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乙烯选择性三聚 / 四聚铬系催化剂及其齐聚机理研究进展

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摘要：线性 α-烯烃是一类重要的有机化工原料和中间体，其下游市场包括聚乙烯、合成润滑油、表面活性剂等，其中 C_4~C_8 组分的消费量占全球线性 α-烯烃消费量的一半以上．采用 1-己烯和 1-辛烯作为共聚单体生产的线性低密度聚乙烯（LLDPE）和高密度聚乙烯（HDPE）产品具有优异的性能，被广泛用于薄膜、管材等领域．为了提高原子经济性，学术界和工业界一直致力于乙烯选择性三聚 / 四聚催化剂的设计与开发，而铬系催化剂是其中研究最广泛、最深入的体系．我们从配体、铬源、助催化剂、反应条件等方面综述了典型的铬系乙烯选择性三聚 / 四聚催化体系，包括雪佛龙菲利普斯乙烯三聚催化体系，Cr/PNP 催化体系，以及其他 N、P、Si 配体等催化体系．我们在文章中也综述了乙烯选择性齐聚的相关机理提案，包括经典的 Cossee-Arlman 机理、单核金属环机理、双核金属环机理、双配位机理及其他机理提案．

关键词：乙烯三聚；乙烯四聚；1-己烯 /1-辛烯；铬系催化剂；反应机理
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线性 α-烯烃(Linear Alpha Olefins, LAOs) 是分子结构中含有唯一末端双键的 C_4 及 C_4 以上的直链碳氢化合物．LAOs 是一类用途广泛的有机化工原料和中间体．在工业生产中，以石蜡为原料的裂解工艺可以得到 C_5~C_{20+} 的直链 α-烯烃，或者从费托法煤制油工艺中通过萃取分离得到碳数连续分布的高品质 α-烯烃．生产 LAOs 的方法以原料的不同可划分为两类：(1) 以石蜡、煤等为原料，生产的 LAOs 中既有偶数碳的 α-烯烃也有奇数碳的 α-烯烃；(2) 以乙烯为原料，生产碳原子数为偶数的 α-烯烃．采用乙烯为原料生产 LAOs 的工艺也分为两类：(1) 非选择性齐聚，获得的产品是 C_4~C_{30+} 的全分布 α-烯烃(雪佛龙菲利普斯化工公司的 Gulf 工艺(Ziegler 一步法)、乙基公司的 Ethyl 工艺(Ziegler 两步法) 等)；(2) 选择性齐聚，获得的产品是具有特定碳数的线性 α-烯烃(雪佛龙菲利普斯化工公司的铬系乙烯三聚工艺、大庆石化公司 1-己烯生产工艺等)[1]．LAOs 下游领域包括聚乙烯共聚单体(C_4~C_8)、合成润滑油(C_8~C_{12})、表面活性剂(C_{12}~C_{18})、增塑剂用醇(C_6~C_{10}) 等．

当前工业生产中 LAOs 装置以乙烯非选择性齐聚工艺为主．下游市场对 α-烯烃有着不同的需求，其中 C_4~C_8 组分作为线性低密度聚乙烯和高密度聚乙烯的共聚单体的消费量占全球线性 α-烯烃消费量的一半以上．其中，1-己烯和 1-辛烯作为共聚单体可以赋予产品更优异的性能和更高的附加值．近年来，市场对高性能聚乙烯的需求，进一步拉大了 1-己烯和 1-辛烯与其他 α-烯烃在下游市场的需求差异．因此，生产全馏分 α-烯烃的传统非选择性齐聚工艺获得的产品分布无法满足市场的需求，这种市场驱动力使得乙烯选择性三聚 / 四聚成为乙烯齐聚领域的研究热点．

针对乙烯选择性三聚 / 四聚的研究，已有论文从不同的角度综述了乙烯选择性三聚 / 四聚的进展[2-11]．在现有金属催化体系中，铬系催化体系是研究最为广泛的乙烯选择性三聚 / 四聚催化体系．我们从配体、铬源、助催化剂、反应条件等方面综述了典型的铬系乙烯选择性三聚 / 四聚催化体系，并简述了乙烯选择性三聚 / 四聚的反应机理．

1 铬系乙烯三聚催化体系

1.1 菲利普斯催化体系

菲利普斯催化体系是首次实现 1-己烯选择性

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大于90%的乙烯三聚催化体系[12]. 20世纪80年代，菲利普斯石油公司(Phillips Petroleum Company)在乙烯聚合催化剂铬环戊二烯基配合物的启发下，研究了铬吡咯化合物的催化性能. 其中，2,5-二甲基吡咯(DMP)因其较高的空气、光、温度稳定性以及优异的催化性能成为优选配体. 以1∶3.3∶7.8∶10.8的摩尔比在甲苯溶剂中混合2-乙基己酸铬($Cr(EH)_3$)、2,5-二甲基吡咯、二乙基氯化铝和三乙基铝制备的催化剂，在115 ℃和10.0 MPa的反应条件下，催化活性为155 246 g/(g_{Cr}·h)，1-己烯的选择性达到93.1%，主要副产物是直链癸烯和支链癸烯(图 1)[13]. 2003年，雪佛龙菲利普斯化工公司(Chevron Phillips Chemical Company)在卡塔尔建成了世界上首个乙烯选择性三聚工业化装置.

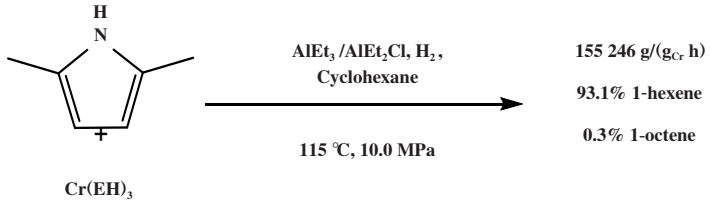


图1 菲利普斯乙烯选择性三聚催化体系

Fig.1 Phillips catalytic system for ethylene trimerization

随后，三菱化学公司(Mitsubishi Chemical Corporation)对该体系进行改进[14]. 将2-乙基己酸铬、2,5-二甲基吡咯、六氯乙烷和三乙基铝以1∶6∶4∶40的摩尔比混合，并控制反应器内部的1-己烯与乙烯的摩尔比低于0.5. 在105 ℃和4.9 MPa的反应条件下，该体系的反应活性为5 391 667 g/(g_{Cr}·h)，1-己烯的选择性为96.3%(图 2). 三菱化学公司改进后的催化体系不仅提高了1-己烯的选择性，而且反应活性是菲利普斯催化体系的30多倍.

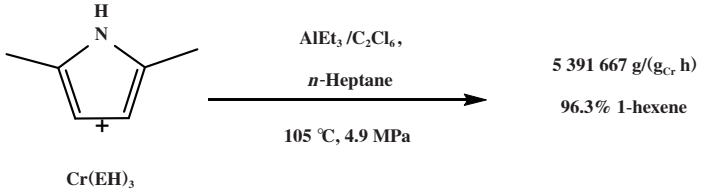


图2 经三菱改进的乙烯选择性三聚催化体系

Fig.2 Mitsubishi-modified catalytic system for ethylene trimerization

除了三菱化学公司，其他公司以及研究团队也探讨了菲利普斯催化体系或者其变体[15-16]. 在均相$Cr(EH)_3$/DMP/TEA/氯化合物催化体系中，随着氯化合物中氯取代数量的增加，观察到1-己烯选择性和乙烯转化率提高. 而含有两个氯的氯化合物大大提高了乙烯三聚的催化活性[15]. 对比研究表明，氯化物的促进效果明显优于氟化物或溴化物，促进效果最好的卤化物是多氯化合物[17]. DMP/Cr(III)/烷基铝/四氯乙烷催化体系催化乙烯三聚反应的结果表明，三乙基铝(TEA)、三甲基铝(TMA)、三正己基铝(TNHA)和三异丁基铝(TIBA)都是乙烯三聚的有效助催化剂. 在80 ℃和2.0 MPa的反应条件下，DMP/Cr(III)/TEA/TCE催化体系的1-己烯选择性最高为92.4%，活性为26 540 g/(g_{Cr}·h)(原文为1 380 000 g/(mol_{Cr}·h))[18]. 添加H_2对2-乙基己酸铬/2,5-二甲基吡咯/三乙基铝/四氯乙烷催化体系1-己烯选择性的影响并不明显，但减少了聚合物的形成并提高了活性[19]. 为了理解乙烯三聚的反应机理，科研人员利用密度泛函理论(DFT)研究了基本组分(即配体、助催化剂和卤代烃化合物)对菲利普斯催化体系催化乙烯三聚反应的影响[20-21].

1.2 Cr-NNN体系

东曹公司(Tosoh Corporation)的研究人员在四氢呋喃(THF)中将三(3,5-二甲基-1-吡唑)甲烷配体与$CrCl_3(THF)_3$反应制备Cr-NNN配合物，在80 ℃和4.0 MPa乙烯压力下，经甲基铝氧烷(MAO)活化后，1-己烯的选择性可达99.1%，反应活性为40 100 g/(g_{Cr}·h)(图 3)[22]. 随后，Li等[23]合成的Cr-NNN(1,3,5-三氮杂环己烷)配合物经MAO活化后，在50 ℃和0.8

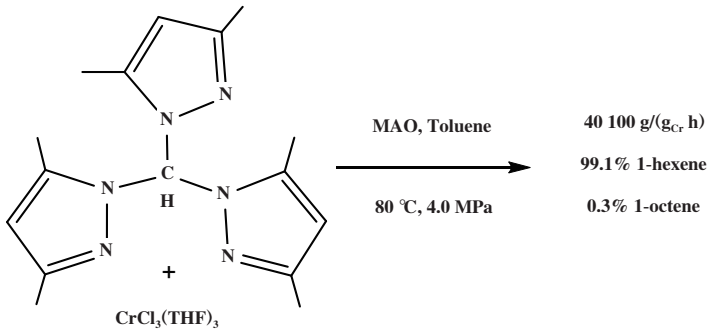


图3 Cr-NNN乙烯选择性三聚催化体系

Fig.3 Cr-NNN catalytic system for ethylene trimerization

MPa压力下可催化乙烯齐聚得到93.1%的总1-己烯和1-辛烯选择性.

