Seminar

低温低压下廉价金属催化的聚烯烃催化高值化降解

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导　师：杨俊锋 青年研究员

张俊良 教授

日　期：2024-10-11

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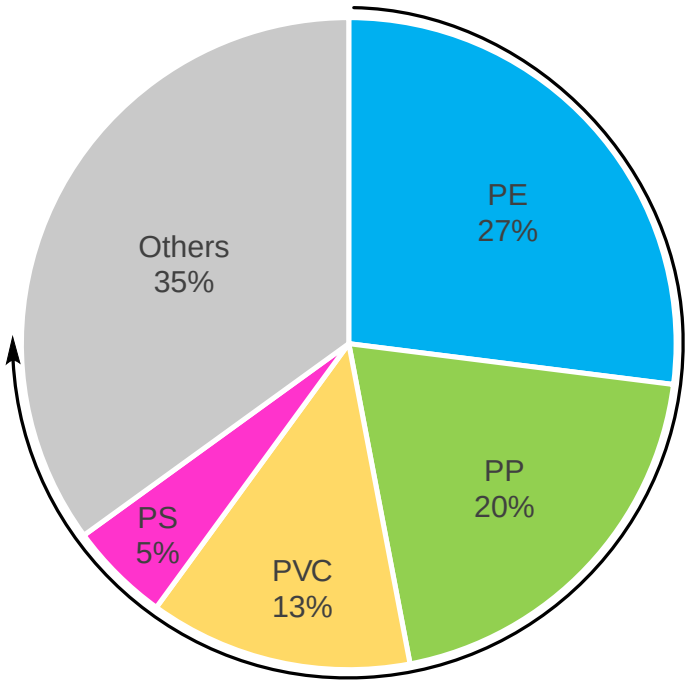
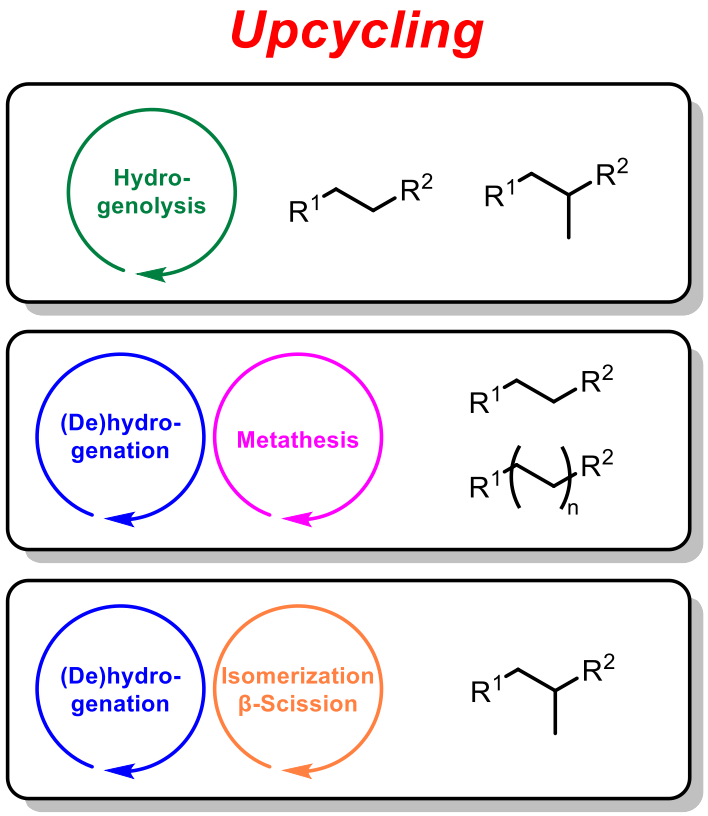
1. 背景
2. 氢解策略
3. 烷烃复分解策略
4. 裂解-串联反应策略
5. 总结与展望





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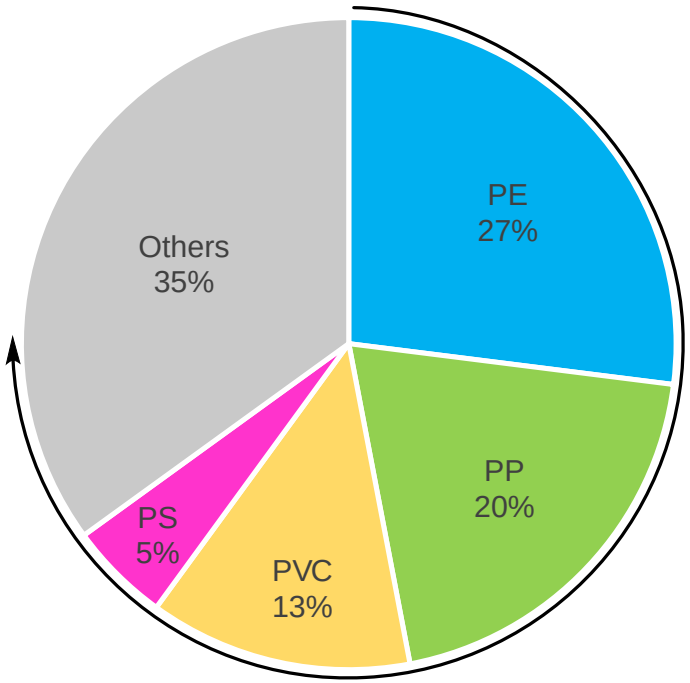
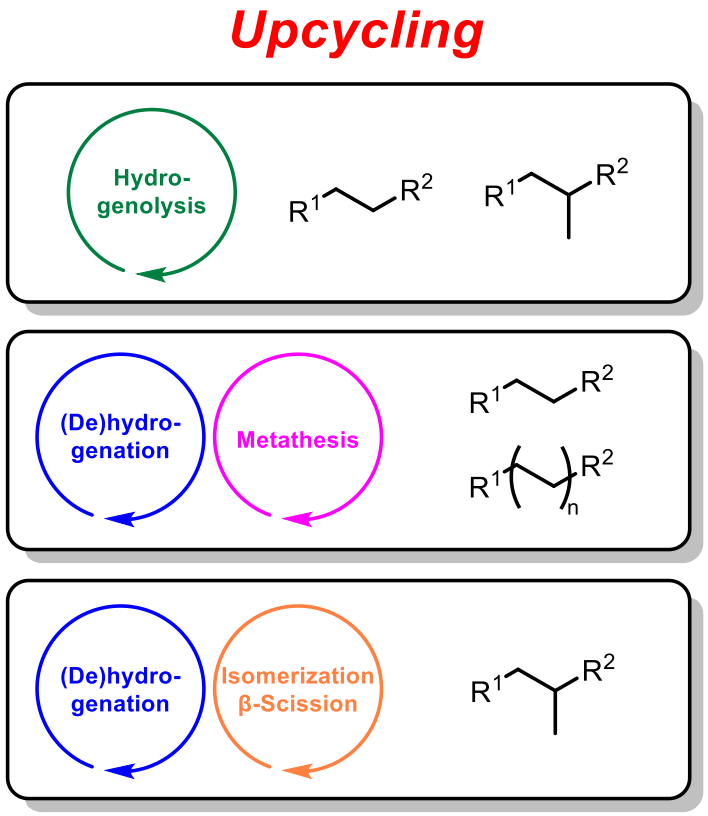
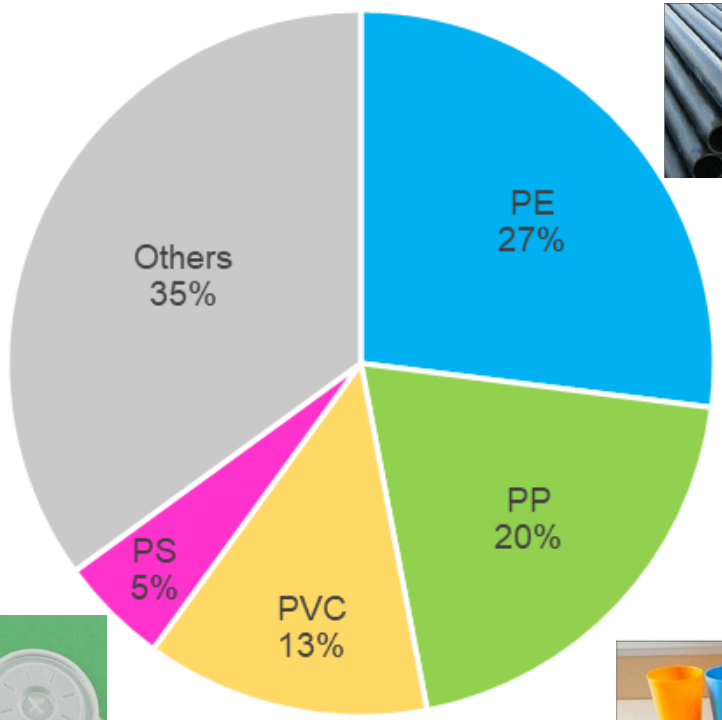




背景：聚烯烃与现代社会

塑料制品占比（2021）



优点	缺点
廉价	使用周期短
稳定	自然分解难

Waste to Waste!

49%

填埋

19%

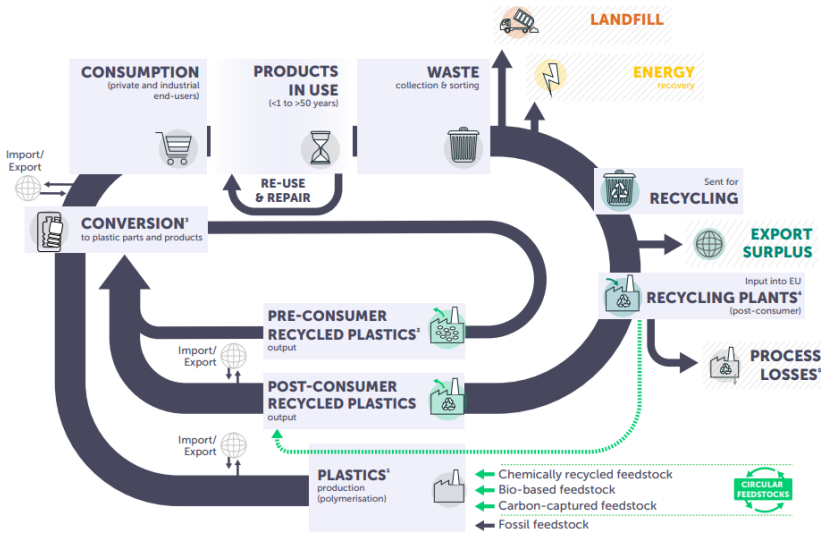
焚烧

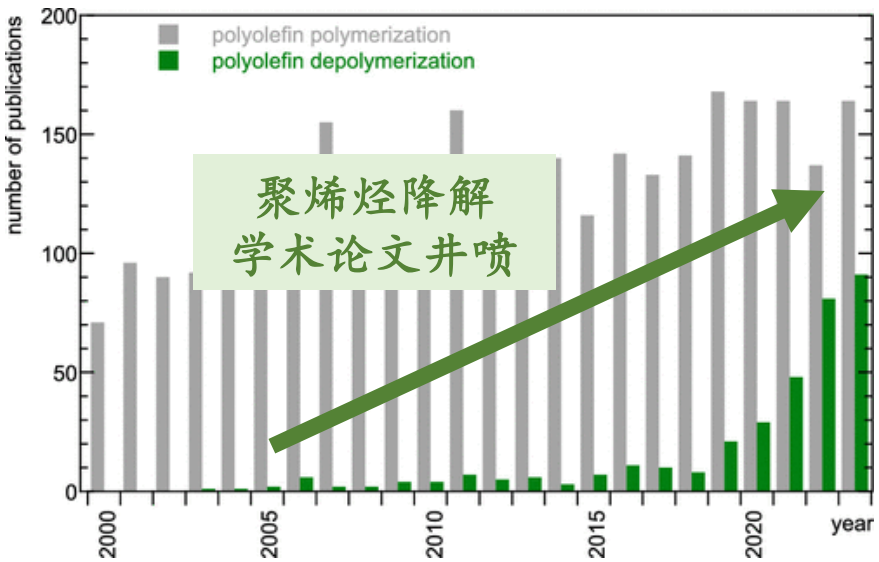
22%

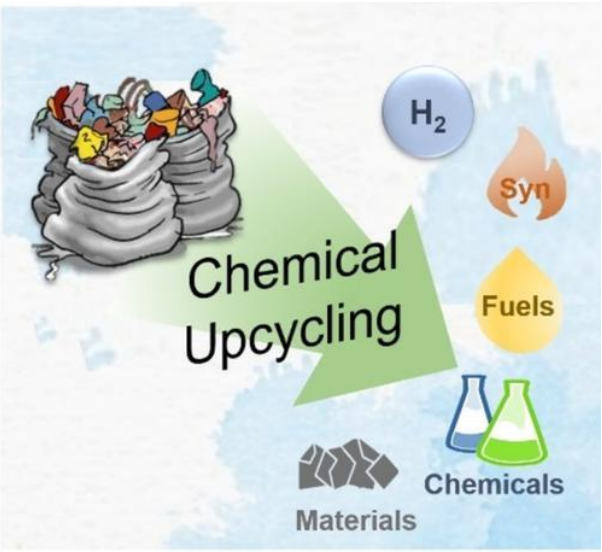
泄漏

Lange, J.-P. *ACS Sustain. Chem. Eng.* **2021**, *9*, 15722-15738.
Ye, E.; *et al*. *ACS Sustainable Chem. Eng.* **2024**, *12*, 1769-1796.
Plastics Europe. *Plastics-The Facts 2022*, Plastics Europe: Brussels, **2022**.

