均相烷烃脱氢具体是指饱和直链或者环烷烃在添加或者不添加氢气接受体的情况下, 经分子催化剂作用失去2个氢原子(无氢气接受体条件下失去1分子氢气)的过程(图1). 约40年前, Crabtree课题组^[10,17]和Felkin课题组^[18,19]首次报道了铈和铱分子催化的烷烃脱氢反应, 反应需要使用当量的氢气接受体以克服烷烃脱氢本身热力学不利的因素. Crabtree

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图1 烷烃脱氢催化剂

Figure 1 Alkane dehydrogenation catalysts

课题组^[17]发现无双键异构能力的叔丁基乙烯(TBE)是理想的氢气接受体. 由于催化剂热稳定差, 造成催化转化数(TON)低. 随后化学家通过设计热稳定性更好的脱氢催化剂来提高该反应的效率. 1996年, 基于早期Shaw课题组^[20,21]在螯型配合物方面的工作, Jensen课题组和Kaska课题组^[22]合作合成了螯型铱催化剂**1a**, 该催化剂结构中双磷原子以及芳环上的 sp^2 碳原子与金属铱中心配位(PCP), 形成的螯型结构大大提高了催化剂的热稳定性, 在使用TBE为氢气接受体或者无氢气接受体情况下^[23], 均表现出高活性, 对环辛烷(以TBE为氢气接受体)和环十烷脱氢(无氢气接受体)反应TON值分别达到1000和360. 随后, 该类PCP骨架的铱催化剂引起金属有机化学家的高度兴趣, 通过设计各种类型的螯型过渡金属配合物, 以期进一步提高该类骨架催化剂的热稳定性以及脱氢活性. 从文献报道来看, 目前PCP骨架主要的改造方式包含磷原子上取代基的修饰^[24-30]、苯环与磷中间的桥联原子的优化^[31-35]以及芳环骨架的改变(图1(a))^[36-39]. Goldman课题组^[24]将催化剂**1a**的磷上叔丁

基改为位阻更小的异丙基, 合成的催化剂**1b**被证明具有更高的烷烃脱氢活性, 如, 该催化剂对于环十烷的无氢气接受体的脱氢, TON可以达到1000. 桥联原子的改变对于催化剂性能的改变尤为显著, 如将催化剂**1a**中的桥联原子由碳原子改变成氧原子, 得到的POCOP类型的催化剂**2**与经典的PCP骨架催化剂**1a**相比在环辛烷的转移脱氢反应中TON值提高了1个数量级^[31,32]. 基于桥联原子的关键作用, 本课题组^[34,40]在螯型配体中引入原子半径相对较大的硫原子, 同时降低磷上的位阻, 由叔丁基改变为异丙基, 合成了PSCOP类型的催化剂**3**. 催化剂**3**对于烷烃脱氢展现出了极高的活性, 例如对于环辛烷与TBE的转移脱氢模板反应, 其催化转化数高达6000, 这是迄今针对环烷烃转移脱氢的最高TON值. 另外, 在反应前60 min内, 催化剂**3**在100℃下对正辛烷的脱氢表现出较高的端位烯烃选择性^[34]. 最后一类pincer铱催化剂是基于芳环骨架改造的配合物. 例如基于蒽骨架的PCP铱催化剂**4**和基于7-6-7环骨架的催化剂**5**, 它们都具有非常高的热稳定性和催化活性^[36,38], 其中

Broolhart课题组^[39]基于三磷烯骨架的PCP铱催化剂**6**,在直链烷烃的转移脱氢反应中表现出极高的催化活性,TON值高达6000.

除了经典的PCP配位的螯型铱催化剂,近年来化学家也发展了许多非PCP配位模式的螯型铱催化剂.例如Braunstein课题组^[41]和Chianese课题组^[42]报道的卡宾结构的CCC配体,本课题组报道的吡啶磷配位的NCP配体^[43]和PNCP四齿配体^[44],Jensen课题组^[45]报道的将磷原子改变成砷原子的AsCAs配体,以及Yamashita课题组^[46]报道的PBP配体等(图1(b)).最近Goldberg课题组^[47,48]、Goldman课题组^[49]和William课题组^[50]报道了双噁唑啉配位的NCN配体,不同于之前报道的PCP体系一价铱介导的C-H键活化过程,这类NCN配位的铱配合物在C-H键活化这一步被证明为是由三价铱介导的.该类高价态铱催化剂不易被极性小分子,如水、氮气或生成的烯烃等抑制,因此在未来的应用范围上可能体现出一定优势.总的来说,非PCP骨架的配体形成的螯型铱配合物在烷烃脱氢反应中表现的活性大幅度低于经典的PCP骨架的配合物.