1.3 Cr-PPP体系

阿莫科公司(Amoco Corporation)使用(2-二甲基膦乙基)(3-二甲基膦丙基)苯基膦配体与$CrCl_3$合成的Cr-PPP配合物经丁基铝氧烷活化后,在60 ℃和3.5 MPa乙烯压力的反应条件下,催化活性达到了26 225 g/(g_{Cr}·h)(原文为48 700 mol乙烯/(mol_{Cr}·h)),1-己烯的选择性为97.3%(图4)[24].

1.4 Cr-PNP体系

英国石油公司(BP)开发了一种双磷PNP配体的铬系乙烯选择性三聚催化剂.以$CrCl_3(THF)_3$为铬源、$Ar_2PN(Me)PAr_2$(Ar=(*o*-OMe)C_6H_4)为配体、MAO为活化剂、甲苯为溶剂,在80 ℃和2.0 MPa压力下催化乙烯三聚得到89.9%的1-己烯,催化活性为1 033 200 g/(g_{Cr}·h)(图5)[25].

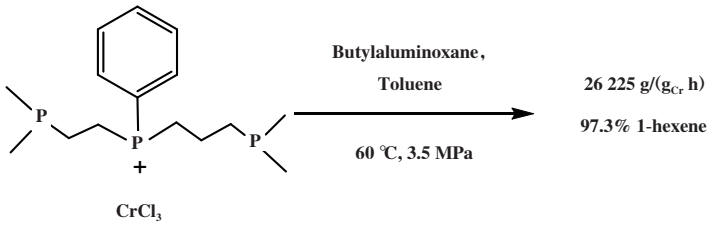


图4 Cr-PPP乙烯选择性三聚催化体系

Fig.4 Cr-PPP catalytic system for ethylene trimerization

萨索尔公司(Sasol Technology)对BP的PNP配体进行改性,开发了一种$R_2P(CH_2)_2N(H)(CH_2)_2PR_2$型三齿配体的铬系乙烯三聚催化剂.以$CrCl_3(THF)_3$为铬源、二乙基膦基乙基胺为配体、MAO为活化剂、甲苯为溶剂,在100 ℃和4.0 MPa压力的反应条件下,1-己烯选择性为97.2%,催化活性为9331 g/(g_{Cr}·h)(图6)[26]. 2009年,Klemps等[27]提出了一种含二齿双膦甲基胺(R' $N(CH_2PR_2)_2$)的铬配合物.Cr-PCNCP配合物经MAO活化后,在70 ℃、3.0 MPa乙烯压力下催化乙烯三聚反应,获得了97.0%的1-己

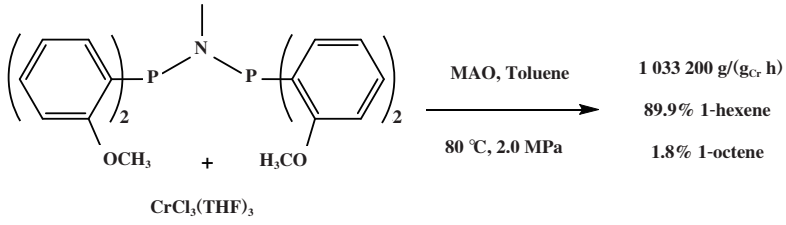


图5 Cr-PNP乙烯选择性三聚催化体系

Fig. 5 Cr-PNP catalytic system for ethylene trimerization

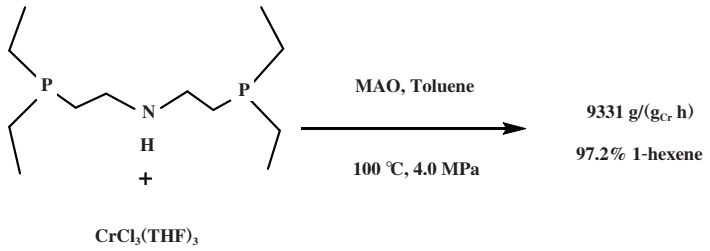


图6 Cr-PC_2NC_2P乙烯选择性三聚催化体系

Fig.6 Cr-PC_2NC_2P catalytic system for ethylene trimerization

烯，反应活性为9783 g/(g_{Cr}·h)(图 7).

Cr-PNP催化体系出现后，许多研究人员探索了反应条件、助催化剂、配体主链、配体上的N-取代基或芳基取代基等对Cr-PNP体系催化乙烯三聚反应的影响[28-40]，并通过实验和理论计算(DFT)方法研究了Cr-PNP体系的催化反应机理[41-49]. Blann

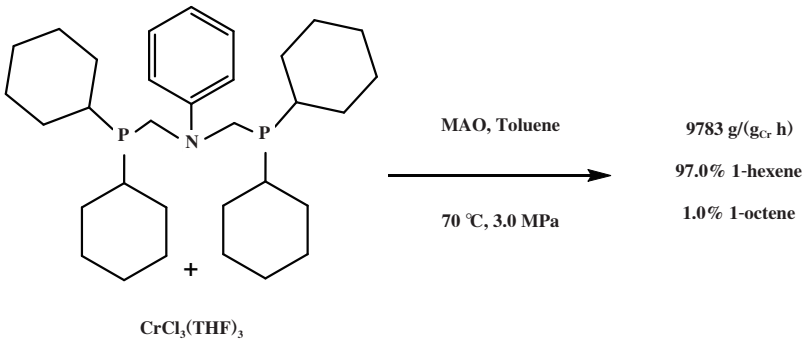


图7 Cr-PCNCP乙烯选择性三聚催化体系

Fig.7 Cr-PCNCP catalytic system for ethylene trimerization

等[33]的实验表明将苯环上的邻位甲氧基取代基改为甲基、乙基、异丙基后，该体系仍然是乙烯三聚催化剂，1-己烯的选择性均超过90%. Alam等[37-38]向PNP配体的N-取代基上引入环戊烷、向一个P-取代基上引入两个$N(R_2)$ (R=Et或者^{i}Pr)基团也可得到1-己烯选择性超过97%的Cr-PNP催化剂. Liu等[50]使用密度泛函理论方法研究了H_2对Cr-PNP体系催化乙烯聚合反应选择性的影响，发现H_2与铬中心的缔合/解离作用可能是该系统高活性和低1-辛烯选择性的关键因素. 目前，超支化铬系催化剂也得到了众多研究者的关注[51-53].

1.5 Cr-SNS体系

McGuinness等[54]利用SNS配体与$CrCl_3(THF)_3$合成了一种新型乙烯三聚催化剂. 在90 ℃和3.0 MPa反应条件下，经MAO活化后进行乙烯三聚反应，得到98.1%的1-己烯，催化活性为160 840 g/(g_{Cr}·h)(图 8). Cr-SNS催化体系需要加入的MAO量较少，且SNS配体的合成相对简单，是一种良好的乙烯三聚工业化候选催化体系.

Temple等[55]对Cr-SNS体系进行了进一步的研究，发现使用2,6-$(CySCH_2)_2$吡啶配体与$CrCl_3(THF)_3$合成的新型Cr-SNS配合物经MAO活化后，在50 ℃

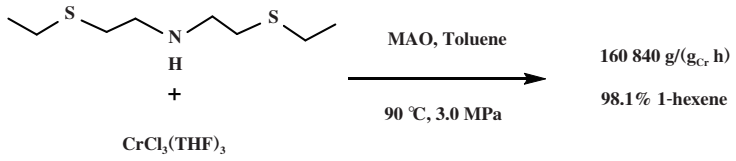


图8 Cr-SNS乙烯选择性三聚催化体系

Fig.8 Cr-SNS catalytic system for ethylene trimerization

和3.5 MPa反应条件下，1-己烯的选择性高达99.8%，催化剂活性为3883 g/(g_{Cr}·h)（图9）. 与萨索尔公司的Cr-SNS[54]相比，两个体系1-己烯的选择性相近. 因此作者认为N-H官能团并不是Cr-SNS体系高1-己烯选择性的主要影响因素.

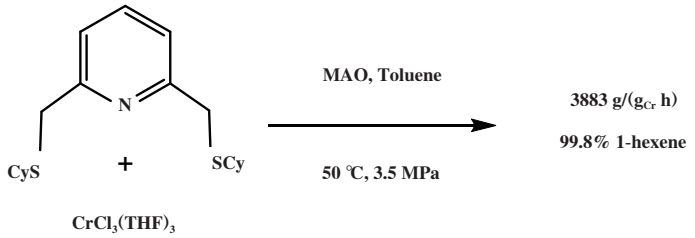


图9 改性的Cr-SNS乙烯选择性三聚催化体系

Fig.9 Modified Cr-SNS catalytic system for ethylene trimerization

1.6 Cr-NON体系

Zhang等[56]使用Pz_2CHCH_2OR（Pz = 吡唑-1-基，R = 己基）配体与$CrCl_3(THF)_3$合成了一种Cr-NON配合物，经MAO活化后，在80 ℃和2.5 MPa反应条件下进行乙烯三聚反应. 该体系反应活性为16 200 g/(g_{Cr}·h)，1-己烯的选择性为98.5%（图10）. 在相同的反应条件下，使用Pz_2CHCH_2SR（Pz = 吡唑-1-基，R = 甲基）配体也可得到95.5%的选择性，但活性仅有2800 g/(g_{Cr}·h).

Zhang等[57]继续探究了配体中第3供体基团（吡啶基、吡唑基、咪唑基以及胺基）对乙烯三聚反应的

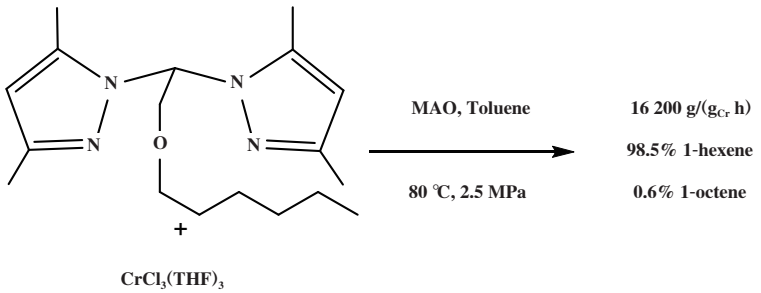


图10 Cr-NON乙烯选择性三聚催化体系

Fig.10 Cr-NON catalytic system for ethylene trimerization

影响，所有合成的Cr-NNN体系在MAO活化后都表现出乙烯三聚催化活性. 其中含有咪唑基的配合物，在80 ℃和3.0 MPa的反应条件下表现出了53 000 g/(g_{Cr}·h)的最高活性和97.6%的1-己烯选择性（图11）.