背景：备受关注的聚烯烃回收与降解







传统回收

Recycling

- **机械法：**不改变聚合物主链结构
- **化学法：**将聚合物降解为单体和/或寡聚物
- **混合法**

聚烯烃回收降解

Waste to Product

技术手段革新？

环境友好产业？

经济效益提高？

实际需求迫切！

高值化

Upcycling

- **技术需求：**温和、高效、清洁
- **经济效益：**高于单体或原材料

Getzler, Yutan D. Y. L.; *et al*. *Nat. Rev. Mater.* **2020**, *5*, 501-516.
Anastasaki, A.; *et al*. *Chem. Sci.* **2024**, *15*, 832-853.
Scott, S. L.; *et al*. *Chem. Rev.* **2024**, *124*, 9457-9579.

背景：聚烯烃的高值化

聚烯烃高值化

高值化核心：面向工业化

产品经济价值高于单体或原材料

产品具有特定（商业）用途

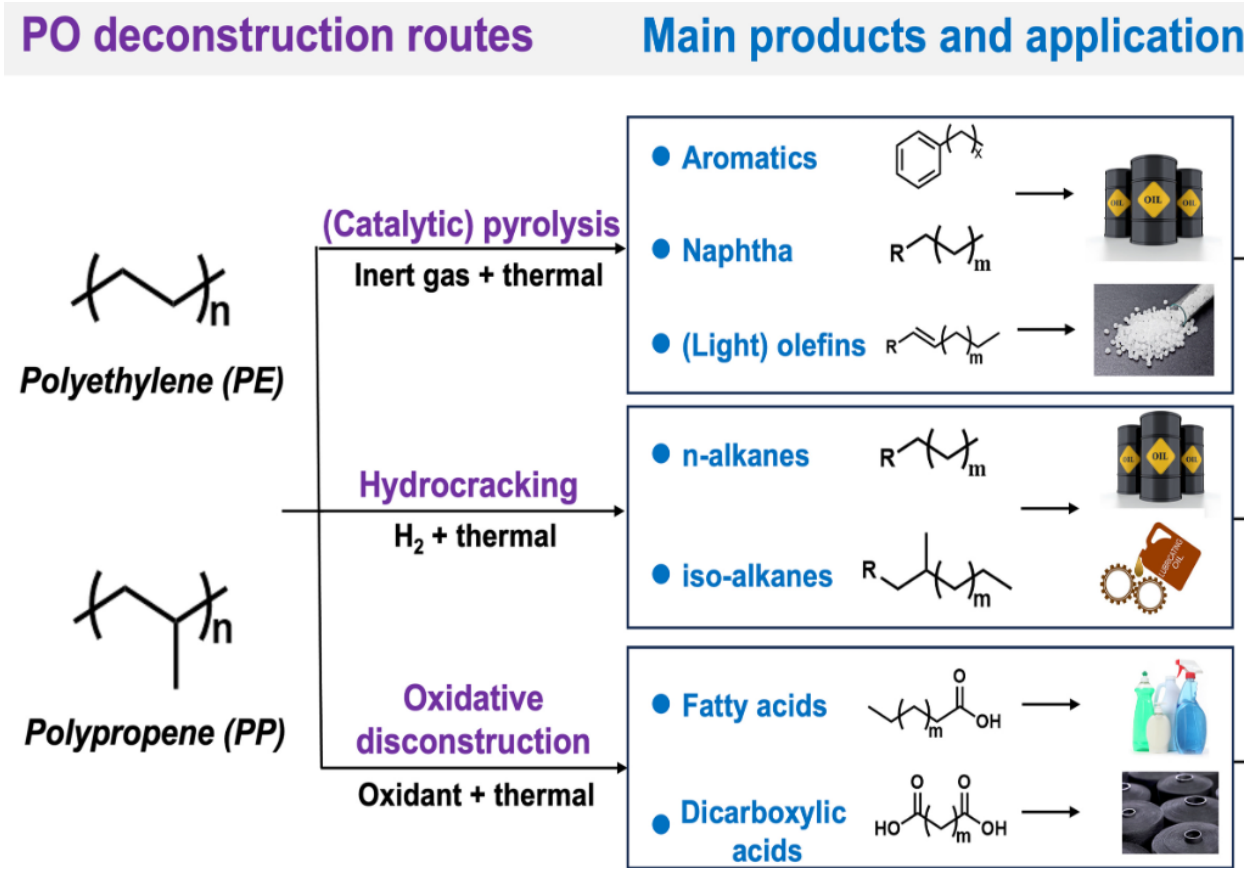
反应条件和操作工况温和

反应选择性好

产物分布窄

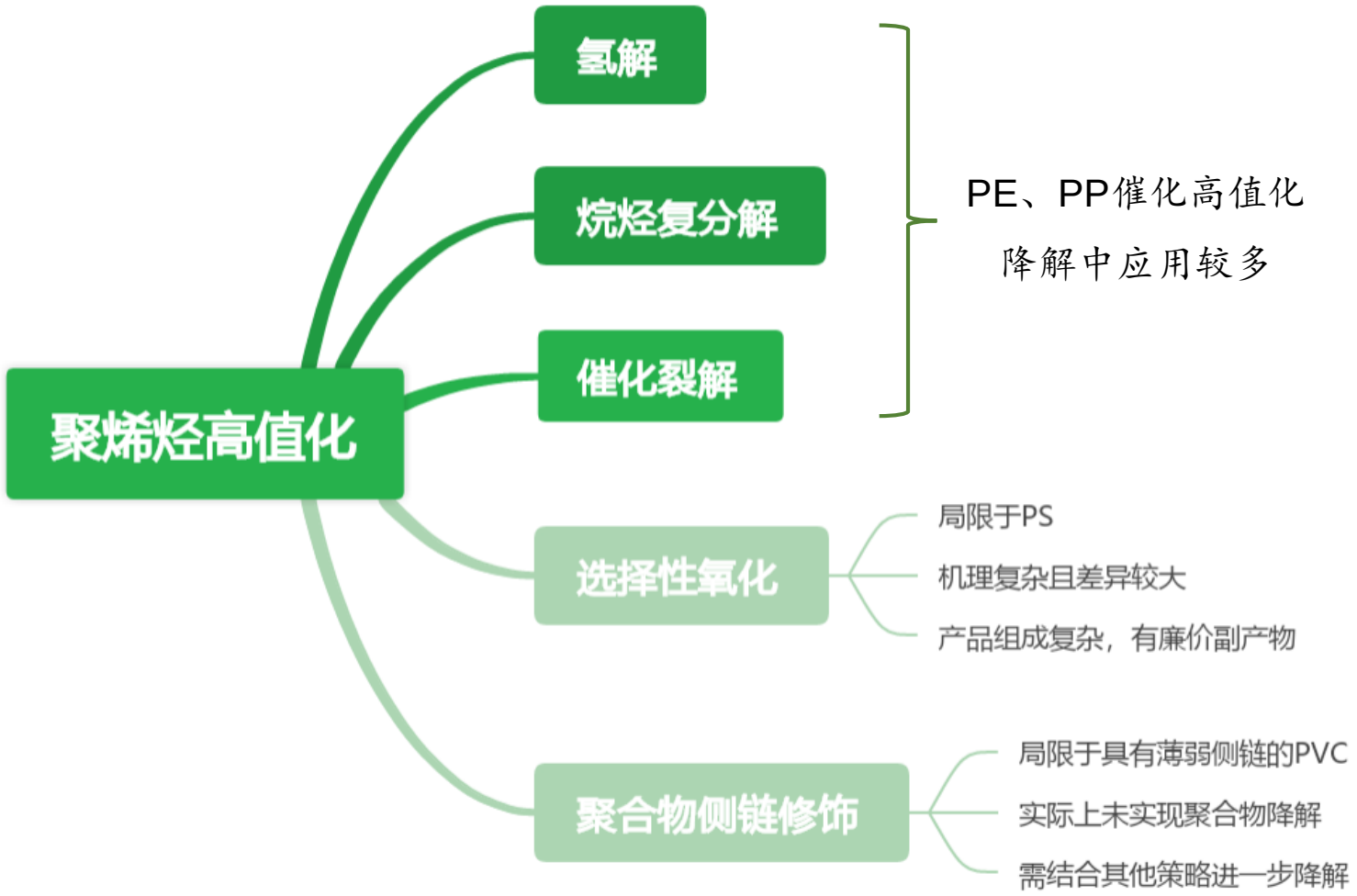
高值化基础：面向基础研究

催化剂的催化效率和选择性

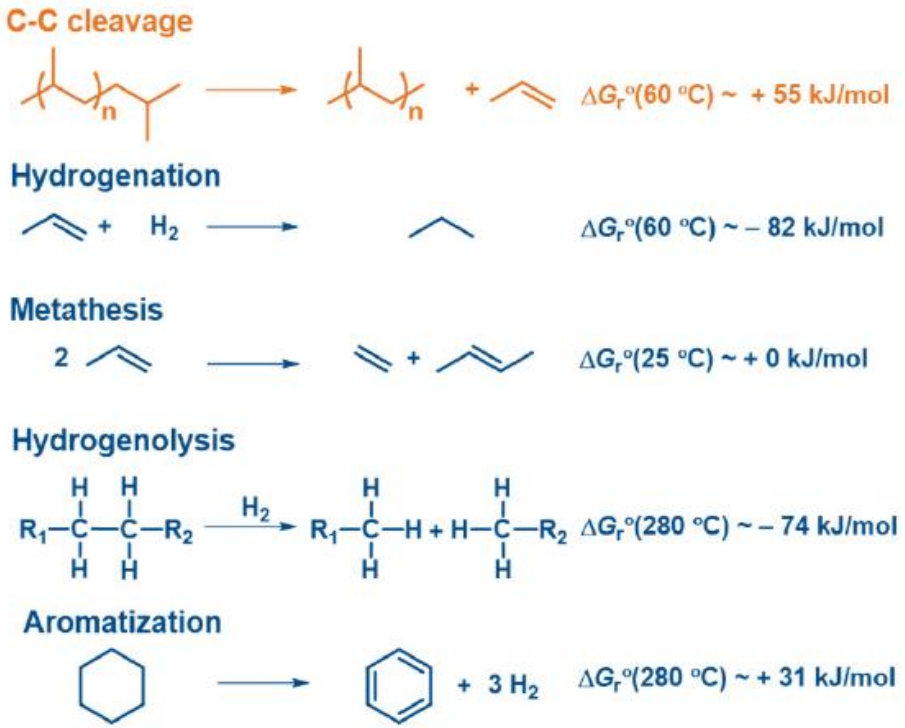


Getzler, Yutan D. Y. L.; *et al*. *Nat. Rev. Mater.* **2020**, *5*, 501-516.
Anastasaki, A.; *et al*. *Chem. Sci.* **2024**, *15*, 832-853.
Scott, S. L.; *et al*. *Chem. Rev.* **2024**, *124*, 9457-9579.
Huang, Z.; *et al*. *CCS Chem.* **2024**, *6*, 313-333.