相较于报道较多的螯型铱配合物催化脱氢,其他金属应用于烷烃脱氢的例子报道相对较少(图1(c)),主要包括由Goldman课题组和Brookhart课题组^[51]报道的PNP配位的铑配合物**11**,Roddic课题组^[52,53]和本课题组^[54]报道的PCP配位的钨和钼配合物**12**和**13**,Vedernikov课题组^[55]报道的双吡啶配位的两性铂配合物**14**.最近,Mindiloo课题组^[56]采用PNP配位的廉价金属钛卡宾配合物**15**也实现了烷烃脱氢反应.该反应以磷叶立德作为氢气接受体,在温和的条件下(75℃)对直链和环烷烃进行脱氢,其中对于直链烷烃可高区域选择性得到端烯烃,但是反应的TON值非常低(小于5,图1(c)).尽管这些金属配合物的活性远低于铱催化剂,但拓展了人们对烷烃脱氢催化模式和机理的认识.

2 基于脱氢策略的烷烃转化

由于均相烷烃脱氢相比于非均相条件下具有反应条件相对温和,产物选择性好(无C-C键断裂副产物)等优点,因此为基于烷烃脱氢反应的进一步转化和官能团化提供了可能.目前,基于烷烃脱氢策略发展的烷烃转化反应主要有烷烃复分解(详见第3部分),烷烃芳构化,烷/烯烃偶合,和利用烷烃脱氢-烯烃异

构-端烯官能团化策略发展的烷烃端位C-H键(形式)官能团化反应(包括烷烃端位硅化、硼化、羰基化和甲胺化反应等).

2.1 烷烃芳构化和烷/烯烃偶合反应

烷基苯类化合物在有机合成以及化学工业中具有广泛的应用^[57].尽管可利用非均相催化剂实现烷烃至相应的烷基苯类化合物的转化,但反应所需的温度高,产率以及选择性均较差^[58-60].螯型铱分子催化剂的发展为均相条件下烷烃的脱氢芳构化反应提供了可能. Goldman课题组和Brookhart课题组^[61]发现,采用经典的PCP铱催化剂可以对长链烷烃实现多次转移脱氢反应,形成的共轭三烯中间体接着发生6 π 电环化反应,生成的产物在TBE存在下继续脱氢,形成芳香产物(图2(a)).随后, Brookhart课题组^[62,63]报道了另一种芳构化方法:以乙烯为氢气接受体,正戊烷脱除两分子的氢气,生成共轭戊二烯,其与另一分子乙烯发生Diels-Alder反应,环化后的产物在Pd/C催化下脱去二分子氢气生成甲苯(图2(a)).

低碳烷烃在自然界广泛存在,但由于其沸点低、能量密度小,无法作为大规模运输的能源,因此发展将低碳烷烃转化成分子量更大的烷烃具有重要的应用价值.基于Goldman等人^[64]和Brookhart课题组^[65]发展的双金属催化的烷烃复分解工作基础, Bercaw和Labinger课题组^[66]提出了烷烃和烯烃偶合的策略,具体过程涉及由螯合PCP铱配合物催化烷烃脱氢,所生成的烯烃中间体和另一分子烯烃原料在钼催化剂作用下发生烯烃二聚反应.值得注意的是这两个催化剂在同一反应条件下兼容,所以脱氢和二聚反应可在同一体系下进行. Bercaw等人^[66]发现在正己烷/正己烯偶合反应中相对于可以铱和钼可分别取得60和30的TON(图2(b)).

2.2 烷烃端位选择性(形式)硅化和硼化

烷烃分子中的一级、二级以及三级C-H键键能相差不大^[67],如何选择性在一级,即端位进行C-H键官能团化是一个难点.自由基机理^[68-70]和卡宾、氮宾插入过程^[71-74]实现的烷烃官能团主要发生在二级和三级C-H键上. Hartwig课题组^[75,76]报道了直链烷烃的端位硼化反应,是为数不多的在烷烃端位实现官能团化的例子.