1.7 Cr-NPN体系

Albahily等[58]使用NPN配体与$CrCl_2(THF)_2$或$CrCl_3(THF)_3$合成了一种用于乙烯三聚的Cr-NPN催化体系. 该体系以Al^iBu_3为助催化剂、在50 ℃和3.5

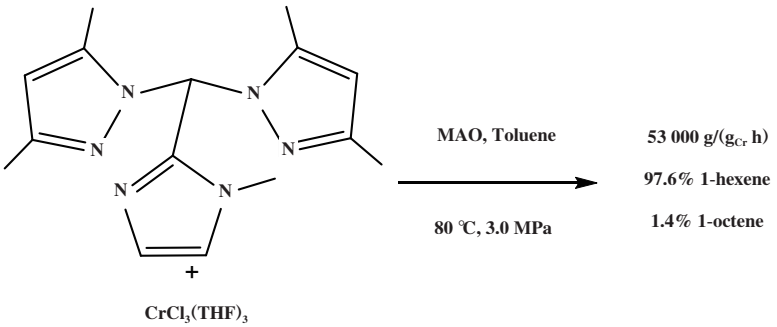


图11 Cr-NNN乙烯选择性三聚催化体系

Fig.11 Cr-NNN catalytic system for ethylene trimerization

MPa反应条件下获得了> 99.9%的1-己烯选择性，反应活性为7693 g/(g_{Cr}·h)（原文为400 g/($mmol_{Cr}$·h)，图 12）.

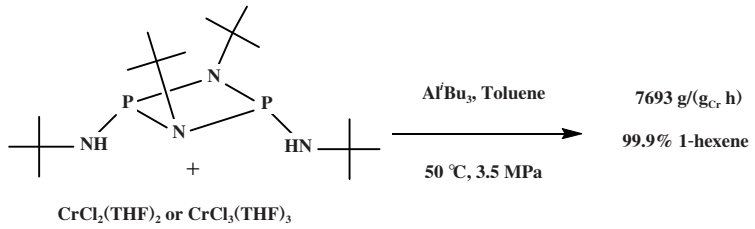


图 12　Cr-NPN乙烯选择性三聚催化体系

Fig.12　Cr-NPN catalytic system for ethylene trimerization

70 ℃、0.2 MPa氢气和6.0 MPa乙烯压力的反应条件下获得了93.6%的1-己烯，反应活性为1 052 002 g/(g_{Cr}·h)（原文为54 700 kg/(mol_{Cr}·h)，图 13）. 随后，Sydora等使用实验方法或者DFT方法继续研究P-取代基、C-取代基、配位模式等对Cr-PNCN催化剂体系的1-己烯和1-辛烯选择性的影响[60-62].

1.9 Cr-PNPNH体系

德国林德公司(Linde AG)和沙特基础工业公司(SABIC)的研究人员[63]使用$Ph_2PN(^iPr)P(Ph)N(^iPr)H$配体与$CrCl_3(THF)_3$合成的Cr-PNPNH配合物经

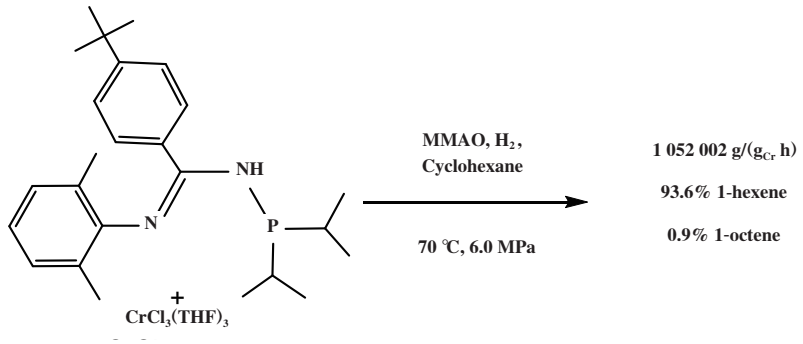


图 13　Cr-PNCN乙烯选择性三聚催化体系

Fig.13　Cr-PNCN catalytic system for ethylene trimerization

Et_3Al活化后，在65 ℃和3.0 MPa乙烯压力的反应条件下获得了90.1%的1-己烯，反应活性为5200 g/(g_{Cr}·h)（图 14）. 这一体系具有选择性高、催化剂稳定性高、使用低成本的Et_3Al以及聚乙烯含量低等

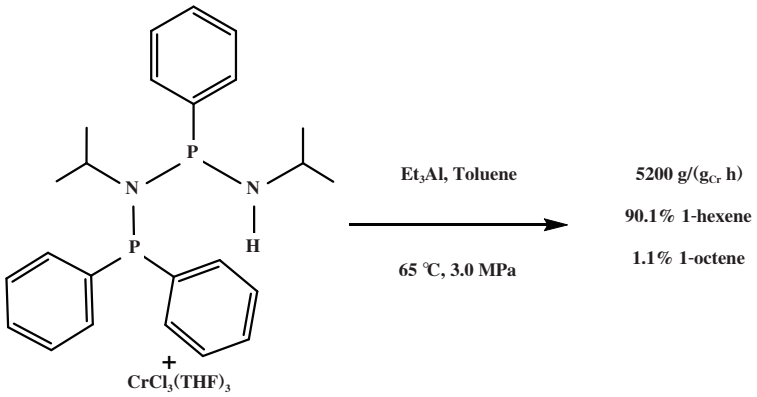


图 14　Cr-PNPNH乙烯选择性三聚催化体系

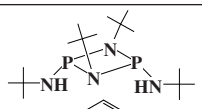
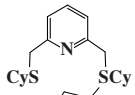
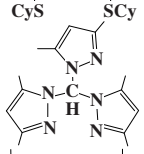
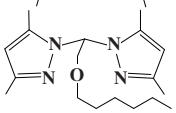
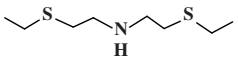
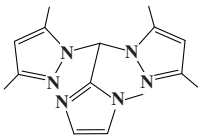
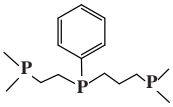
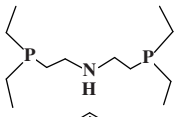
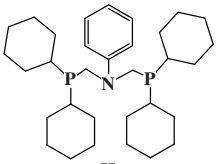
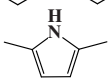
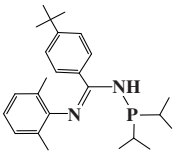
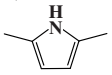
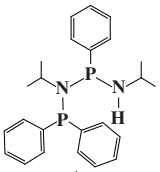
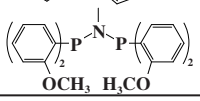
Fig.14　Cr-PNPNH catalytic system for ethylene trimerization

优点，也是一种良好的乙烯三聚工业化候选催化体系.

表1按1-己烯的选择性从高到低依次列出了典型的高选择性乙烯三聚催化体系，其中1-己烯选择

表 1 典型的铬系乙烯三聚催化体系

Table 1 Chromium-based catalysts for ethylene trimerization

Entry	Chromium compound	Ligand	Activator, Modificator	Solvent	Temperature /℃	Pressure /MPa	Activity, /($g \cdot g_{Cr}^{-1} \cdot h^{-1}$)	1-C_6 /%	1-C_8 /%
1	$CrCl_2(THF)_2$ or $CrCl_3(THF)_3$		Al^iBu_3	Toluene	50	3.5	7 693	99.9	–
2	$CrCl_3(THF)_3$		MAO	Toluene	50	3.5	3 883	99.8	–
3	$CrCl_3(THF)_3$		MAO	Toluene	80	4.0	40 100	99.1	0.3
4	$CrCl_3(THF)_3$		MAO	Toluene	80	2.5	16 200	98.5	0.6
5	$CrCl_3(THF)_3$		MAO	Toluene	90	3.0	160 840	98.1	–
6	$CrCl_3(THF)_3$		MAO	Toluene	80	3.0	53 000	97.6	1.4
7	$CrCl_3$		Butylalumi-noxane	Toluene	60	3.5	26 225	97.3	–
8	$CrCl_3(THF)_3$		MAO	Toluene	100	4.0	9 331	97.2	–
9	$CrCl_3(THF)_3$		MAO	Toluene	70	3.0	9 783	97.0	1.0
10	$Cr(EH)_3$		$AlEt_3$, C_2Cl_6	*n*-Heptane	105	4.9	5 391 667	96.3	–
11	$CrCl_3(THF)_3$		MMAO, H_2	Cyclohexane	70	6.0	1 052 002	93.6	0.9
12	$Cr(EH)_3$		$AlEt_3$/ $AlEt_2Cl$, H_2	Cyclohexane	115	10.0	155 246	93.1	0.3
13	$CrCl_3(THF)_3$		Et_3Al	Toluene	65	3.0	5 200	90.1	1.1
14	$CrCl_3(THF)_3$		MAO	Toluene	80	2.0	1 033 200	89.9	1.8

性最高可达99.9%. 除已工业化的菲利普斯催化体系之外, Cr-PNP催化体系是研究最为广泛, 受关注程度最高的乙烯三聚催化体系. 高选择性乙烯三聚催化体系最常用的铬源和溶剂分别是$CrCl_3(THF)_3$和甲苯. 乙烯三聚反应通常以MAO为助催化剂, 但关于助催化剂作用机理方面的研究相对薄弱. 高选择性乙烯三聚催化剂的反应温度普遍在50 ℃以上, 反应压力范围为2.0 ~ 10.0 MPa的中等压力.

2 铬系乙烯四聚催化体系

2.1 Cr-PNP体系

2004年, 萨索尔公司的Bollmann等报道了第一个高选择性乙烯四聚催化体系, 该体系通过调整Cr-PNP配体中N-取代基以及P-取代基实现了较高的1-辛烯选择性[64]. 在众多候选配体中, N-取代基为异丙基、P-取代基为苯基的候选配体与$Cr(acac)_3$合成的Cr-PNP配合物经MAO活化后, 在45 ℃和4.5 MPa反应条件下获得了67.5%的1-辛烯选择性, 催化活性为272 400 g/(g_{Cr}·h) (图 15). Cr-$N^iPr(PPh_2)_2$催化体系经乙基铝氧烷/三甲基铝(EAO/TMA)活化后, 在45 ℃和4.5 MPa反应条件下获得了70.5%的1-辛烯, 但催化活性仅有之前的1/10. 该体系的主要副产物是甲基环戊烷和亚甲基环戊烷.