背景：聚烯烃高值化的难点与挑战



- **难点：** C(sp^3)-C(sp^3)键吸热断裂在热力学上非常不利
- **解决策略：** 将C-C键吸热断裂与放热反应耦合

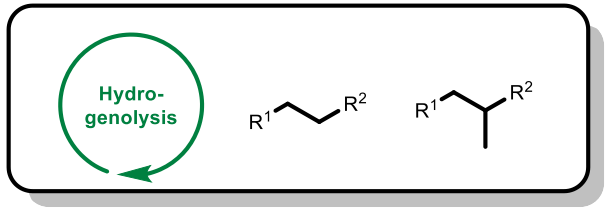


Beckham, G. T.; *et al*. *Nat. Catal.* **2021**, *4*, 539-556.
Beckham, G. T.; *et al*. *Annu. Rev. Chem. Biomol. Eng.* **2022**, *13*, 301-324.
Lercher, J. A. *et al*. *Science* **2023**, *379*, 807-811.
Scott, S. L.; *et al*. *Chem. Rev.* **2024**, *124*, 9457-9579.

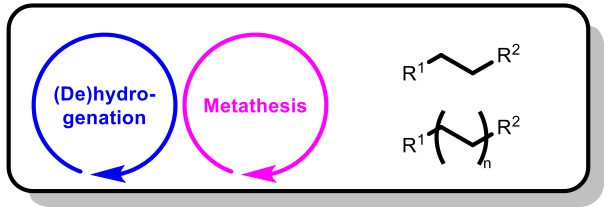
背景：聚烯烃高值化的现状与机遇

聚烯烃高值化

- 氢解
- 烷烃复分解
- 催化裂解
- 选择性氧化
- 聚合物侧链修饰



稀有金属cat. = [W], [Ru], [Rh], [Pt]
廉价金属cat. = [Zr], [Ta], [Co], [Ni]



稀有金属cat. = [W], [Re], [Ru], [Ir], [Pd], [Pt]
廉价金属cat. = [Zr], [Ta]

稀有金属cat. = [Mo], [W], [Pd], [Pt]
廉价金属cat. = [Zr], [Ta], [Co], [Ni]
非过渡金属cat. = Si/Al zeolite, Lewis-acidic IL

主流策略的局限性：

- 多使用**贵金属**催化剂
- 反应温度普遍需要**高温**（>200 ℃）
- 氢解、选择性氧化需要**高压**（≥5 bar）气体参与

汇报聚焦：

- 廉价金属催化剂
- 低温（<200 ℃）
- 低压（近常压，≤2 bar）
- 挑战最大的PE、PP

Scott, S. L.; *et al*. *Chem. Rev.* **2024**, *124*, 9457-9579.

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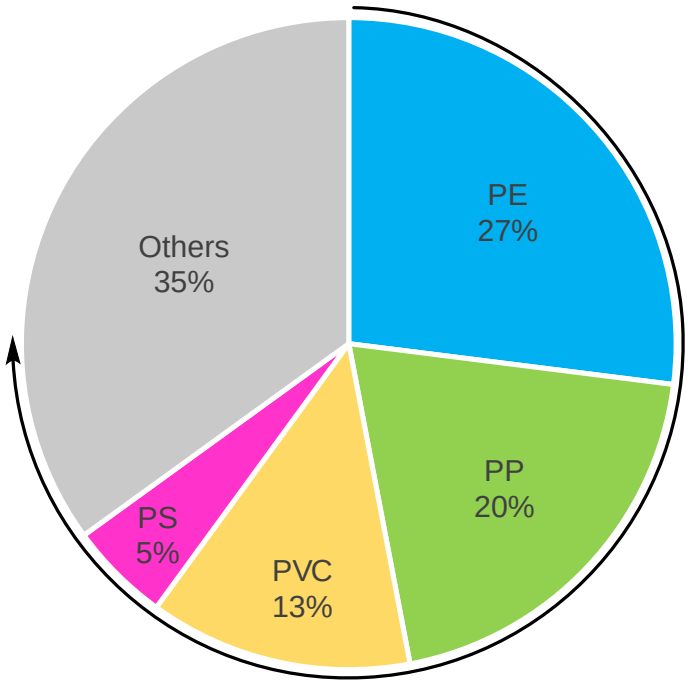
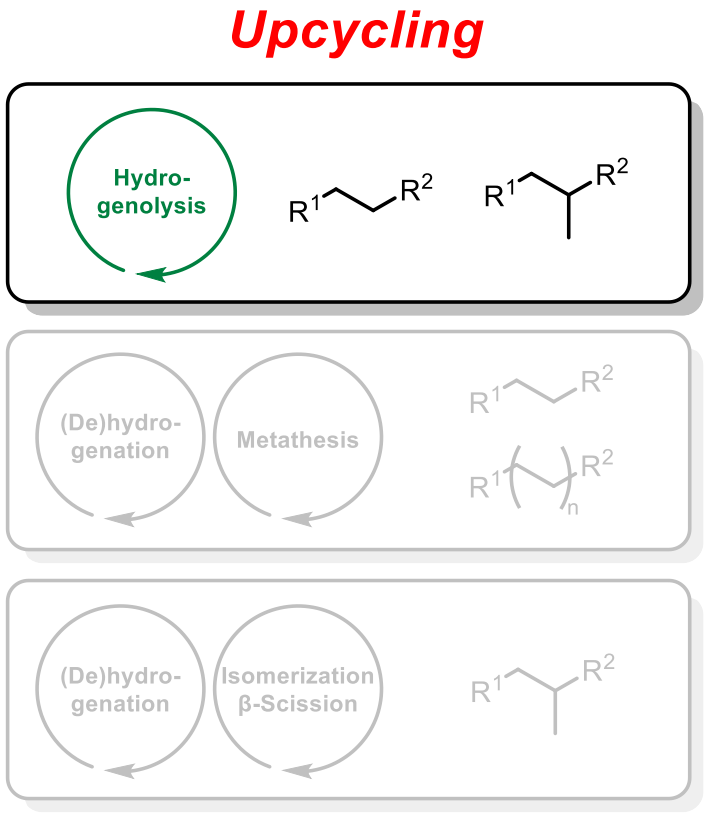
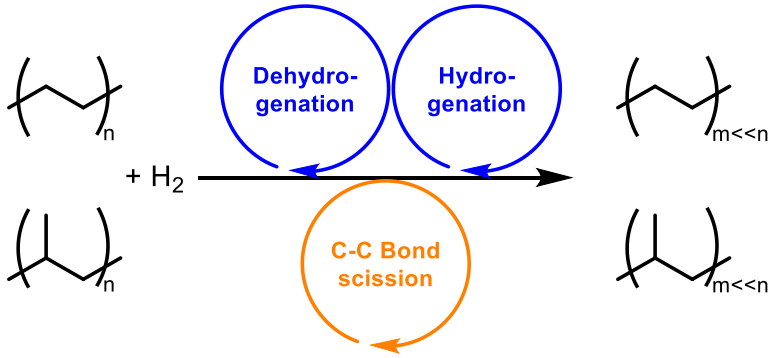
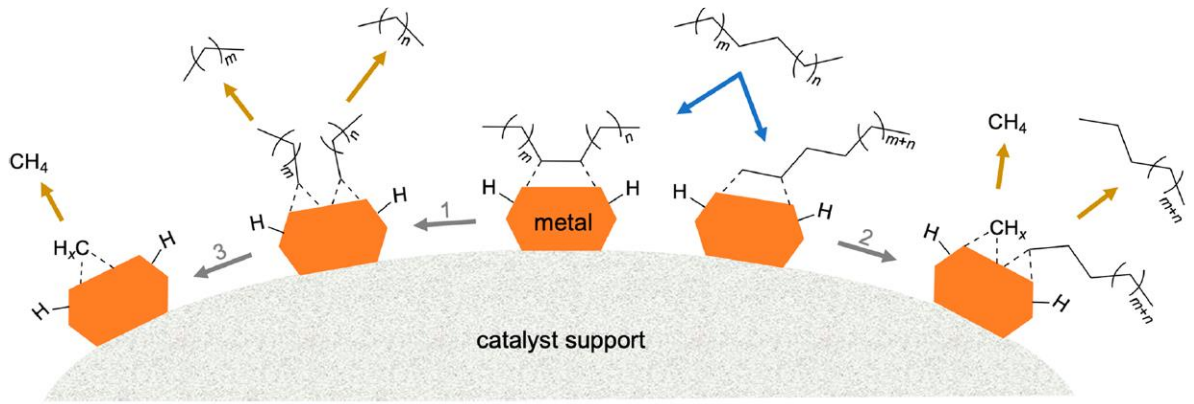




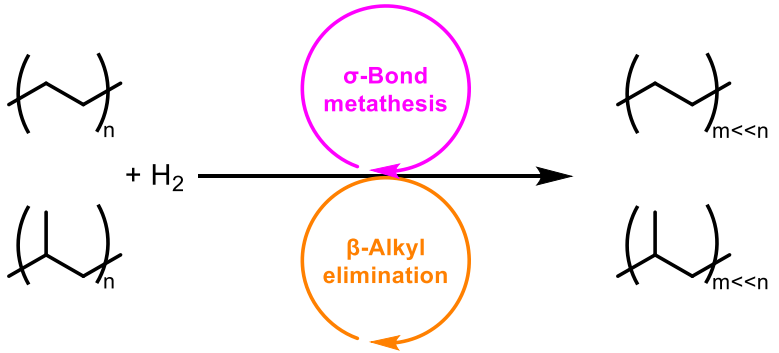
聚烯烃的催化氢解

后过渡金属
纳米颗粒@非/弱酸性基底
[Ru], 200-250 °C, 20-60 bar H_2
[Pt], 250-350 °C, 10-20 bar H_2
[Co], 200-300 °C, 20-40 bar H_2
[Ni], 280-350 °C, 30-70 bar H_2





前过渡金属
氢化物
[Zr], [Hf], [Ta], [W]
≤200 °C
≤2 bar H_2



机理核心：

- 金属**单功能**催化剂@**非/弱酸性**基底
- 反应**不经历**碳正离子中间体
- 催化剂**表面吸附**活化聚烯烃C-H键和C-C键

优势：

- 化学原理最简单
- 实际操作最简易成熟

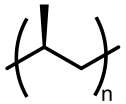
局限：

- 聚烯烃各C-C键键能差异不大，选择性差

Weckhuysen, B. M.; *et al*. *Angew. Chem. Int. Ed.* **2020**, *59*, 15402-15423.
Iglesia, E.; *et al*. *J. Phys. Chem. C* **2016**, *120*, 8125-8138.
Scott, S. L.; *et al*. *Chem. Rev.* **2024**, *124*, 9457-9579.