近年来,采用串联双金属催化体系来实现烷烃

图2 烷烃的脱氢芳构化和烷/烯烃偶合反应

Figure 2 Dehydroaromatization of alkane and alkane-alkene coupling reaction

的端位官能团化逐渐被报道. 最新报道的是一类由本课题组^[77,78]发展的基于烷烃脱氢反应引发的官能团化反应. 其具体过程是直链烷烃首先在具有高活性的烷烃脱氢催化剂作用下实现烷烃脱氢, 在该过程中由于脱氢催化剂同时具有烯烃异构的活性, 因此不可避免会生成热力学更稳定的内烯烃混合物; 接着在不分离的条件下加入另一种同时具有烯烃异构以及对端烯选择性反马氏官能团化的催化剂, 来实现将内烯烃转化成端位官能团化产物, 从而在形式上实现直链烷烃的端位官能团化过程(图3). 后来报道的是另一类基于烷烃自由基卤化反应进而发生后续的官能团化的反应, 如Baudoin课题组^[79]报道的直链烷烃溴化异构芳基化反应, Martin课题组^[80]报道的直链烷烃溴化再发生异构羧基化反应. 本文主要介绍第一类烷烃脱氢-烯烃异构-烯烃官能团化的进展.

直链硅化合物在工业上具有重要的应用, 例如,

它可以应用于分离涂层、硅橡胶、航空润滑油和有机硅黏合剂等. 从价廉量广的烷烃制备直链硅化合物具有潜在应用价值. 本课题组设计了烷烃脱氢, 烯烃异构再硅氢化的策略, 实现了首例直链烷烃端位选择性硅化^[77,81]. 为实现该目标, 双催化体系需要满足以下条件: 首先两个催化体系必须要能兼容, 其次至少需有一个催化剂可高效催化烯烃异构, 最后端烯烃的反马氏硅氢化反应速率必须远远高于内烯烃的硅氢化速率. 烷烃脱氢部分我们选用本课题组发展的PSCOP铱配合物³^[34]. 对于异构硅氢化步骤, 经过对催化剂的大量筛选, 我们发现吡啶二亚胺铁配合物可以满足上述条件^[82]. 当用二乙基硅烷作为硅源, 可以76%的分离收率得到正辛烷端位硅化的产物, 从而实现了从直链烷烃到直链硅化合物的转化. 基于同样的策略, 采用本课题组^[43,83]发展的联吡啶磷配位的PNN铁配合物, 可以实现从直链烷烃到直链硼酸酯类化合物的高区域选择性转化(图4(a)).

图3 基于烷烃脱氢发展的烷烃端位官能团化策略

Figure 3 Alkane functionalization with terminal selectivity based on alkane dehydrogenation

2.3 烷烃端位选择性(形式)羰化和胺甲基化

醛和胺类化合物是化学工业上两类重要的合成中间体和原料,需求量巨大.例如,目前以烯烃的氢甲酰化反应制备衍生的醛及醇、酸等氧化物年产量已经超过1000万吨^[84].目前,制备直链醛主要依赖于 α 烯烃的反马氏氢甲酰化反应,而 α 烯烃工业上主要是由乙烯的寡聚反应来制备(即所谓的SHOP)^[85].如果可以直接以广泛存在的烷烃为起始原料高效选择性地来制备相应的直链醛,无疑具有一定的实用价值.

目前从烷烃直接制备相应的直链醛的报道很少,已知的体系主要是在紫外光照射下进行的,该方法效率低^[86],生成的醛类产物在反应条件下不稳定,容易发生Norris II类型的裂解反应^[87,88].Jaynes和Hill^[89]报道的烷烃羰基化反应经由自由基历程,主要生成支链醛,且不可避免地会生成自由基偶联副产物.

最近,本课题组^[78]基于烷烃脱氢反应,设计了烷烃先进行脱氢,生成的内烯烃混合物经由异构氢甲酰化反应生成直链醛的策略,从而实现了从直链烷烃到直链醛的转化(图4(b)).在烷烃脱氢步骤还是使用本课题组^[34]报道的高活性的PSCOP型铱催化剂

我们发现美国联合碳化公司发展的biphephos配体^[90,91]在脱氢后的体系中可以兼容,表现较好直链选择性,同时产率优秀.以此为最佳配体,对底物的考察发现该双催化体系不仅对于常见的直链烷烃(C5-C10以及C12)具有良好的效果,对于烷基链上带有硅基取代基的底物也可以兼容,而其相应的产物可作为制备含硅表面活性剂以及硅树脂的原料(图4(b))^[78].