随后, 众多研究人员探索了N-取代基、苯环取代基等对Cr-PNP乙烯选择性四聚体系活性和选择性的影响[33-34,65-74]. Blann等[65]研究了N-取代基对体系选择性的影响, 向N上引入大体积的烷基取代基后体系仍然保持50% ~ 60%的1-辛烯选择性. Kuhlmann等[67]研究了将环烷基引入PNP配体的N-取代基对Cr-PNP体系催化性能的影响, 引入环庚基的Cr-PNP体系经MMAO-3A活化后, 在60 ℃和4.5 MPa反应条件下催化乙烯四聚生成67.4%的1-辛烯, 反应活性为737 536 g/(g_{Cr}·h) (图 16). Blann等[33]的实验表明向苯环中引入两个乙基取代基, 体系的1-己烯和1-辛烯选择性分别为55.6%和34.1%; 而减少一个乙基取代基, 体系的1-辛烯选择性有显著提高(1-己烯: 19.5%, 1-辛烯: 62.1%). 一般来说, 较小的铬中心空间位阻有利于1-辛烯的生成, 而1-己烯形成于更拥挤的铬中心. Overett等[34]研究了苯环取代基对Cr-PNP乙烯四聚催化剂选择性的影响, 向苯环取代基的邻位引入一个甲氧基基团会使体系由四聚催化剂转变为三聚催化剂(1-己烯: 61.7%, 1-辛烯: 16.7%); 然而引入一个相同体积的乙基基团, 体系的1-己烯和1-辛烯的选择性未见明显变化. 显然, Cr系乙烯齐聚催化剂的选择性受到多种因素的共同影响, 某种单一因素并不能用于预测体系的选择性.

由于MAO的价格较高, 研究人员尝试采用简单

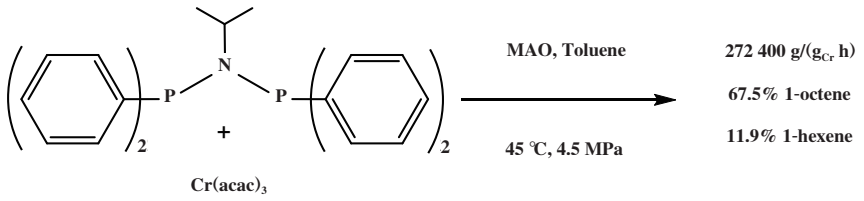


图 15 Cr-PNP乙烯选择性四聚催化体系

Fig.15 Cr-PNP catalytic system for ethylene tetramerization

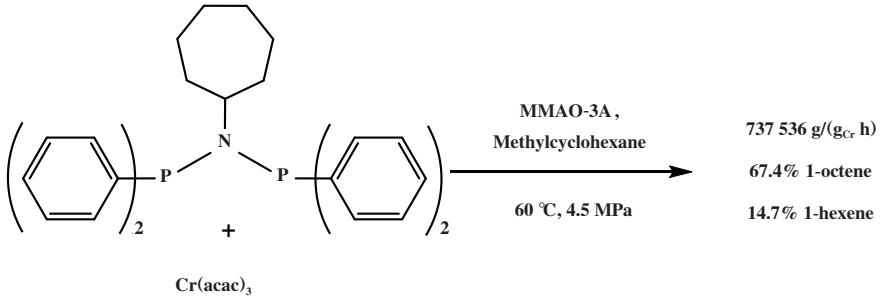


图 16 改性的Cr-PNP乙烯选择性四聚催化体系

Fig.16 Modified Cr-PNP catalytic system for ethylene tetramerization

易得的助催化剂来取代MAO助催化剂. 早在2007年, McGuinness等[29-30]就使用Cr-PNP体系研究了各种助催化剂的影响, 发现使用氟化硼烷和硼酸盐助催化剂与烷基化试剂结合得到的Cr-PNP催化剂的选择性与使用MAO的Cr-PNP体系相当. 使用[Ph_3C][$Al(OC(CF_3)_3)_4$]和$AlEt_3$作为Cr-PNP体系的助催化剂, 在45 ℃和4.0 MPa反应条件下获得了71.5%的1-辛烯选择性, 催化活性为125 600 g/(g_{Cr}·h)[30]. 近年来, Lee等[75-78]使用阴离子[$B(C_6F_5)_4$]$^-$与阳离子[Cr-PNP]$^+$配合物合成的催化剂经烷基铝助剂活化后可催化乙烯四聚生成1-辛烯, 并且所得1-辛烯的选择性与使用MAO的Cr-PNP催化体系相当. 一般认为MAO最重要的作用是与铬源、配体作用形成乙烯齐聚活性中心. Hirscher等[79]以芳基铬(III)配合物为前体, 与PNP配体和$HBAr'_4$反应后用于催化乙烯齐聚. 该体系不使用任何烷基铝助剂, 并且能够达到Cr-PNP/MAO体系的1-己烯/1-辛烯选择性.

2.2 Cr-PCCP体系

除了PNP配体外, 萨索尔公司还研究了其他双磷配体. 与PNP配体类似的PCP配体的性能较差[80-81], 而PCCP配体则表现出较好的选择性和活性. 使用PCCP配体合成的Cr-PCCP配合物催化乙烯齐聚可以达到80%的1-己烯和1-辛烯总选择性(1-辛烯选择性约为60%), 活性最高可达7 200 000 g/(g_{Cr}·h)[80]. Cr-PCCP/MMAO-3A催化体系, 采用具有刚性芳香基骨架的PCCP配体, 在60 ℃和5.0 MPa反应条件下获得了56.8%的1-辛烯和13.0%的1-己烯, 反应活性为2 240 000 g/(g_{Cr}·h)(图17)[80].

随后, 研究人员还探索了碳桥长度、饱和度、取代基等条件对乙烯齐聚活性和选择性的影响[80,82-87]. SK能源(SK Energy)的研究人员使用双(二苯基膦基-1,2-二甲基乙烷)配体与$CrCl_3(THF)_3$合成的Cr-PCCP配合物, 经MMAO-12A活化后, 在25 ℃和3.0 MPa的反应条件下获得了77.4%的1-辛烯和9.4%的1-己烯, 反应活性为580 005 g/(g_{Cr}·h) (原文为30 158 kg/(mol_{Cr}·h), 图18)[82].

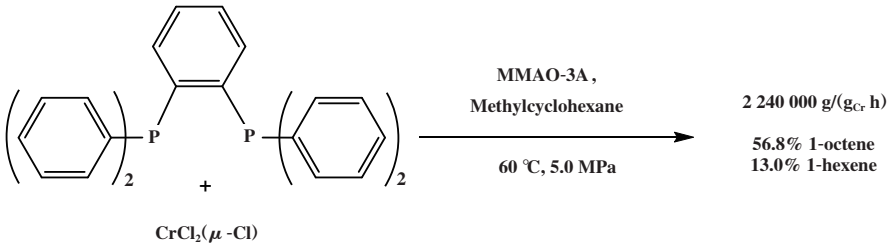


图17 Cr-PCCP乙烯选择性四聚催化体系

Fig.17 Cr-PCCP catalytic system for ethylene tetramerization

2.3 Cr-PNC$_3$NP体系

Shaikh等[88]使用$Ph_2PN(R)(CH_2)_nN(R)PPh_2$($n$ = 3, R = Me)二齿配体和$CrCl_2(THF)_2$合成的Cr-PNC$_3$NP配合物经DMAO活化后, 在80 ℃和4.0 MPa反应条件下获得了93.1%(原文为91%(摩尔分数))的高1-辛烯选择性, 反应活性为1833 g/(g_{Cr}·h) (图19). 且除1-己烯外该体系不产生聚乙烯等副产物. 对反应条件优化后, 以$CrCl_3(THF)_3$为铬源、以DMAO/Et_3Al为活化剂, 反应活性提高了近14倍, 1-辛烯选择性

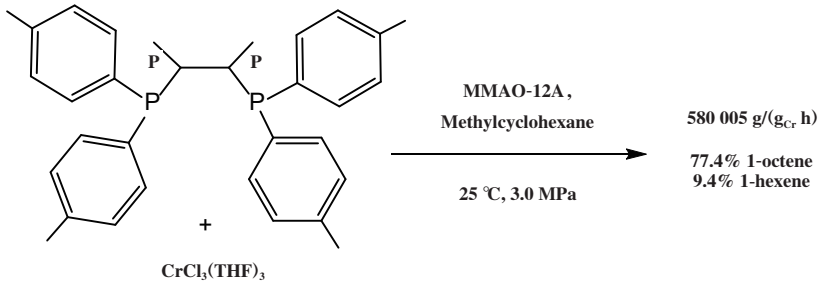


图18 Cr-PCCP乙烯选择性四聚催化体系

Fig.18 Cr-PCCP catalytic system for ethylene tetramerization

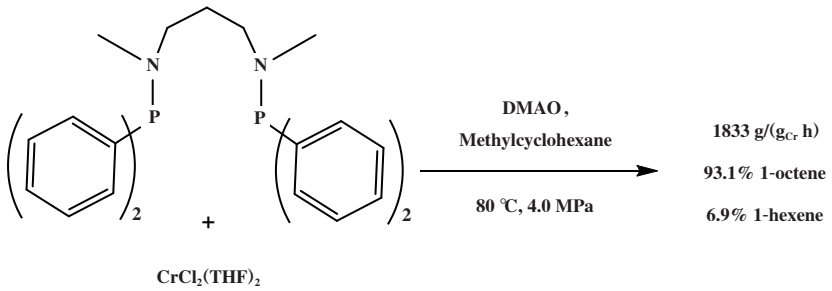


图 19　Cr-PNC$_3$NP 乙烯选择性四聚催化体系

Fig.19　Cr-PNC$_3$NP catalytic system for ethylene tetramerization

略微降低，但同时也生成了 4.1 g 聚乙烯．随后，Gao 等[89]使用 1,4-双(二苯基膦)哌嗪配体与 $CrCl_3(THF)_3$ 合成的配合物催化乙烯得到分布较宽的 α-烯烃．

2.4 Cr-PN 体系

Yang 等[90]使用混合 N, P-配体、$Cr(acac)_3$ 和 MAO 原位生成的催化剂进行乙烯低聚实验，发现使用二苯基磷吡啶配体合成的 Cr-PN 配合物，在 40 ℃和 5.0 MPa 反应条件下进行乙烯低聚反应时，1-辛烯选择性可达 73.7%，反应活性为 16 309 g/(g_{Cr}·h)(原文为 848 g/($mmol_{Cr}$·h)，图 20)．通过调整反应条件(温度、乙烯压力、催化剂负载量和配体/Cr 比)，可以调节 1-己烯/1-辛烯的摩尔比在 0.3~20 之间变化．