负载型前过渡金属氢化物催化聚烯烃氢解

M_n ~125,000 g/mol
LDPE
or



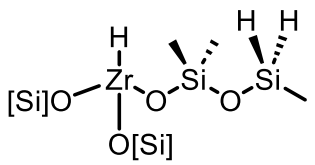
M_n ~250,000 g/mol
iPP

[Zr-H]@silica or silica-alumina

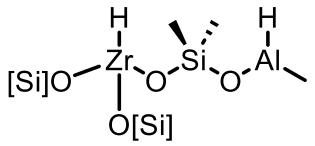
H_2 (1 atm), 150 °C
Full Conversion after 62 h

Hydrogenolysis rate:
Ti>Zr>Hf, Ta>W

Light alkane
C_1-C_{17} after 5 h
<C_9 after 62 h

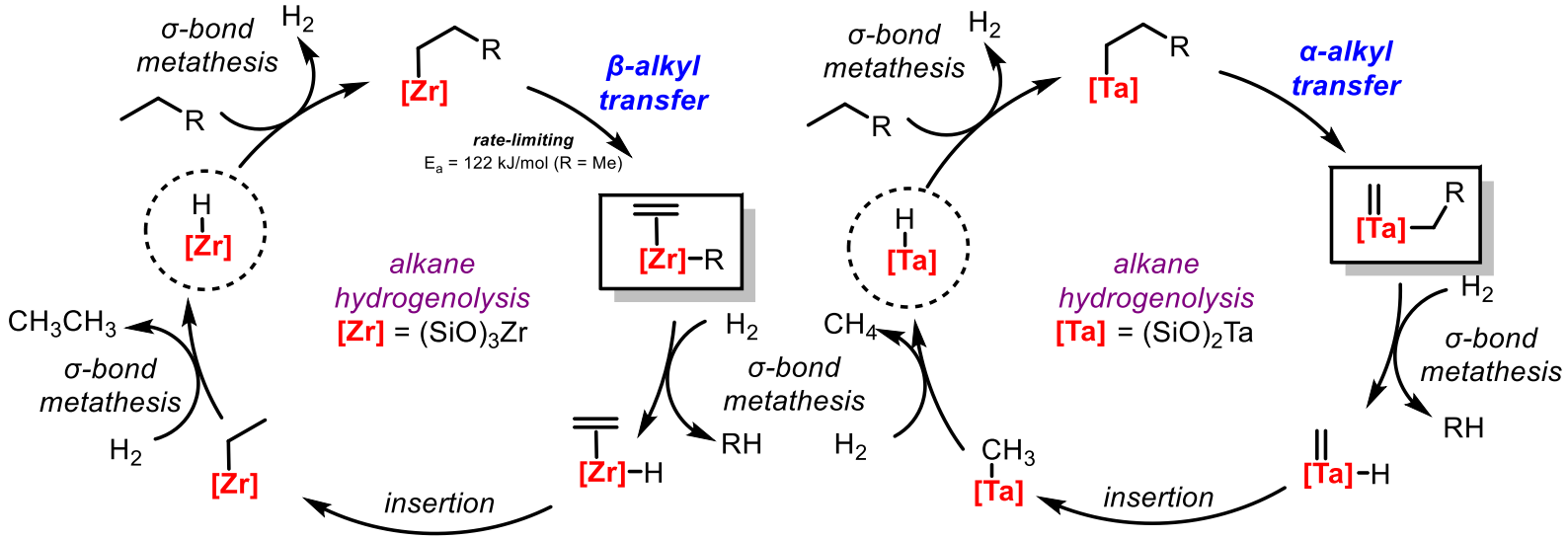


[Zr-H]@silica



[Zr-H]@silica-alumina

Proposed mechanisms: Zr(IV) vs. Ta(V)



Basset, J.-M.; *et al*. *Angew. Chem. Int. Ed.* **1998**, *37*, 806-810.; Basset, J.-M.; *et al*. *Angew. Chem. Int. Ed.* **2000**, *39*, 1962-1965.; Parrinello, M.; *et al*. *J. Phys. Chem. B* **2000**, *104*, 2901-2907.; Basset, J.-M.; *et al*. *Acc. Chem. Res.* **2016**, *49*, 664-677.

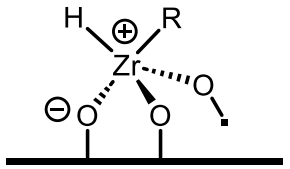
负载型前过渡金属氢化物催化聚烯烃氢解

酸性基底-阳离子型氢化物增强效应

M_n ~11,620 g/mol
PE
(also iPP, POE)

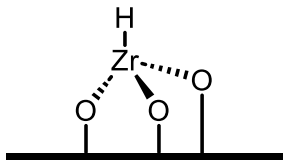
$[Zr\text{-}H]^+$@SAO
(0.02-0.03 mol% Zr)
→
H_2 (0.5-2 atm)
200 °C **>99%** after 48 min
150 °C **>95%** after 120 min

C_{10}-C_{20} light alkane

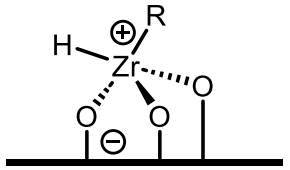


SO_4/Al_2O_3
$[Zr\text{-}H]^+$@SAO
>200× rate than [Zr-H]@silica

Different types of [Zr-H]:



中性[Zr-H]
表面弱Brønsted酸性
具有C_2H_4聚合活性
C-C键氢解速率慢



正离子型$[Zr\text{-}H]^+$
表面强Brønsted酸性
配位不饱和，高度缺电子
C-C键氢解速率快

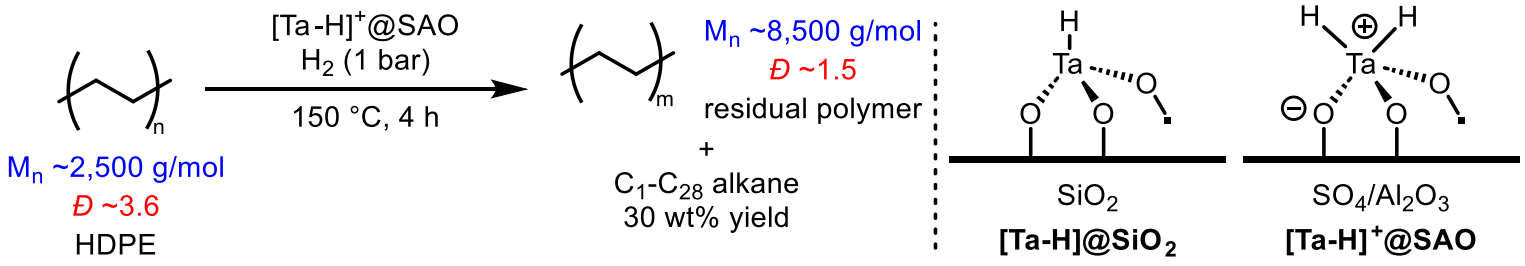
创新点：

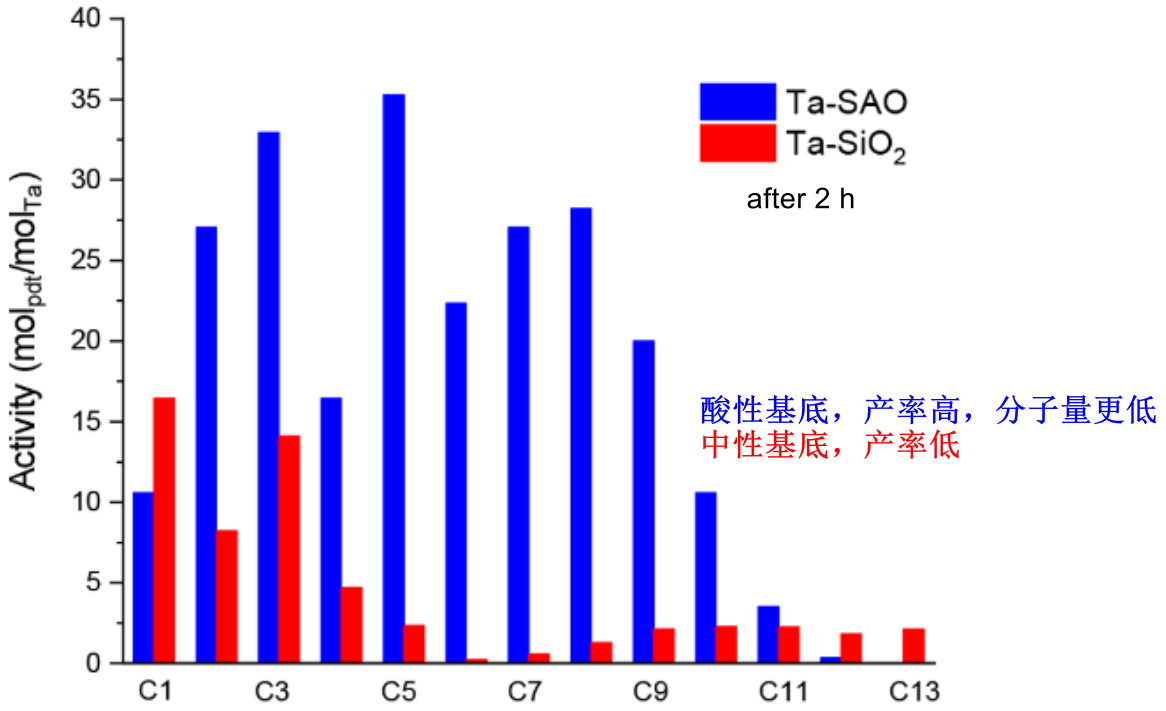
- 负载物改性
- Zr负载量低（0.02-0.03 mol%）
- 反应速率显著提升（200倍）
- iPP和POE降解效率更高（1 h完全降解）

Marks, T. J.; *et al*. *Nat. Commun.* **2022**, *13*, 7187.

负载型前过渡金属氢化物催化聚烯烃氢解

酸性基底-阳离子型氢化物增强效应





Conley, M. P.; *et al*. *J. Am. Chem. Soc.* **2023**, *145*, 4964-4968.

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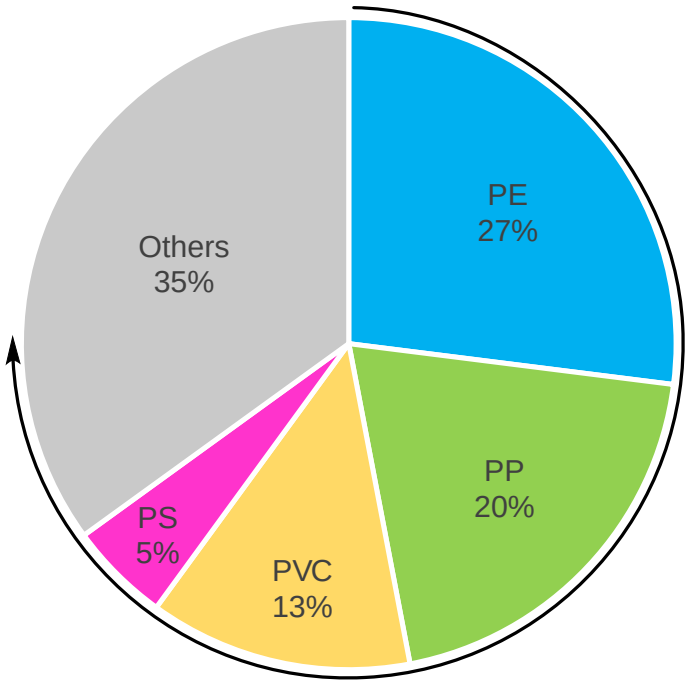
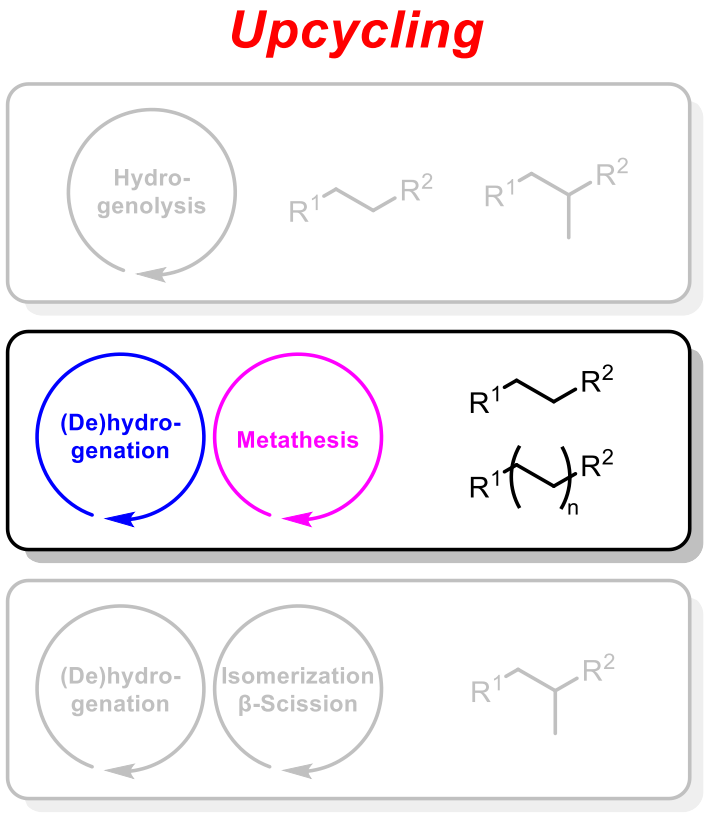
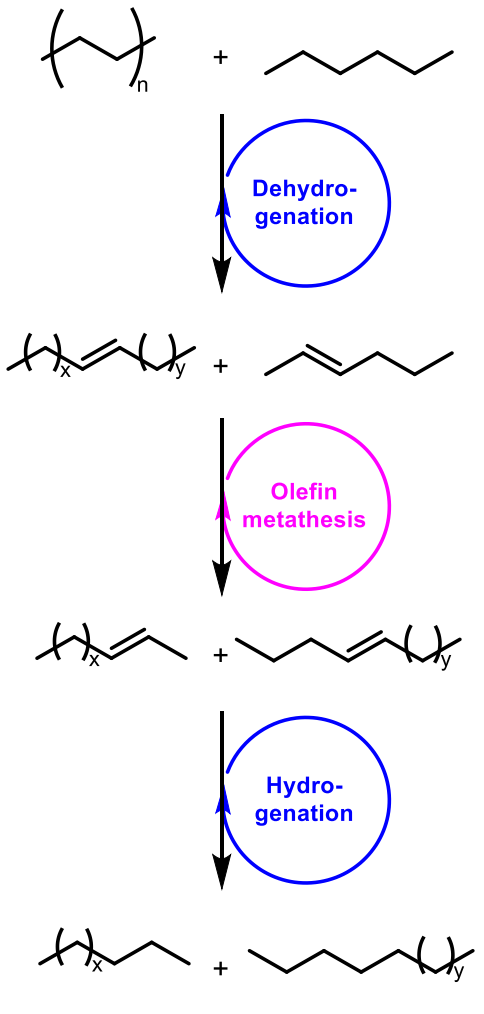