乙烯作为比叔丁基乙烯更便宜也更实用的氢气接收体,在该体系中也得到应用.在正辛烷转化成正壬醛的反应中,我们^[78]以乙烯为氢气接收体,在最优条件下,对于铱和铑的催化TON可以分别达到577和1110.

此外,采用类似的策略,我们也实现了以烷烃为原料制备直链胺化合物的反应.通过对反应条件的考察,发现Beller课题组^[92,93]报道的iphos配体对反应的产率,产物中对胺的选择性以及胺的直链选择性综合效果最好.此外,实验结果表明不同的胺源对产率和直链选择性影响较大.例如,对正戊烷的胺甲基化反应中,若使用硫代吗啉作为胺源,反应的产率和直链与支链比分别为60%和24:1,而在同样条件下,若以哌啶作为胺源,该值分别为95%和6:1^[78].

图4 基于烷烃脱氢的烷烃端位选择性官能团化反应

Figure 4 Terminal selective alkane functionalization via alkane dehydrogenation

3 烷烃复分解和聚乙烯可控降解

早期Burnett和Hughes^[94]报道了在非均相条件下,以氧化铝负载的铂作为脱氢催化剂,二氧化硅负载的氧化钨作为烯烃复分解催化剂,实现了丁烷的复分解反应. Basset课题组^[95,96]采用钼为烯烃复分解催化剂,也实现了该转化,但催化转化数都非常低,且后者无法选择性生成直链烷烃产物. 而均相分子催化的烷烃复分解最早由Goldman课题组和Brookhart课题组^[64,65,97]报道,其具体过程是直链烷烃首先在14电子螯型铱活性催化物种作用下进行脱氢反应,生成的烯烃经由烯烃复分解催化剂(Schorrock催化剂或者 $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ 催化剂)作用进行烯烃复分解,所生成的烯烃中间体和第一步脱氢反应中生成的铱二氢物种反应,再生14电子的铱活性催化物种,同时自身被还原生成碳链长度增长或者缩短的烷烃. 这种方法可以将低碳烷转化成碳数增加的烷烃,其中碳数在9~20的烷烃是柴油的理想组成体(图5(a)),但该过程不可避免地会产生碳数减少的烷烃. 烷烃复分解过程为低碳烷烃资源的有效利用提供了可能^[64]. 该催化体系也同样适用于烷烃和烷基苯的交叉复分解反应^[98].

聚乙烯因为优良的物理和化学性能在生活中得到广泛的使用,其年产量超过一亿吨. 但是,由于聚乙烯难以降解,使用后被废弃闲置,因此也造成环境污染问题. 从化学结构上看,聚乙烯分子可以看做是大分子量的“长链”烷烃,它们均由 $\text{C}(\text{sp}^3)-\text{C}(\text{sp}^3)$ 单键和 $\text{C}(\text{sp}^3)-\text{H}$ 键组成. 传统烷烃复分解的目的是将低价值低碳烷烃生成碳数增加的可作为运输燃油的烷烃,我们想反其道而行之,设想在加入另一种低分子量的烷烃后,高分子量的聚乙烯是否可以与低碳烷烃进行“交叉”烷烃复分解,进而将聚乙烯的分子量降低^[99,100].

反应的具体历程首先是在螯型铱脱氢催化剂存在下,聚乙烯和低碳烷烃分子都进行脱氢反应,该过程在聚乙烯和低碳烷烃分子中引入不饱和双键. 由于脱氢催化剂同时具有烯烃异构的活性^[5,14,101],聚乙烯脱氢产生的端位双键可被异构至链中间,生成的内烯烃在烯烃复分解催化剂的作用下与低碳烯烃发生交叉复分解反应,使聚乙烯链长缩短. 随后铱的二氢物种将生成的不饱和碳链还原,再生铱的活性物种,完成一次烷烃交叉复分解(CAM)过程,也即第一

图5 烷烃复分解、聚乙烯降解及塑料袋和塑料瓶的降解

Figure 5 Alkane metathesis, degradation of polyethylene and degradation of plastic bag and bottle

次降解. 在体系中, 相对于聚乙烯我们使用过量的低碳烷烃作为反应试剂和溶剂, 第一次降解产物可与低碳烷烃发生再次烷烃交叉复分解, 不断重复该过程可实现聚乙烯的逐步降解至分子量在一百至数百间、适用于燃油的烷烃(图5(b)).