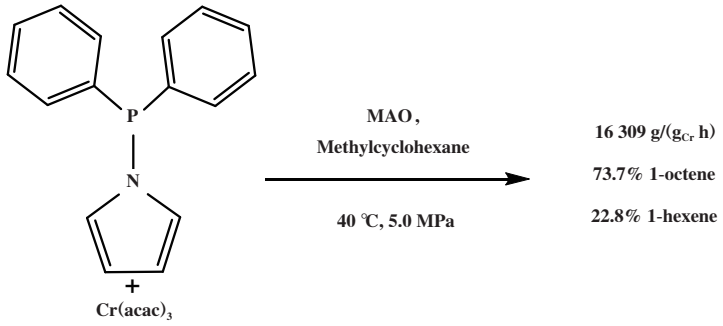


图 20　Cr-PN 乙烯选择性四聚催化体系

Fig.20　Cr-PN catalytic system for ethylene tetramerization

2.5 Cr-PCSiCP 体系

Zhang 等[91]使用 $Ph_2PCH_2Si(CH_3)_2CH_2PPh_2$ 硅桥连配体与 $CrCl_3(THF)_3$ 合成了一种 Cr-PCSiCP 配合物，经 DMAO/$AlEt_3$ 活化后，在 0 ℃和 1.0 MPa 反应条件下获得了 86.4% 的 1-辛烯，催化活性仅为 217 g/(g_{Cr}·h)(原文为 11 300 g/(mol_{Cr}·h)，图 21)．而降低铬源用量并在 45 ℃和 4.0 MPa 反应条件下，1-辛烯选择性降低至 78.4%，催化活性提高至 80 975 g/(g_{Cr}·h)

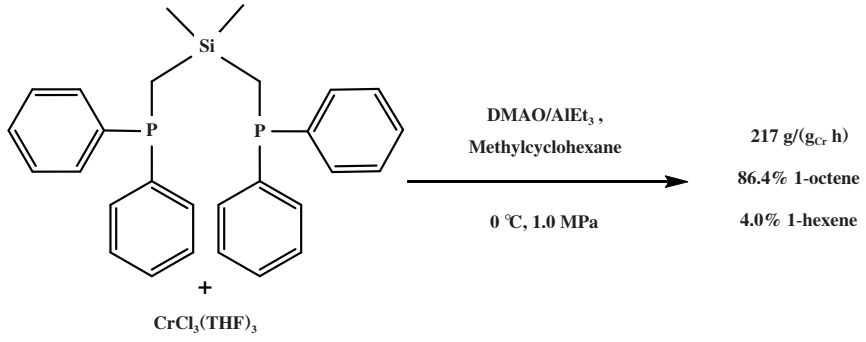


图 21　Cr-PCSiCP 乙烯选择性四聚催化体系

Fig.21　Cr-PCSiCP catalytic system for ethylene tetramerization

(原文为4 210 400 g/(mol_{Cr}·h)).

通过改变配体的骨架结构对Cr-PCSiCP体系进行调整，发现使用硅桥连的PCSiNP配体合成的配合物经DMAO/$AlEt_3$活化后，在15 ℃和4.0 MPa反应条件下获得了83.3%的1-辛烯，体系的催化活性为43 461 g/(g_{Cr}·h)(图22)[92].

Alam等[93]使用Si桥连的PPP配体合成的配合物经DMAO/$AlEt_3$活化后，在45 ℃和4.0 MPa反应条件下获得了71.0%的1-辛烯，体系的催化活性为3173 g/(g_{Cr}·h)(图23). 而采用减少一个连接Si和P的CH_2碳桥的配体也能达到72.0%的1-辛烯选择性.

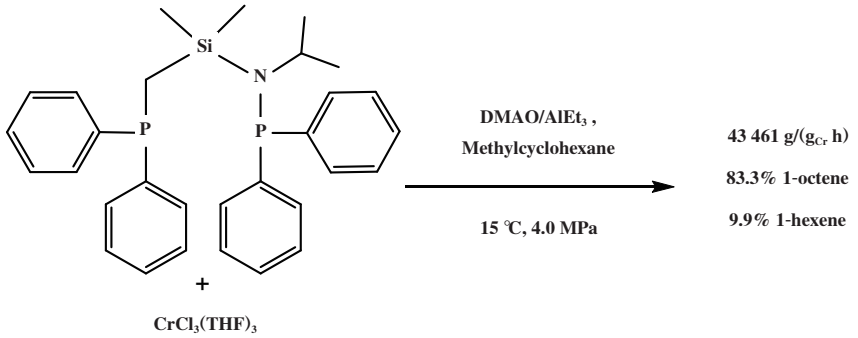


图22 Cr-PCSiNP乙烯选择性四聚催化体系

Fig.22 Cr-PCSiNP catalytic system for ethylene tetramerization

2.6 Cr-PCN体系

Radcliffe等[94]使用1-膦基甲亚胺配体(^{i}Pr)$_2$P-C(Ph)=N(*o*-Xyl)与Cr(EH)$_3$合成的一种Cr-PCN配合物经MMAO-3A活化后，以$ZnEt_2$为助剂，在60 ℃、4.0 MPa乙烯压力的反应条件下获得了96.7%的总1-己烯和1-辛烯选择性(1-己烯 = 35.6%, 1-辛烯 = 61.1%)，反应活性为491 000 g/(g_{Cr}·h)(图24).

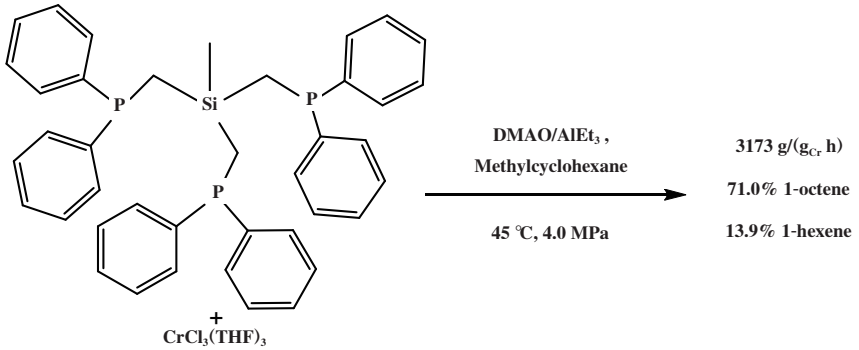


图23 Cr-(Si)PPP乙烯选择性四聚催化体系

Fig.23 Cr-(Si)PPP catalytic system for ethylene tetramerization

表2中按1-辛烯的选择性从高到低依次列出了典型的高选择性乙烯四聚催化体系. 其中1-辛烯选

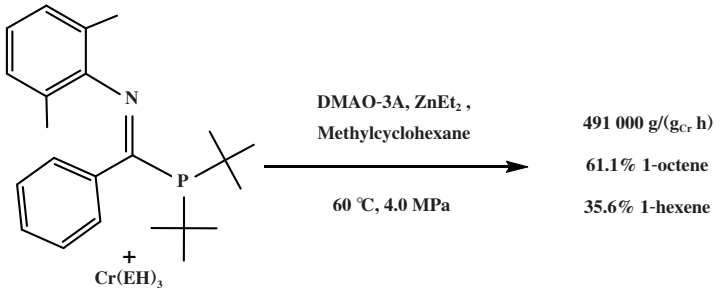
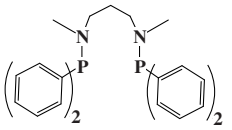
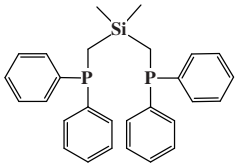
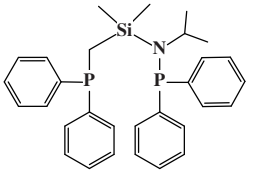
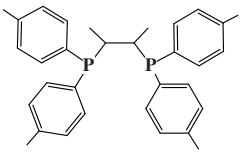
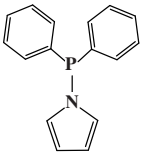
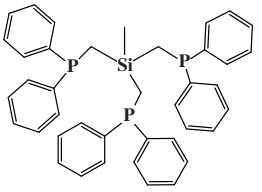
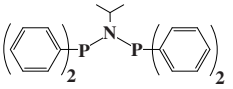
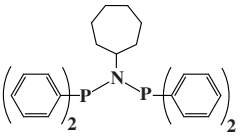
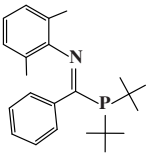
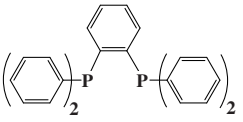


图24 Cr-PCN乙烯选择性四聚催化体系

Fig.24 Cr-PCN catalytic system for ethylene tetramerization

表 2 典型的铬系乙烯四聚催化体系

Table 2 Chromium-based catalysts for ethylene tetramerization.