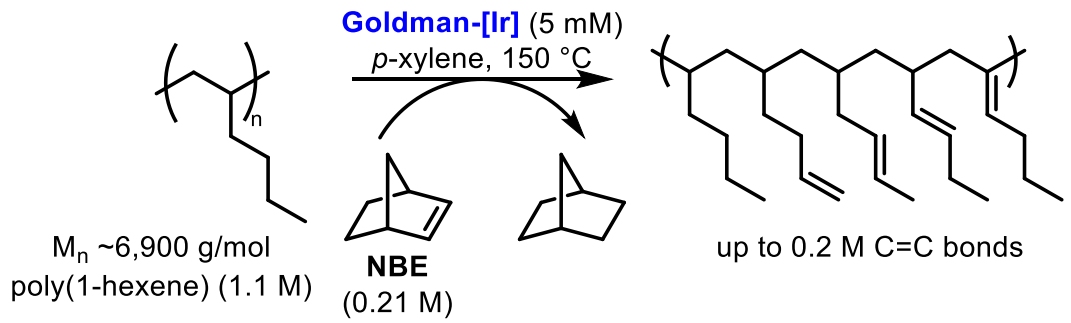


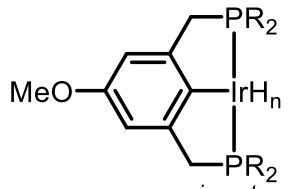
贵金属催化的聚烯烃烷烃复分解

General process:



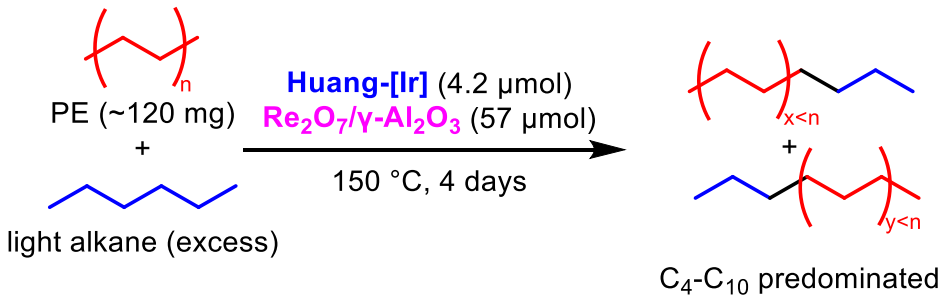
Catalytic combination: (de)hydrogenation + olefin metathesis

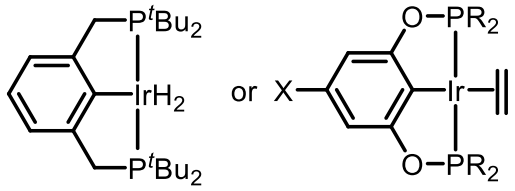




n = 2 or 4, R = ^{i}Pr, ^{t}Bu

Goldman (2005)

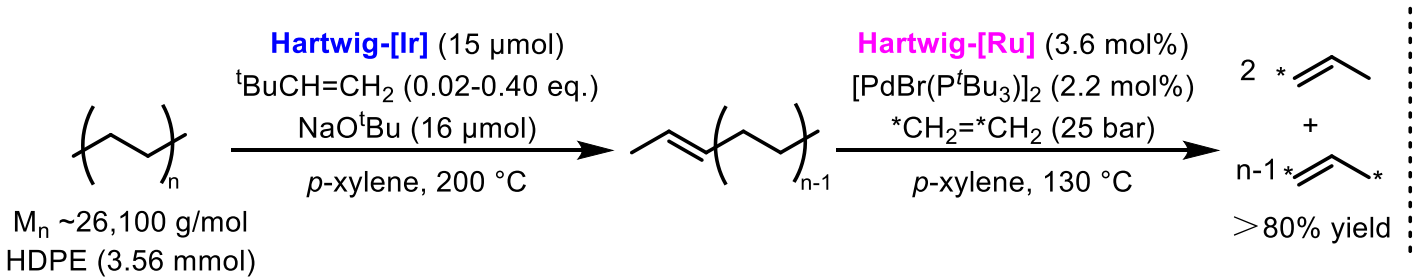


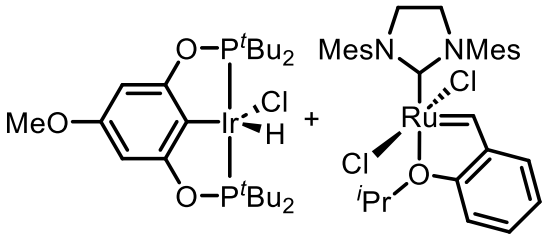


Huang (2016)

R = *i*Pr, X = OMe

R = *t*Bu, X = OP^{t}Bu$_2$

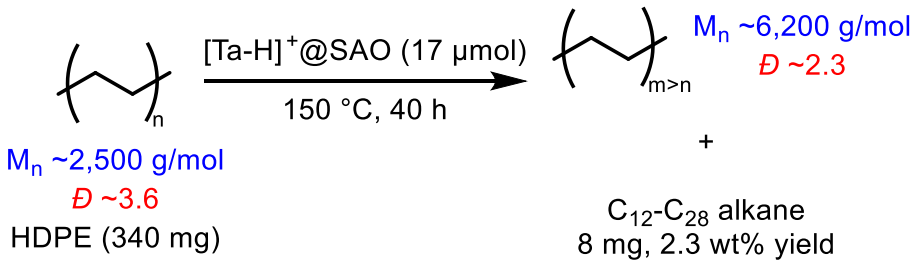


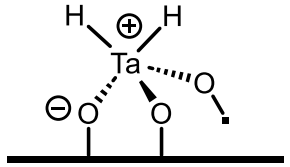


Hartwig (2022)

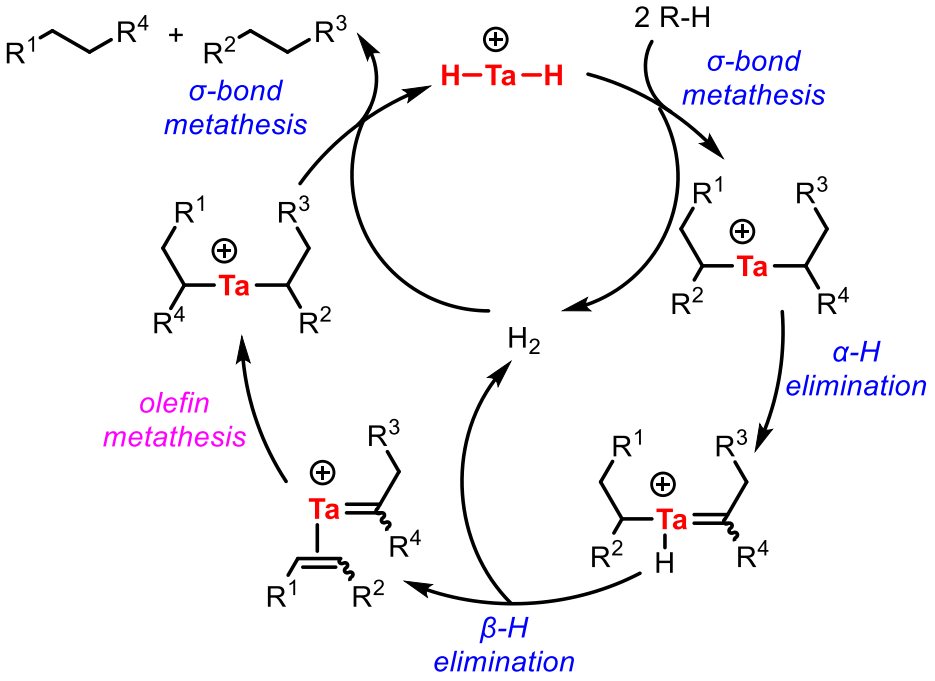
Goldman, A. S.; *et al*. *Chem. Commun.* **2005**, *27*, 3388-3390.; Huang, Z.; *et al*. *Sci. Adv.* **2016**, *2*, e1501591.; Hartwig, J. F.; *et al*. *Science* **2022**, *377*, 1561-1566.

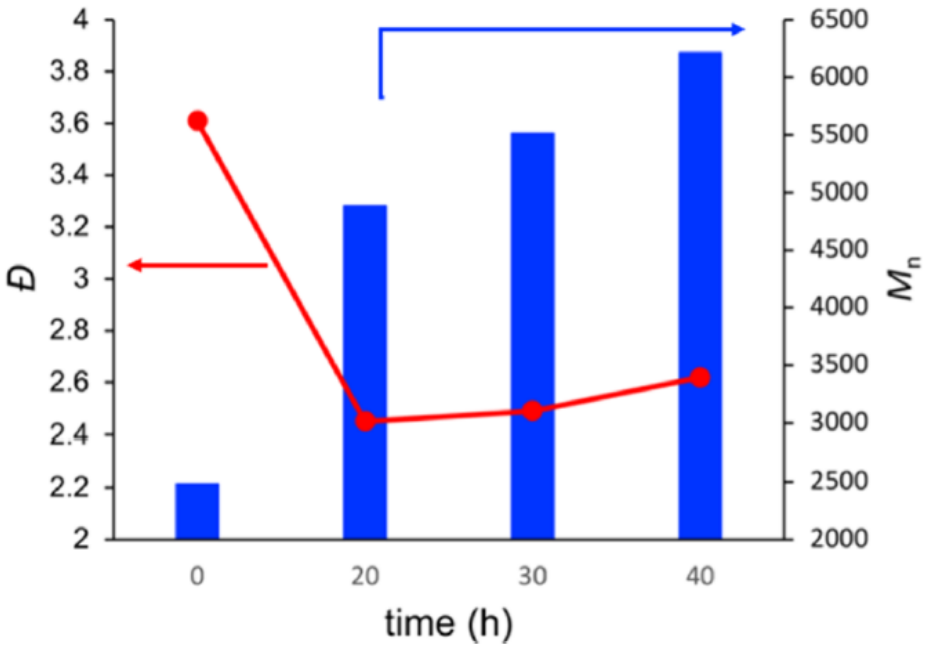
聚烯烃自身烷烃复分解





Proposed mechanism of PO's self-metathesis:





随反应进行，剩余的HDPE：

M_n持续上升

Đ迅速下降，后缓缓上升

Conley, M. P.; *et al. J. Am. Chem. Soc.* **2023**, *145*, 4964-4968.