实验结果表明, 利用Ir和Re双金属催化体系, 各种不同类型的聚乙烯链, 如低密度聚乙烯、高密度聚乙烯(分子量达174万)、以及含有抗氧化剂, 硬脂酸锌等添加剂的聚乙烯均在相对温和的条件下(175℃)可以很好地得到降解. 甚至对于商业化的聚乙烯塑料盒、聚乙烯保鲜膜和聚乙烯购物袋降解反应也可以发生, 突出了该方法的实用性(图5(c))^[99]. 在通用反应条件下(175℃, 4 d), 各类聚乙烯链经降解后得到的主要产物为燃油和少量聚乙烯蜡. 但通过改变使用的烷烃脱氢催化剂, 或者缩短反应的时间, 可以提高产物中聚乙烯蜡的比例. 所得到的这类聚乙烯蜡具有分子量较低, 分布较窄的特点, 可在聚合物加工中用作润滑剂、分散剂、树脂修饰试剂等使用^[99].

在该体系中, 除了采用正己烷、正辛烷作为烷烃交叉复分解试剂, 也可以使用轻质石油醚作为试剂. 石油醚相比正己烷等来源更加广泛, 价格更低, 因此采用其作为烷烃交叉复分解试剂无疑更具优势, 此外使用的石油醚可以通过简单蒸馏的方式回收利用^[99].

4 总结与展望

目前对烷烃的官能团化反应主要有基于Shilov系统发展起来的烷烃的亲电活化反应, 卡宾氮宾等活性物种对烷烃C-H键的插入反应, 经由自由基机理的高价金属氧化物(例如卟啉配位的铁、锰等)催化的烷烃氧化和卤化反应等. 后两类反应一般优先活化烷烃中的二级以及三级C-H键, 对一级C-H键的选择性较差. 金属介导的C-H键活化以烷烃脱氢反应为代表, 可以选择性地在烷烃的一级C-H键上发生活化. 在低价态金属的作用下, 烷烃的C-H键发生氧化加成反应, 经由后续 β -H消除, 释放出相应的烯烃. 然而, 随着反应的进行, 初始阶段生成的 α 烯烃会在

催化剂作用下逐渐异构成热力学更稳定的内烯烃^[101]. 本文集中于介绍烷烃脱氢和基于脱氢的烷烃进一步官能团化反应, 后者主要包括: (1) 在烷烃分子中不引入杂原子官能团的转化, 已报道的有烷烃的芳构化反应, 烷烃与烯烃的偶合反应和烷烃(交叉)复分解反应; (2) 在烷烃分子中引入杂原子的官能团化转化, 已报道的有烷烃的硅化、硼化、羰基化和胺化反应.

目前, 均相烷烃脱氢领域尽管取得了很大进展, 但离实际应用, 特别是工业规模上的应用仍有距离. 我们认为亟待发展的方向包括以下6个方面: (1) 发展低成本、易回收利用的氢气接受体来取代目前应用较多的叔丁基乙烯、降冰片烯、乙烯丙烯氢气接受体等. 最理想的情况是在保证催化效率的前提下不使用氢气接受体实现烷烃的直接脱氢. (2) 发展经由高氧化态历程诱导的烷烃脱氢体系. 与经典的PCP铱相比, 高氧化态的催化循环对于一些常见的配位小分子如氮气、水、丙酮敏感性可能较低, 对官能团兼容性更高, 可以降低分子催化的烷烃脱氢反应对惰性环境的苛刻要求. 在这方面Goldman, Goldberg课题组^[49]和William课题组^[50]发展的NCN型铱催化剂已取得了初步成功, 但是TON值仍很低. (3) 目前采用的热条件下的烷烃脱氢反应在反应的后期往往生成内烯烃为主要产物, 同时也不可避免地生成过度脱氢的副产物, 因此如何提高产物中 α 烯烃的比例也是一个需要努力的方向. Goldman课题组^[102]采用固气两相反应条件、利用乙烯或丙烯作为氢气接受体提升了 α 烯烃的比例, 但无论是选择性还是活性仍有很大提升空间. (4) 发展廉价金属配合物应用于烷烃脱氢反应. 目前已知的基本都是以贵金属铱、铑、钌为中心的催化剂. 由Mindiola课题组^[56]报道的廉价金属钛可以催化脱氢反应, 但催化效率极低, 仍有待发展. (5) 基于烷烃脱氢反应发展更加多元化的后续烯烃转化, 进而在烷烃分子中区域选择性甚至立体选择性地引入官能团. (6) 将洁净的光、电催化和过渡金属催化相结合, 发展高效、实用、绿色的烷烃转化新方法, 也是未来的发展方向之一.