Entry	Chromium compound	Ligand	Activator, Modificator	Solvent	Temperature /℃	Pressure /MPa	Activity /($g \cdot g_{Cr}^{-1} \cdot h^{-1}$)	1-C_6 /%	1-C_8 /%
1	$CrCl_2(THF)_2$		DMAO	Methylcyclohexane	80	4.0	1833	6.9	93.1
2	$CrCl_3(THF)_3$		DMAO/ $AlEt_3$	Methylcyclohexane	0	1.0	217	4.0	86.4
3	$CrCl_3(THF)_3$		DMAO/ $AlEt_3$	Methylcyclohexane	15	4.0	43 461	9.9	83.3
4	$CrCl_3(THF)_3$		MMAO-12A	Methylcyclohexane	25	3.0	580 005	9.4	77.4
5	$Cr(acac)_3$		MAO	Methylcyclohexane	40	5.0	16 309	22.8	73.7
6	$CrCl_3(THF)_3$		DMAO/ $AlEt_3$	Methylcyclohexane	45	4.0	3173	13.9	71.0
7	$Cr(acac)_3$		MAO	Toluene	45	4.5	272 400	11.9	67.5
8	$Cr(acac)_3$		MMAO-3A	Methylcyclohexane	60	4.5	737 536	14.7	67.4
9	$Cr(EH)_3$		MMAO-3A $ZnEt_2$	Methylcyclohexane	60	4.0	491 000	35.6	61.1
10	$CrCl_2(\mu\text{-}Cl)$		MMAO-3A	Methylcyclohexane	60	5.0	2 240 000	13.0	56.8

择性最高可达93.1%，但该条件下活性偏低，大多数活性较高的乙烯四聚催化体系的1-辛烯选择性在50%~80%之间．乙烯四聚催化体系的主要产物还包括1-己烯，两种产物的总选择性最高可达95%以上．Cr-PNP催化体系也是乙烯四聚催化体系中研究最为广泛的一类乙烯四聚体系，经过配体的设计可以调控Cr-PNP催化体系的选择性在乙烯三聚和乙烯四聚之间转换．

3 乙烯三聚/四聚反应机理

3.1 乙烯齐聚Cossee-Arlman机理

1964年，Cossee和Arlman提出Ziegler-Natta催化剂催化烯烃聚合反应机理，该机理认为活性中心Ti上存在一个空位，烯烃分子在空位与Ti中心配位后插入Ti烷基键进行链增长反应，链终止则通过β-H向Ti中心或者单体转移进行[95-96]．目前，Cossee-Arlman机理(图25)也通常被用来解释金属催化剂催化烯烃聚合及齐聚反应，其主要步骤包括：(1)金

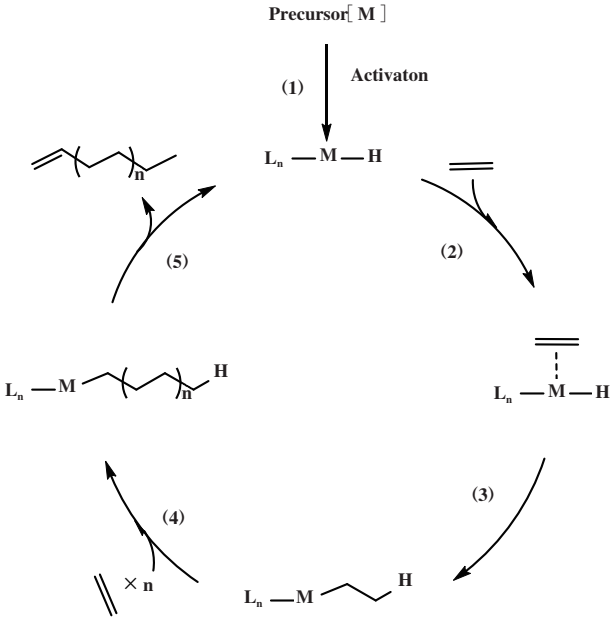


图25 乙烯聚合、齐聚的Cossee-Arlman反应机理

Fig.25 Proposed Cossee-Arlman mechanism of ethylene polymerization/oligomerization

属催化剂前体与助催化剂反应生成金属氢或者金属烷基活性中心；(2)一分子乙烯配位到金属活性中心的空位点；(3)乙烯插入金属-氢键或者金属-烷基键实现一个链节的增长，并形成新的空位点；(4)乙烯配位到金属中心并继续插入金属-碳键进行链增长；(5)通过β-H消除释放相应的α-烯烃，实现金属活性中心的再生．遵循Cossee-Arlman机理的催化体系的选择性取决于烯烃单体的插入速率与β-H消除速率的差异，若插入速率与消除速率相当则体系生成具有统计学分布的α-烯烃．

3.2 金属环机理

3.2.1 乙烯三聚金属环机理

1977年，Manyik等[97]首先提出在乙烯三聚成1-己烯的过程中存在铬环戊烷中间体．后来，Briggs等[98]提出在乙烯三聚过程中，关键中间体铬环戊烷进一步扩环为铬环庚烷，整个催化循环包括：(1)两个乙烯分子与铬中心配位；(2)配位乙烯氧化耦合产生铬环戊烷中间体；(3)第三分子乙烯插入铬环戊烷，扩环形成铬环庚烷；(4)铬环庚烷经历β-H转移释放1-己烯(图26)．金属环机理比传统的Cossee-

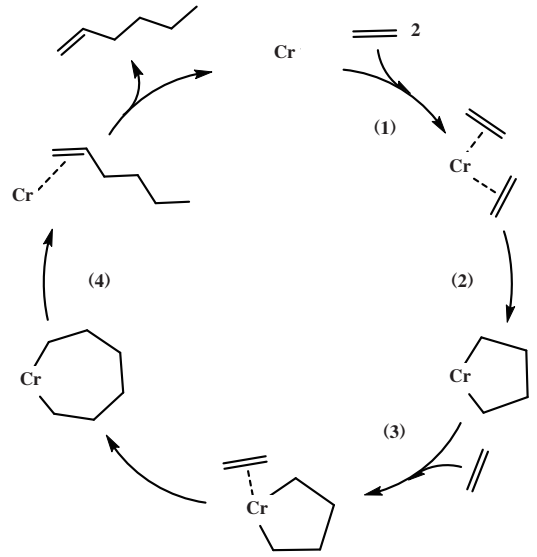


图26 乙烯三聚金属环机理

Fig.26 Proposed metallacycle mechanism of ethylene trimerization

Arlman聚合机理更能合理地解释乙烯三聚反应对1-己烯的高选择性．根据金属环机理，金属环庚烷中间体的扩环反应和β-H转移反应的竞争决定了体系1-己烯的选择性．

关键金属环中间体的分解经历一步路径或两步路径(图27)．一步路径即协同的β-H转移，β-H在铬中心的协同作用下直接转移至α'-C，然后发生还原消除得到α-烯烃．两步路径中，β-H先转移至金属中心形成金属烯基氢配合物，再发生还原消除生成α-烯烃．由于金属五元环结构中的几何限

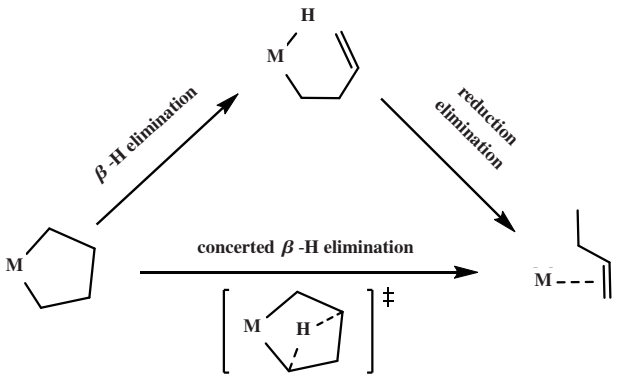


图 27　以铬环戊烷为例的金属环中间体分解的一步路径和两步路径

Fig.27　The decomposition of the key metallacycle intermediates undergoes a one-step process or follows a two-step pathway

制，理论计算中无法定位到金属环戊烷通过协同的 β-H 转移进行环分解的过渡态，因此金属五元环中间体遵循两步法氢转移进行开环反应[45,99-100]. 而金属环庚烷通过一步路径进行环分解的能垒低于两步路径的环分解能垒，表明 1-己烯经协同的 β-H 转移路径生成[27,50,99-103].

金属环机理得到了氘同位素标记等实验的支持[104-110]. Emrich 等[104]使用 $(Me_2NC_2H_4C_5Me_4)Cr(Cl)_2$ 与乙烯反应获得铬环戊烷和铬环庚烷，且铬环庚烷分解释放 1-己烯. 在乙烯和过量三甲基膦存在下，用活性 Mg 还原 $CpCr(THF)Cl_2$ 获得了单乙烯铬配合物 $(\eta^2\text{-}CH_2{=}CH_2)Cr$. 最近，Chabbra 等[108]通过原位电子顺磁共振光谱与催化剂前体和底物的选择性同位素标记，在实验中观察到了 Cr(I) 双乙烯物种 $[Cr(C_2H_4)_2(CO)_2(PNP)]^+$. 氘同位素标记实验是以等摩尔混合的 C_2D_2 和 C_2H_2 进行乙烯聚合实验，若遵循金属环机理则会获得 C_6D_{12}、$C_6D_8H_4$、$C_6D_4H_8$、C_6H_{12}；若遵循 Cossee-Arlman 机理则会获得 H 或 D 数量为奇数的同位素异构体. Agapie 等[105]以 1∶1 混合的 C_2D_2 和 C_2H_2 为原料，采用合成的 Cr-PNP^{OMe} 催化剂进行多次实验，均获得了比例为 1∶3∶3∶1 的同位素异构体 C_6D_{12}、$C_6D_8H_4$、$C_6D_4H_8$、C_6H_{12}. 以上实验结果均支持乙烯三聚生成 1-己烯遵循金属环反应机理.

3.2.2　乙烯四聚金属环机理

Overett 等[106]使用 Cr-PN(^{i}Pr)P 乙烯四聚催化剂进行氘同位素标记实验，其结果也支持用金属环机理来解释乙烯四聚反应. 乙烯四聚金属环机理从铬环庚烷中间体开始：(1) 第四分子乙烯配位到铬环庚烷中间体的铬中心；(2) 乙烯迁移插入铬环庚烷中间体形成铬环壬烷中间体；(3) 铬环壬烷中间体通过一步法 β-H 转移释放 1-辛烯(图 28). 根据金属环机理，

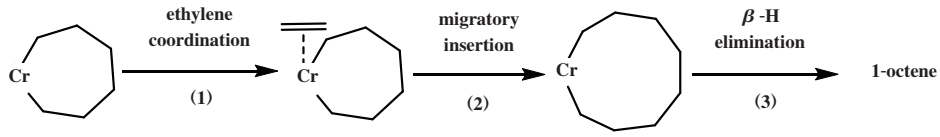


图 28　乙烯四聚金属环机理

Fig.28　Proposed metallacycle mechanism of ethylene tetramerization

铬环庚烷中间体进行环增长与环分解反应之间的竞争决定了体系 1-辛烯的选择性.