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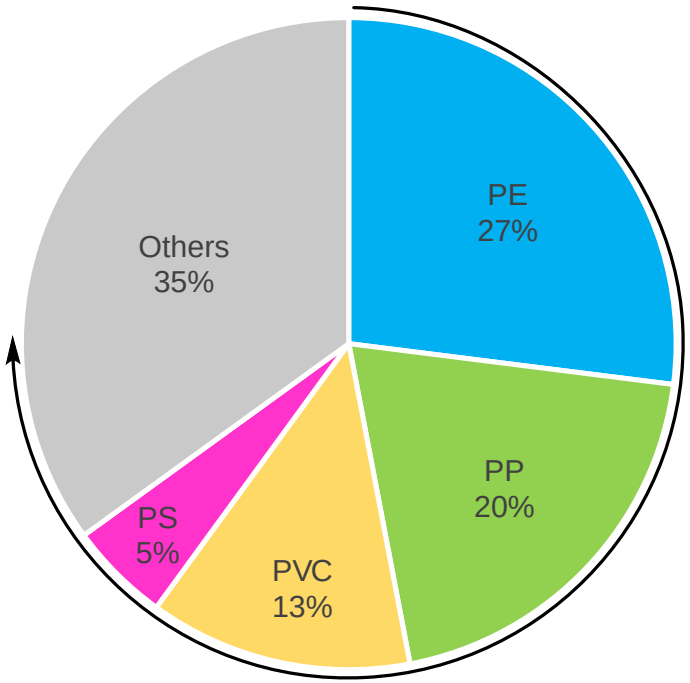
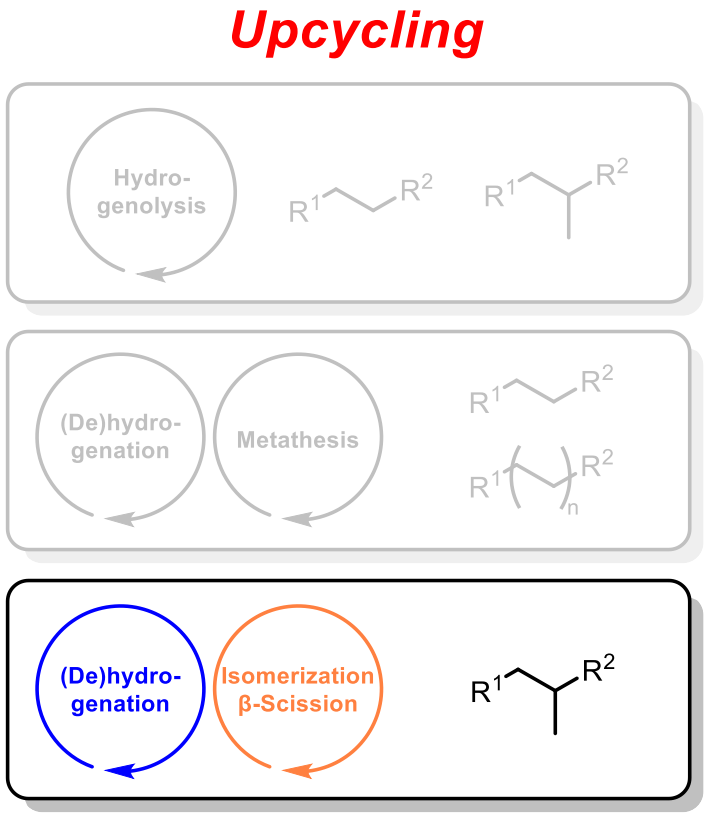
1. 背景
2. 氢解策略
3. 烷烃复分解策略
4. 裂解-串联反应策略
5. 总结与展望





催化裂解

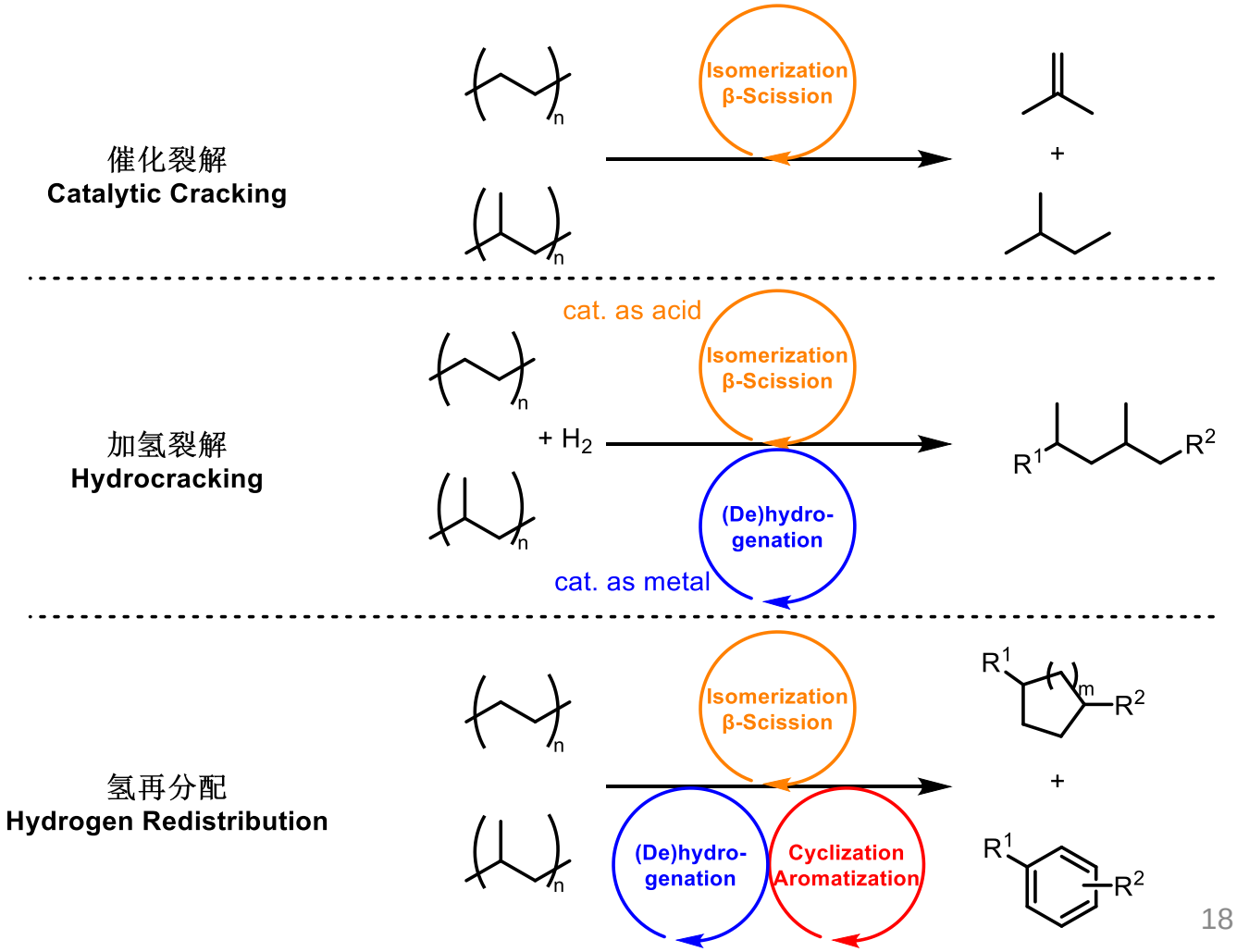
高压H_2参与（20-150 bar）

聚烯烃等长链烷烃 → 催化裂解-串联反应 <200 ℃ → 催化加氢裂解 180-480 ℃ → 热裂解 >500 ℃ → 低分子量短链烷烃

机理核心：

- 酸性催化剂介导**碳正离子**生成
- 碳正离子的**β-裂解**使主链降解

能量补偿： 串联显著放热反应

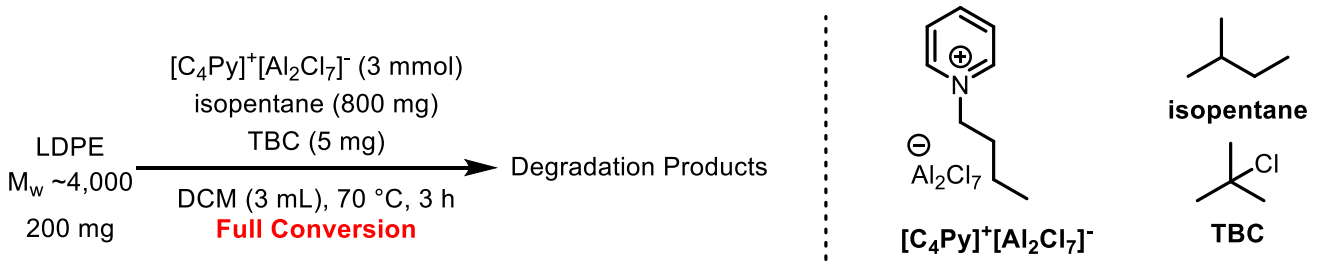


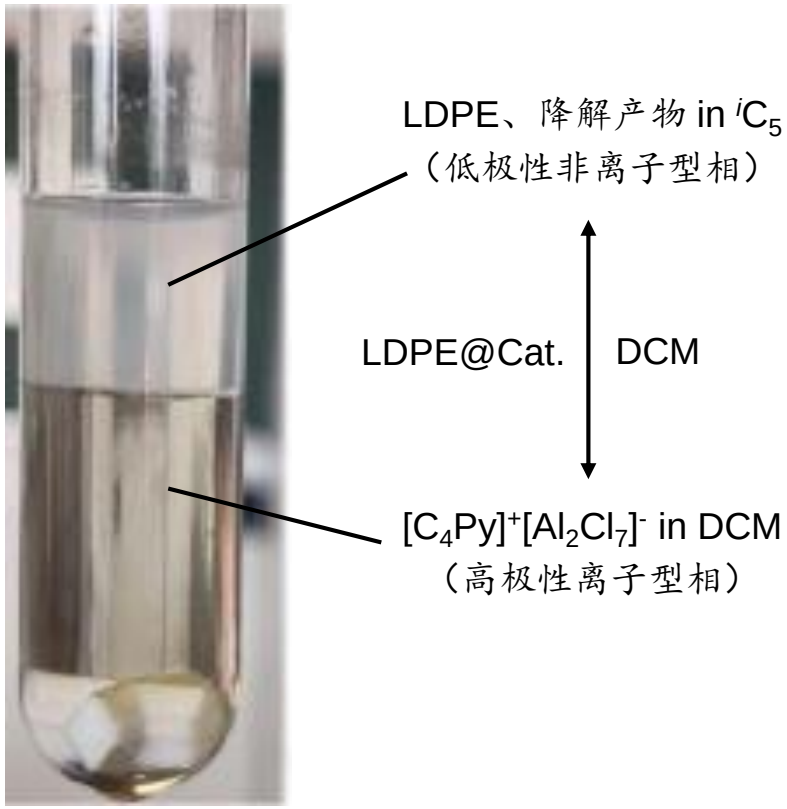
Pramanik, B. K.; *et al*. *J. Environ. Chem. Eng.* **2022**, *10*, 108865.
Xiao, F.-S.; *et al*. *J. Am. Chem. Soc.* **2022**, *144*, 14269-14277.
Ruan, R.; *et al*. *Energy Convers. Manag.* **2022**, *254*, 115243.
Alsheikh, F.; *et al*. *Int. J. Environ. Anal. Chem.* **2023**, *103*, 5920-5937.
Vlachos, D. G.; *et al*. *Sci. Adv.* **2021**, *7*, eabf8283.
Vlachos, D. G.; *et al*. *React. Chem. Eng.* **2021**, *7*, 41-54.
Lin, B.-L.; *et al*. *Sci. Adv.* **2023**, *9*, eadg5332.
Cargnello, M.; *et al*. *ACS Sustain. Chem. Eng.* **2023**, *11*, 12623-12630.
Bao, X.; *et* al. Natl. *Sci. Rev.* **2024**, *11*, nwae097.