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Summary for “过渡金属分子催化的烷烃转化进展”

Transition-metal complex-catalyzed alkane functionalization

Xinxin Tang & Zheng Huang*

State Key Laboratory of Organometallic Chemistry, Center for Excellence in Molecular Synthesis, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

* Corresponding author, E-mail: huangzh@sioc.ac.cn

The selective conversion of simple alkane feedstocks to high-value organic compounds constitutes one of major challenges in organic synthesis. There are three general catalytic methods for alkane functionalizations: reactions via radical intermediates and through carbene/nitrene insertion pathways typically occur preferentially at the secondary and tertiary C–H bonds, whereas transition metal-mediated C–H bond activation holds promise for the functionalization of primary C–H bonds. From a practical point of view, the installation of a functional group at the terminal position of alkanes is of particular attractive for large-scale synthesis of specialty or commodity chemicals. This review focuses on the area of molecular transition-metal-catalyzed alkane transformations through catalytic alkane dehydrogenation.

In the first section, the development of iridium pincer and related complexes for alkane dehydrogenation is summarized. Among various catalysts, the PCP type Ir pincer complexes have proven to be most active toward transfer dehydrogenation of alkanes. α -Olefins are the kinetic products at the early stage of the dehydrogenation process, but they can be rapidly isomerized to internal alkenes. Recently, other non-phosphorus-ligated Ir and non-Ir metal dehydrogenation catalysts have also been developed, but they are generally less efficient than the PCP Ir catalysts.

The second section first describes two dehydrogenation-based alkane transformations without the incorporation of heteroatom-containing functionality. The dehydroaromatization reaction involves multiple steps of dehydrogenation of linear alkanes to form conjugate trienes, which undergo electrocyclization and another step of dehydrogenation to generate aromatic products. The alkane-alkene coupling reaction employs an Ir pincer catalyst for dehydrogenation and a tantalum catalyst for alkene/alkene coupling, thus providing a method for upgrading light alkanes to higher alkanes that may be suitable to transportation fuel. Following that, the selective installation of functional groups at the terminal positions of alkanes through a dehydrogenation-alkene isomerization-hydrofunctionalization strategy using a dual catalyst system is described. Several combinations between a PSCOP Ir pincer dehydrogenation catalyst and molecular Fe or Rh catalysts for tandem isomerization and hydrofunctionalization of terminal alkenes have been developed for terminal selective alkane silylation, borylation, carbonylation, and aminomethylation.

The third section covers alkane metathesis and its application to polyethylene (PE) degradation. The alkane metathesis reaction described here consists of two catalysts, one Ir dehydrogenation catalyst and one olefin metathesis catalyst. The metathesis process can find potential application in upgrading low carbon number *n*-alkanes to higher-molecular-weight fuel alkanes. A cross-alkane metathesis strategy has been developed for PE degradation. Using excess of low-value light alkanes as the reagent/solvent, PE with molecular weight up to 1.7 million undergoes multiple times of cross-alkane metathesis at 175 °C to produce liquid fuels or high-quality waxes. The catalysts can tolerate the commercial HDPE, LDPE and LLDPE, and enable the efficient degradation of postconsumer PE plastic wastes.

Finally, the review discusses the limitations of the known catalytic approaches and future opportunities in this field. Catalyst development will be the central theme of research, and insights into the factors controlling the activity and selectivity gained in mechanistic studies will guide the design of more efficient dehydrogenation catalysts. The cooperative catalysis involving enantioselective catalysts will provide a protocol for synthesis of valuable fine chemicals from simple saturated hydrocarbons. Lastly, we should not overlook the potential of cooperation between photo- or electro-catalysis and transition-metal catalysis, which may allow the exploitation of alkane feedstocks more cleanly and efficiently.

alkane dehydrogenation, dual-metal catalysis, iridium pincer complex, terminal alkane functionalization, polyethylene degradation

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