3.2.3　铬金属中心氧化态和自旋态

Agapie 等[105]针对 Cr-PNP^{OMe} 催化剂催化乙烯三聚的实验研究发现，采用 $NaB[C_6H_3(CF_3)_2]_4$ 活化后的 Cr-PNP^{OMe} 催化体系表现出较高的乙烯三聚活性，这一实验现象表明乙烯三聚催化体系的活性中心为铬阳离子中心. Qi 等[100]基于菲利普斯催化体系设计了 10 种可能的活性中心模型，使用密度泛函理论研究了菲利普斯催化体系中 DMP 在乙烯聚合反应中的作用，发现阳离子模型的计算结果与实验结果相符. 对于金属环机理中铬氧化态的问题，大多数实验和计算研究都支持乙烯三聚 / 四聚催化体系的铬中心遵循 Cr(I)/Cr(III) 循环[20,27,44,102-103,111-115]. Yang 等[20]研究了菲利普斯体系催化乙烯三聚的金属环机理，发现 Cr(I)/Cr(III) 循环更能合理解释该体系的 1-己烯选择性. Rucklidge 等[111]使用 PNP-型配体制备了 Cr(0) 和 Cr(I) 羰基配合物进行乙烯齐聚实验，发现 Cr(I) 配合物 / 烷基铝可以催化乙烯四聚获得 1-辛烯，而 Cr(0) 配合物在相同反应条件下无活性. 这一发现支持了 Cr(I) 和 Cr(III) 催化循环. 针对 Cr-SNS 体系，Yang 等[102]研究了金属活性中心的氧化态，计算表明六重态的双乙烯配位的 Cr(I) 物种进行氧化耦合形成铬环戊烷之前会经过最小能量交叉点

(MECP)转变为四重态基态. 双乙烯配位的Cr(I)物种从六重态到四重态的自旋交叉降低了形成铬环戊烷的能垒, 表明乙烯三聚反应路径上各中间体和过渡态的铬中心氧化态在Cr(I)和Cr(III)之间变化. 此外, Monillas等[112]使用合成的Cr(I)-N, N配合物在不加助催化剂的条件下催化乙烯三聚生成1-己烯, 并且发现单核Cr(III)环戊二烯与乙烯聚合也能生成1-己烯, 这些结果同样支持Cr(I)/Cr(III)循环.

采用DFT计算方法研究铬中心的氧化态和自旋态, 其计算结果通常取决于计算水平的选择. McGuinness等[44]针对Cr-PNP催化剂开展了基于不同理论方法的基准测试, 发现M06L泛函比较适用于铬系催化乙烯齐聚反应的计算. 作者使用M06L泛函的计算结果表明Cr(I)/Cr(III)循环比Cr(II)/Cr(IV)循环更可能发生, 并且催化循环中包含从六重态到四重态的自旋交叉反应. 此外, Cr(II)/Cr(IV)循环也得到了一些研究者的支持[41,116-118]. Rensburg等[117]使用DFT方法研究了菲利普斯催化剂催化乙烯三聚的反应机理, 计算结果表明Cr(II)和Cr(IV)物种的基态是三重态, 并且该催化循环中无自旋交叉发生. Bhaduri等[118]使用DFT方法研究了中性和阳离子物种的催化循环, 发现阳离子$[Cr(II)Cl_2]^+$模型的Cr(II)/Cr(IV)金属环路径是最有利的路径, 并且所有结构表现为单重态基态. 与Cr(I)/Cr(III)催化循环相比, Cr(II)/Cr(IV)催化循环并未得到学术界的一致认可.

3.2.4 乙烯三聚反应中的C_{10}副产物

Cr-PNP^{OMe}催化剂催化乙烯三聚可以生成高达90%的1-己烯, 该反应还生成10%左右的C_{10}副产物[25]. Do等[119]使用Cr-PNP^{OMe}催化剂进行乙烯和α-烯烃的共齐聚来研究乙烯三聚反应中C_{10}副产物的形成机理. 实验结果表明, Cr-PNP^{OMe}催化乙烯和1-己烯聚合可以生成94%的C_{10}产物. 作者使用GC/MS分析了C_{10}产物并提出C_{10}产物的形成路径(图29), 主要步骤包括: (1)乙烯配位并插入铬环戊烷生

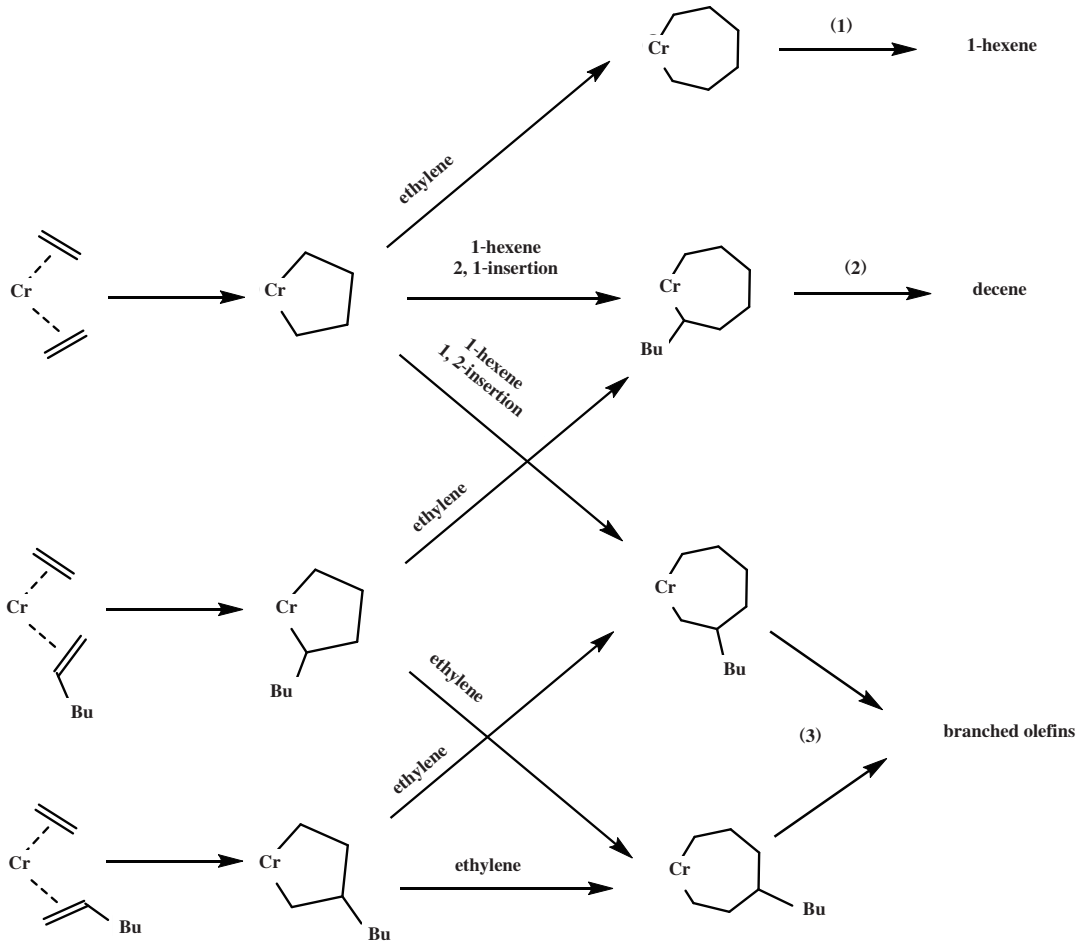


图29 乙烯三聚反应的C10副产物的生成路径

Fig.29 C_{10} Alkenes formed via co-trimerization of ethylene and 1-hexene

成铬环庚烷，随后释放1-己烯；(2)1-己烯配位并以2,1-插入铬环戊烷或者乙烯从低位阻Cr—C键一侧进行配位并插入2-丁基铬环戊烷后，经β-H消除生成癸烯；(3)1-己烯配位并以1,2-插入铬环戊烷，或者乙烯配位并插入2-丁基铬环戊烷或者3-丁基铬环戊烷后，经β-H消除生成含有支链的C_{10}烯烃. 作者认为乙烯三聚生成1-己烯与乙烯/1-己烯共聚相互竞争. Zilbershtein等[120]使用菲利普斯催化体系研究了乙烯三聚反应中副产物癸烯的形成，作者通过NMR和GC/MS确定反应产物中存在图29中所预期的乙烯与1-己烯共三聚生成的癸烯和支链烯烃，该研究结果支持上述C_{10}副产物的形成路径. 此外，Gong等[48]通过DFT方法研究了Cr-PNP^{OMe}体系的乙烯与1-己烯共三聚机理，计算得到的C_{10}产物分布与实验结果一致.

3.2.5 乙烯四聚反应中的C_6副产物

Overett等[106]使用Cr-PNP/MMAO体系催化乙烯四聚除获得了70%左右的1-辛烯外，还发现以1∶1的比例形成的甲基环戊烷和亚甲基环戊烷两种副产物. 作者提出铬环庚烷重排为铬甲基环戊基氢配合物主要有协同反应和分步反应(包括β-H转移和插入成环)两种途径. 铬甲基环戊基氢配合物生成甲基环戊烷和亚甲基环戊烷也可能存在两种方式：(1)还原消除产生甲基环戊烷或β-H转移生成亚甲基环戊烷；(2)通过双金属歧化机理生成两种环状副产物(图 30). 作者认为双核机理可以解释实验中观察到的1∶1比例的甲基环戊烷和亚甲基环戊烷. Britovsek等[45]使用DFT方法研究了Cr-PNP体系，计算发现乙基己烯基铬中间体通过己烯基尾部插入形成乙基甲基环戊基铬中间体的能垒低于通过C—C还原消除形成1-辛烯和β-H反向转移形成1-己烯的能垒，且乙基甲基环戊基铬中间体的β-H转移生成甲基环戊烷和亚甲基环戊烷的能垒仅差5.9 kJ/mol，符合实验观察到的1∶1的产率. Zhang等[91]在Cr/硅桥连的双磷配体体系催化的乙烯聚合反应的产物中观察到了非1∶1比例的甲基环戊烷和亚甲基环戊烷，作者认为双金属歧化机理不能解释此现象，且形成甲基环戊烷和亚甲基环戊烷的活性中心可能与乙烯齐聚活性中心不同. Boelter等[86]采用多种双磷配体进行乙烯齐聚的实验结果表明，甲基环戊烷与亚甲基环戊烷的比率随配体的改变在1.25~5.00之间变动，因此作者支持通过还原消除产生甲基环戊烷或β-H转移生成亚甲基环戊烷.