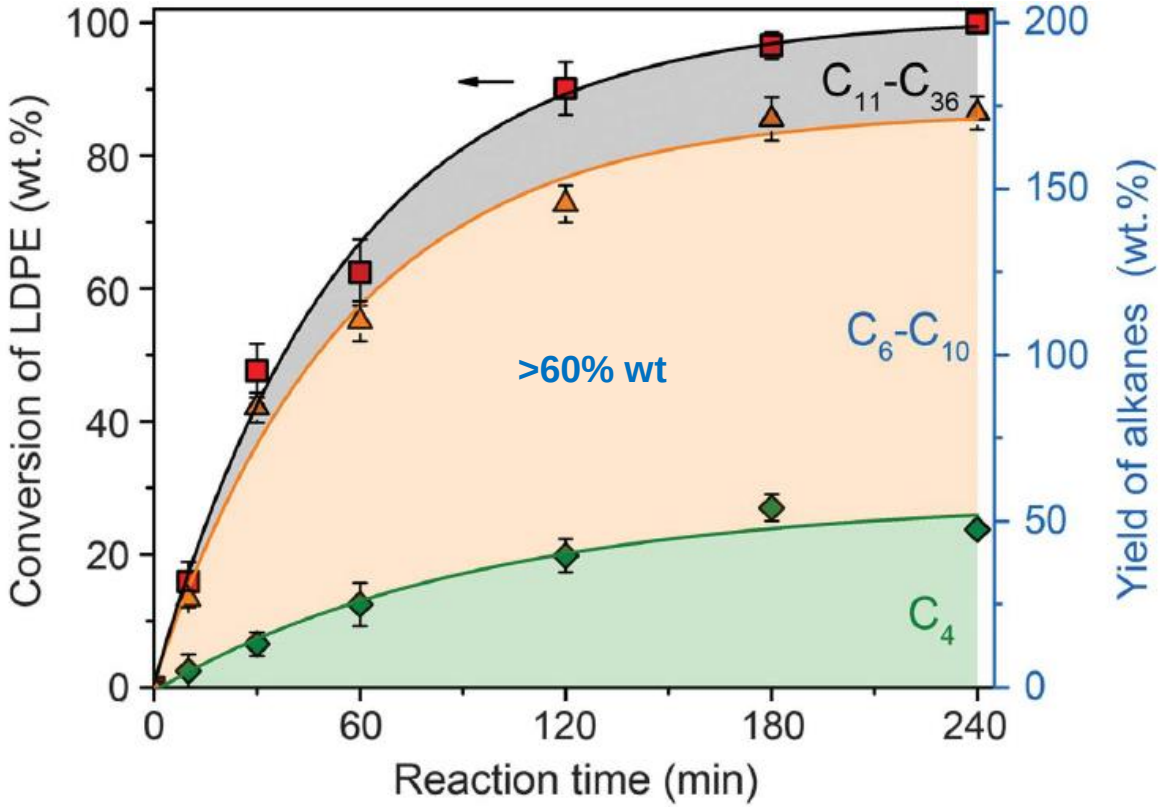
聚烯烃催化裂解的传统催化剂

催化裂解类别	催化剂（共反应物）	反应温度(℃)	主要产物	参考文献
催化裂解	silica-alumina	480	烯烃、支链烷烃、芳烃	Zhang, F.; *et al*. *ACS Catal.* **2022**, *12*, 14882-14901.
	$MgCl_2/AlCl_3$	370	气体烃类	Berlin, A. A.; *et al*. *Prog. Polym. Sci.* **1990**, *15*, 193-215.
	ZSM-5	280	C_3-C_6的烯烃	Xiao, F.-S.; *et al*. *J. Am. Chem. Soc.* **2022**, *144*, 14269-14277.
	H-MFI zeolite	200	C_3-C_7的烷烃、烯烃	Sarazen, M. L.; *et al*. *Appl. Catal. B Environ.* **2023**, *338*, 123028.
加氢裂解	金属纳米颗粒/无定形多孔酸性氧化物基底（20-150 bar H_2）	350-450	短链烷烃	Scott, S. L.; *et al*. *Chem. Rev.* **2024**, *124*, 9457-9579.
	Pt/USY or Pt/Hbeta（20 bar H_2）	275-330	C_4-C_6的支链烷烃	Garforth, A. A.; *et al*. *Ind. Eng. Chem. Res.* **2019**, *58*, 20601-20609.
	$Pt/WO_3/ZrO_2$和HY沸石（30 bar H_2）	250	C_5-C_{22}的烷烃	Vlachos, D. G.; *et al*. *Sci. Adv.* **2021**, *7*, eabf8283.
	MoS_x-Hbeta（25 bar H_2）	180	C_4-C_{12}的支链烷烃	Lin, B.-L.; *et al*. *Sci. Adv.* **2023**, *9*, eadg5332.

离子液体催化串联裂解-烷基化策略

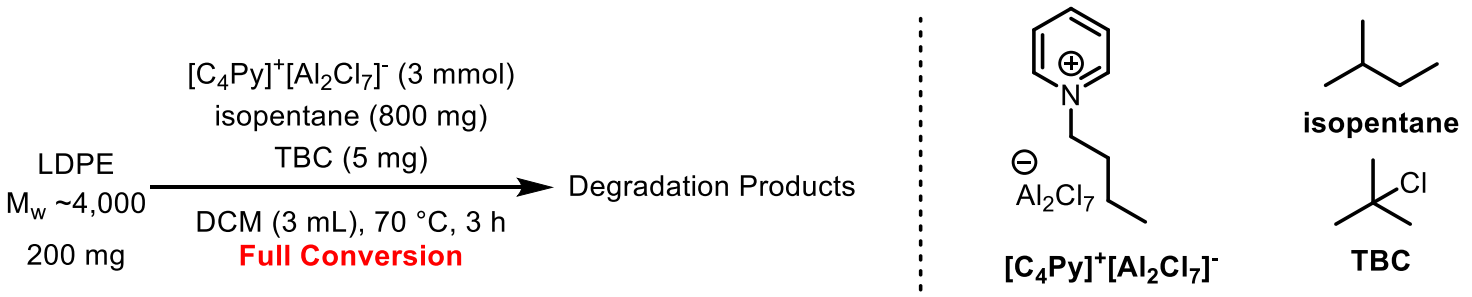






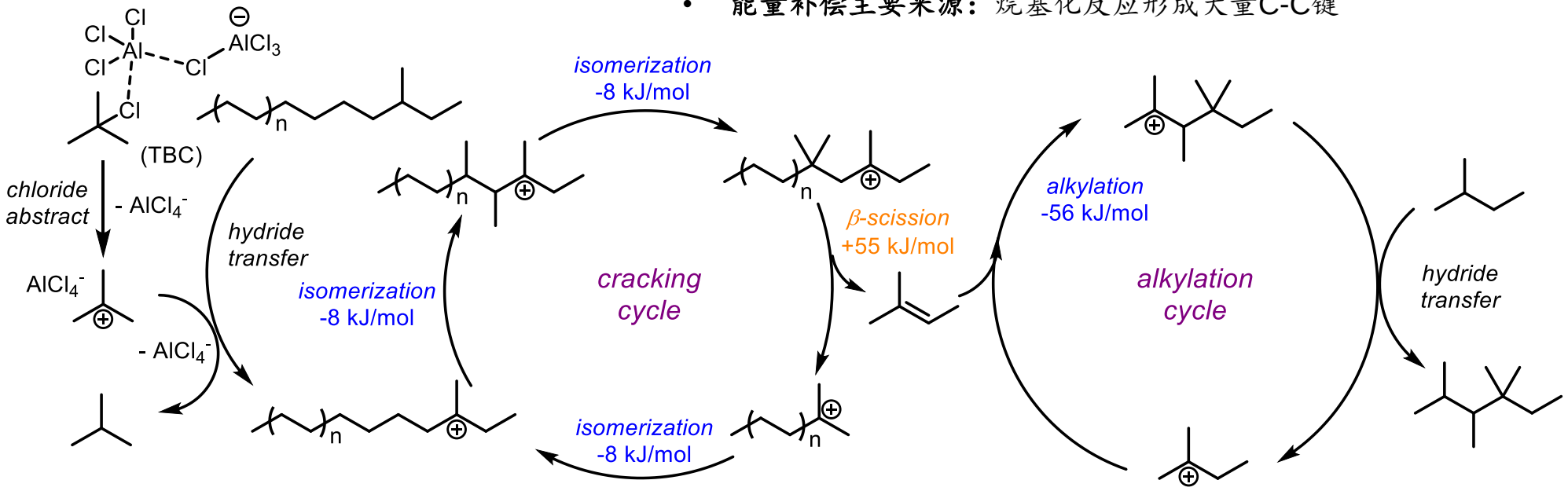
Lercher, J. A. *et al*. *Science* **2023**, *379*, 807-811.

离子液体催化串联裂解-烷基化策略



Proposed Mechanism:

- 表观活化能：17±2 kJ·mol^{-1}（此前报道值： 163-303 kJ·mol^{-1}）
- 能量补偿主要来源：烷基化反应形成大量C-C键

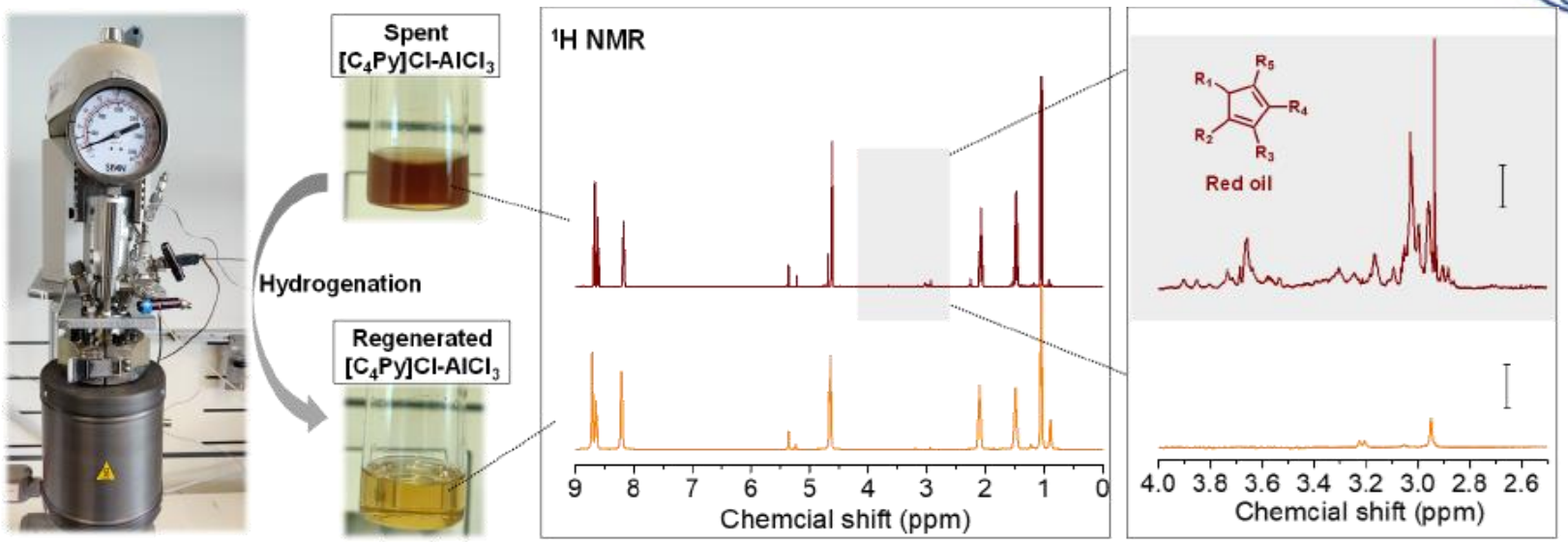


Lercher, J. A. *et al*. *Science* **2023**, *379*, 807-811.
Lercher, J. A. *et al*. *Nat. Commun.* **2024**, *15*, 5785.