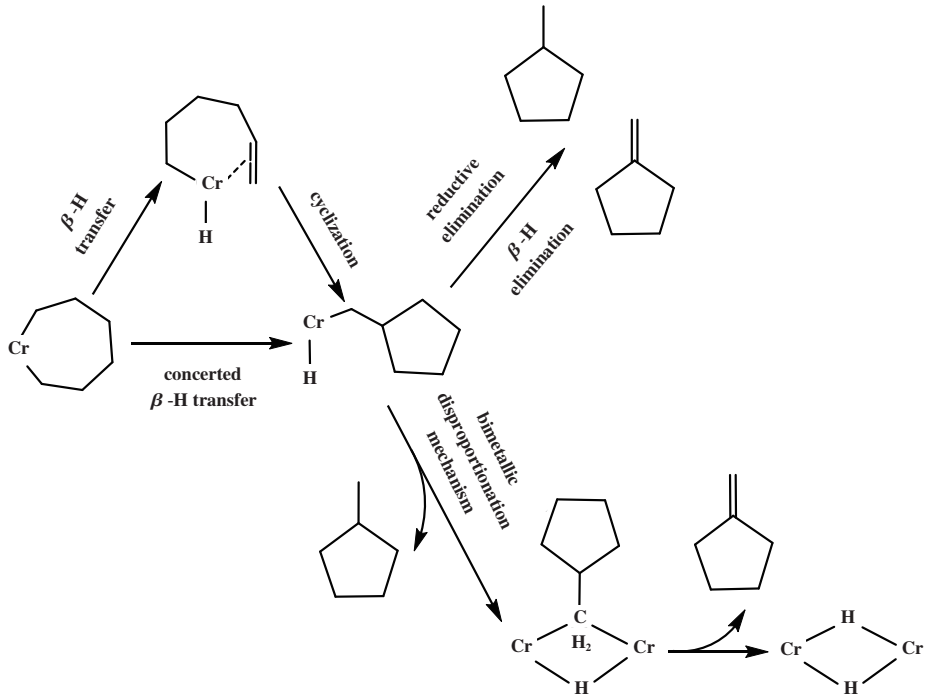


图30 副产物甲基环戊烷和亚甲基环戊烷的可能路径

Fig.30 Proposed mechanisms for the formation of methylcyclopentane and methylenecyclopentane

3.3 乙烯四聚双金属机理及双配位机理

Wilke等[121]提出炔烃选择性四聚生成环辛四烯路径中存在双金属环戊二烯中间体. 在此启发下，

Peitz等[122]提出了乙烯四聚双金属机理. 乙烯四聚双金属机理的关键中间体是双金属铬环戊烷, 其反应步骤包括:(1)双金属配合物吸附4分子乙烯配位到两个金属中心;(2)随后两个金属中心上的两分子乙烯氧化耦合形成两个金属环戊烷;(3)两个五元环单元C—C偶联形成更大的双金属十元环;(4)最后双金属十元环通过β-H转移释放1-辛烯(图31). 双金属机理避开了1-己烯的形成, 而直接经由双金属十元环中间体释放1-辛烯. 乙烯四聚双金属机理将乙烯三聚和四聚催化体系之间的选择性差异归因于铬源与配体之间形成双金属配合物的能力.

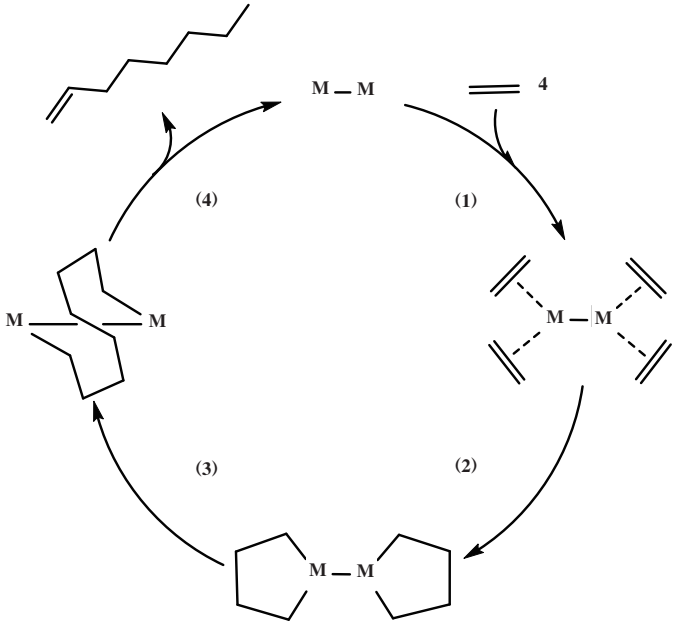


图31 乙烯四聚双金属机理

Fig.31 Proposed binuclear mechanism for ethylene tetramerization

Hirscher等[110]通过同位素标记实验对乙烯四聚双金属机理进行了评估. 作者认为在乙烯双金属机理中, 选择性由金属环戊烷的C—C偶联反应与乙烯插入的相对速率决定. 两者都不涉及C—H或者Cr—H键的形成或裂解, 因此不存在一级同位素效应. 然而实验获得的KIE=3.0 ± 0.3(同位素效应)表明该反应是一级同位素效应控制的反应. 该实验结果并不支持乙烯四聚双金属机理.

Britovsek等[45]提出双配位机理来解释Cr-PNP催化体系催化乙烯齐聚中1-辛烯的形成(图32). 双配位机理反应路径包括:(1)一分子乙烯在铬环戊烷

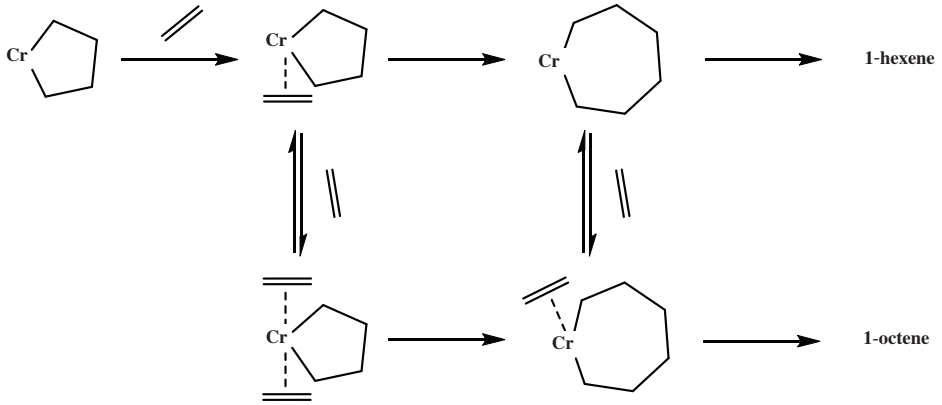


图32 乙烯四聚双配位机理

Fig.32 Proposed double-coordination mechanism for ethylene tetramerization

上进行配位(单配位)后形成单乙烯铬环戊烷中间体，随后经过迁移插入形成铬环庚烷，再通过 β-H 还原消除释放1-己烯；(2)两分子乙烯在铬环戊烷中间体上进行配位(双配位)形成双乙烯铬环戊烷中间体，随后经过两分子配位乙烯的连续迁移插入形成铬环壬烷，再经过还原消除生成1-辛烯. 双配位机理中反应经双乙烯铬环戊烷中间体形成1-辛烯，而1-己烯主要经单乙烯铬环戊烷中间体形成. 催化反应的选择性取决于单配位路径和双配位路径之间的竞争.

4 结论

自2002年以来，工业界和学术界对铬系乙烯选择性三聚、四聚催化体系的研发热度持续增加. 乙烯选择性三聚催化剂，如菲利普斯铬系催化体系、Cr-PNP体系、Cr-SNS体系等，对1-己烯的选择性可达99.9%. 乙烯四聚催化剂，如Cr-PNP体系、Cr-PCCP体系等，对1-辛烯选择性普遍在50% ~ 80%之间. 调控体系的1-己烯、1-辛烯选择性也是设计开发高效乙烯三聚/四聚反应催化剂的一大难点，尤其是提高1-辛烯的选择性. $Cr(EH)_3$/DMP/二乙基氯化铝/三乙基铝乙烯三聚催化体系早在2003年就由雪佛龙菲利普斯化工公司成功实现工业化生产. 2014年，萨索尔公司采用Cr-PNP催化体系进行乙烯四聚的工业化试验. 国内大庆石化公司日前已完成5000 t/a 1-己烯的工业化试验，其乙烯四聚工业试验项目也在建设中. 乙烯三聚/四聚工业化面临的另一个难题是减少聚乙烯的形成，但目前对乙烯三聚/四聚反应中聚乙烯的形成机理尚未有定论[123-124]. 为了加快乙烯三聚/四聚催化剂的工业化应用，我们仍需进一步对乙烯齐聚的反应机理、活性中心、金属氧化态以及助催化剂等方面进行更为深入的研究.

乙烯选择性三聚/四聚领域仍存在诸多挑战与机遇. 一方面，随着现代实验表征技术的发展，科研工作者可以原位追踪催化活性中心上发生的反应动态；另一方面，高性能计算机和算法的发展也促进了以机器学习和密度泛函理论为代表的数学统计和分子模拟方法在新型催化剂筛选和设计领域的应用. 通过结合实验表征和理论计算对催化反应机理进行精准解析，必将加速新型催化剂的开发进程，最终实现乙烯高选择性三聚、四聚的工业规模生产.

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Selective Ethylene Tri-/tetramerization Catalyzed by Chromium-Based Catalysts and Oligomerization Mechanism

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Abstract: Linear alpha olefins are important chemical raw materials and intermediates, which are used in the production of polyethylene, synthetic lubricants, surfactants, etc. 1-hexene and 1-octene are used as co-monomers to enhance the performance of linear low-density polyethylene (LLDPE) and high-density polyethylene (HDPE), which are widely used in the production of films, tubes and other high-grade materials. About half of linear alpha olefins (C_4~C_8) are consumed by polyethylene manufacturers. Therefore, both academia and industry have long been devoting to develop effective catalysts for the selective oligomerization of ethylene into 1-hexene and 1-octene. Chromium catalysts are believed to be advantageous compared to other catalysts. In this review, the chromium-based catalysts with excellent catalytic performance for ethylene tri-/tetramerization are summarized, including the Phillips catalyst system for ethylene trimerization, the well-studied Cr/PNP catalysts for ethylene tri-/tetramerization, and other catalysts baring N-, P-, Si-based ligands. The catalyst development can be accelerated trough mechanistic understanding, including the linear Cossee-Arlman mechanism, the mononuclear metallacycle mechanism, the binuclear metallacycle mechanism, the double-coordination mechanism and other mechanisms. With the mechanistic understandings on the chromium active oxidation states, the spin multiplicity of the catalyst systems, the electronic and steric effects of the ligands, the multiple conformers of the key intermediates, and other crucial factors, this catalyst system will surely become more and more mature through close collaboration between industrial and academia, and will finally be realized in industrial application for mass production of alpha olefins with tunable high selectivity.

Key words: ethylene trimerization; ethylene tetramerization; 1-hexene/1-octene; chromium catalyst; mechanism