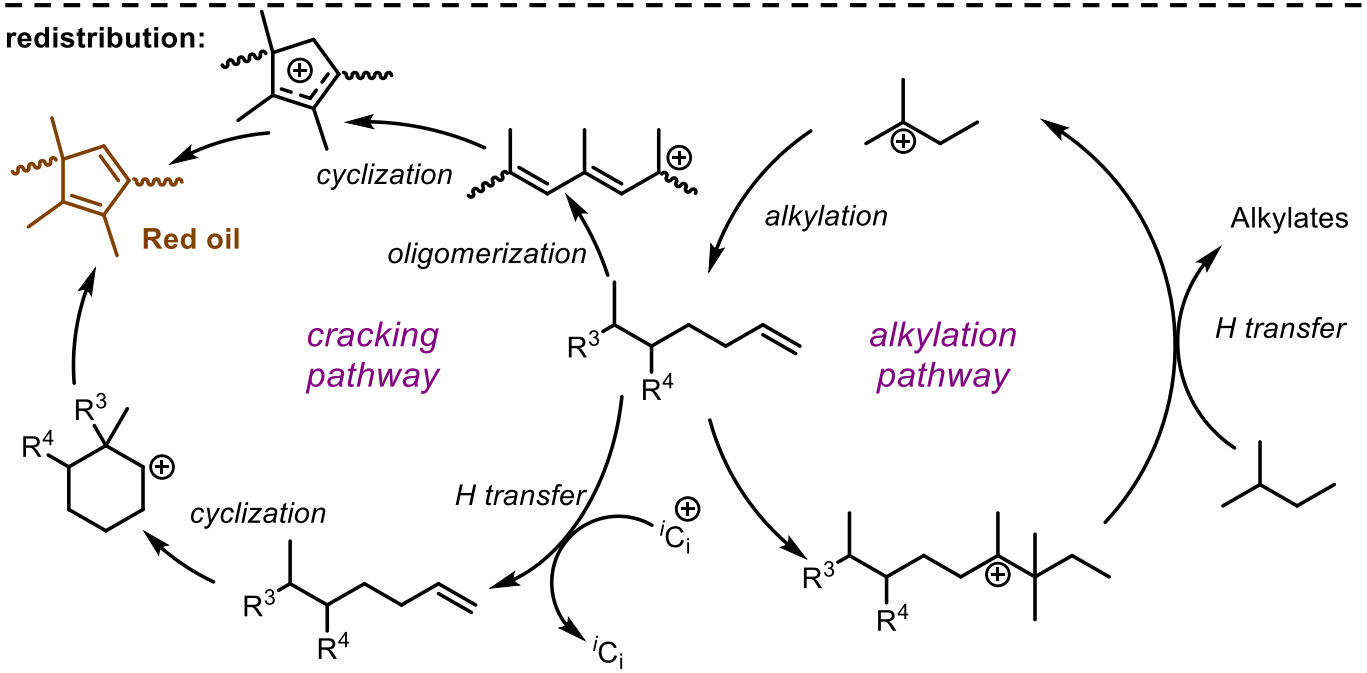
离子液体催化串联裂解-烷基化策略

催化剂的循环与再生

- 循环：至少**5**次，均能保持LDPE完全转化
- 活性丧失：环状芳香烃络合
- 再生：氢化



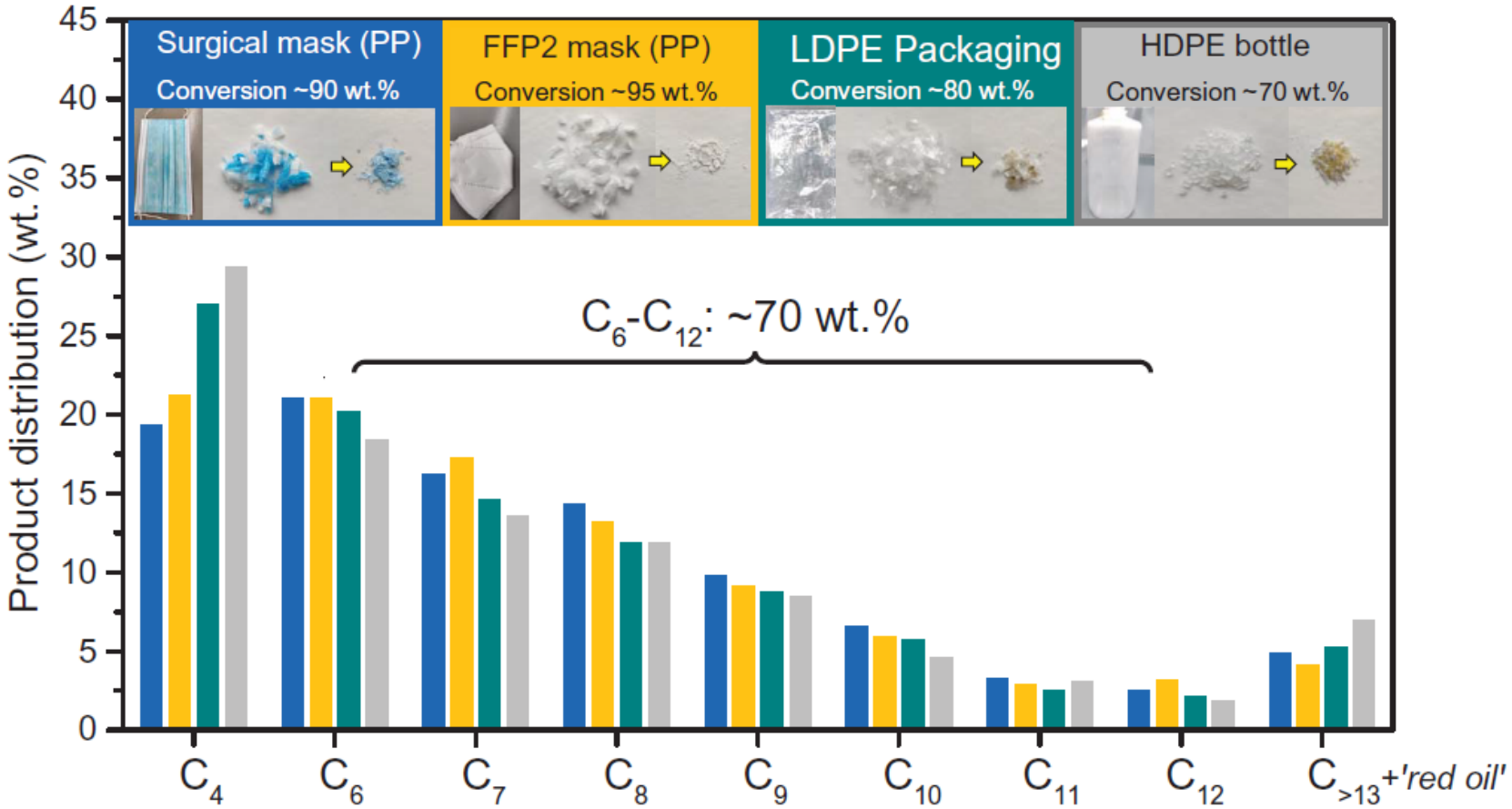
Red oil generation by hydrogen redistribution:



Lercher, J. A. *et al*. *Science* **2023**, *379*, 807-811.

离子液体催化串联裂解-烷基化策略

聚烯烃商品的降解尝试



- 工艺对HDPE、PP等聚烯烃亦可兼容
- 工艺对实际塑料制品中的添加剂、涂层等表现出较好的鲁棒性

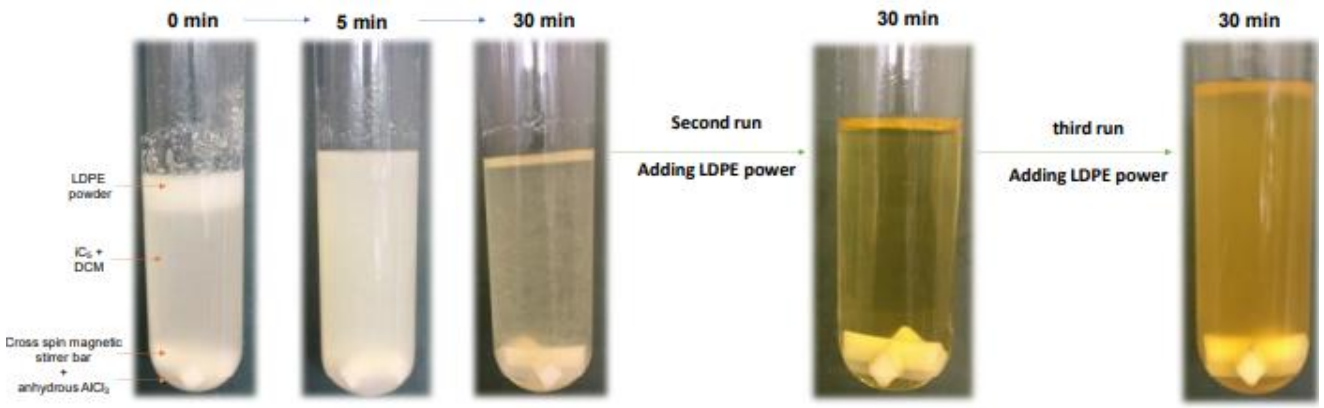
Lercher, J. A. *et al*. *Science* **2023**, *379*, 807-811.

Lewis酸催化串联裂解-烷基化策略

LDPE
M_w ~4,000
200 mg

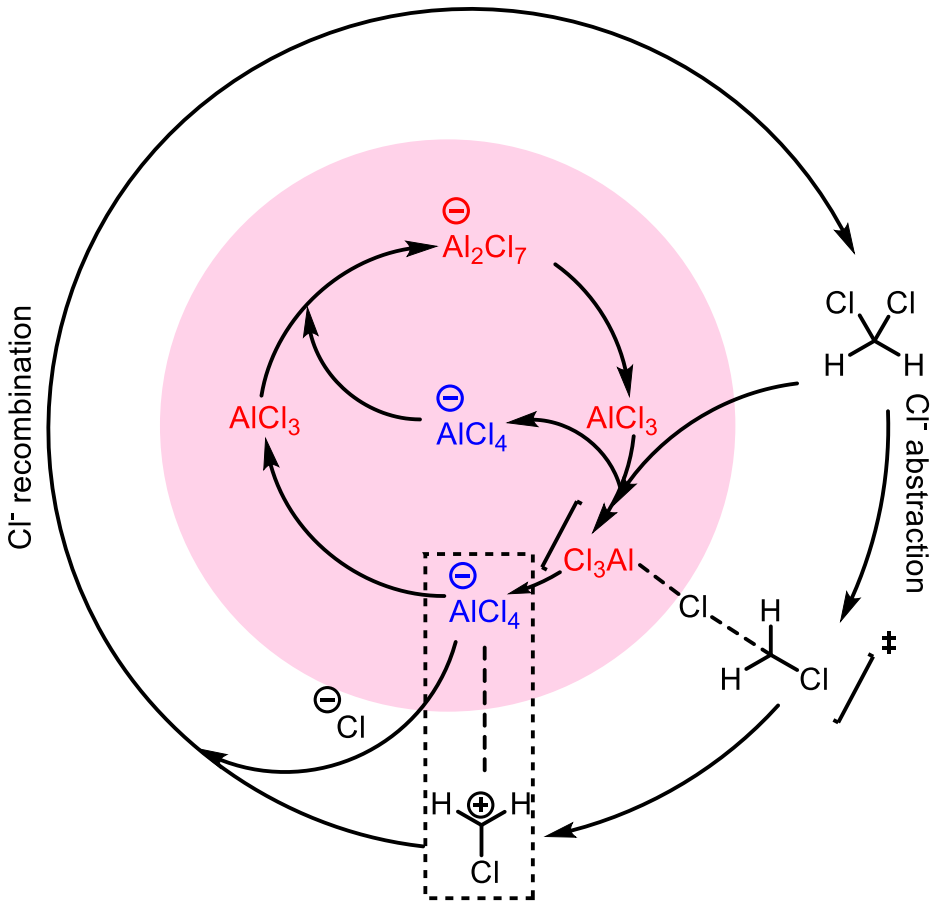
$AlCl_3$ (1 mmol)
isopentane (800 mg)
DCM (3 mL), 70 °C, 10-30 min
Full Conversion

→ Degradation Products



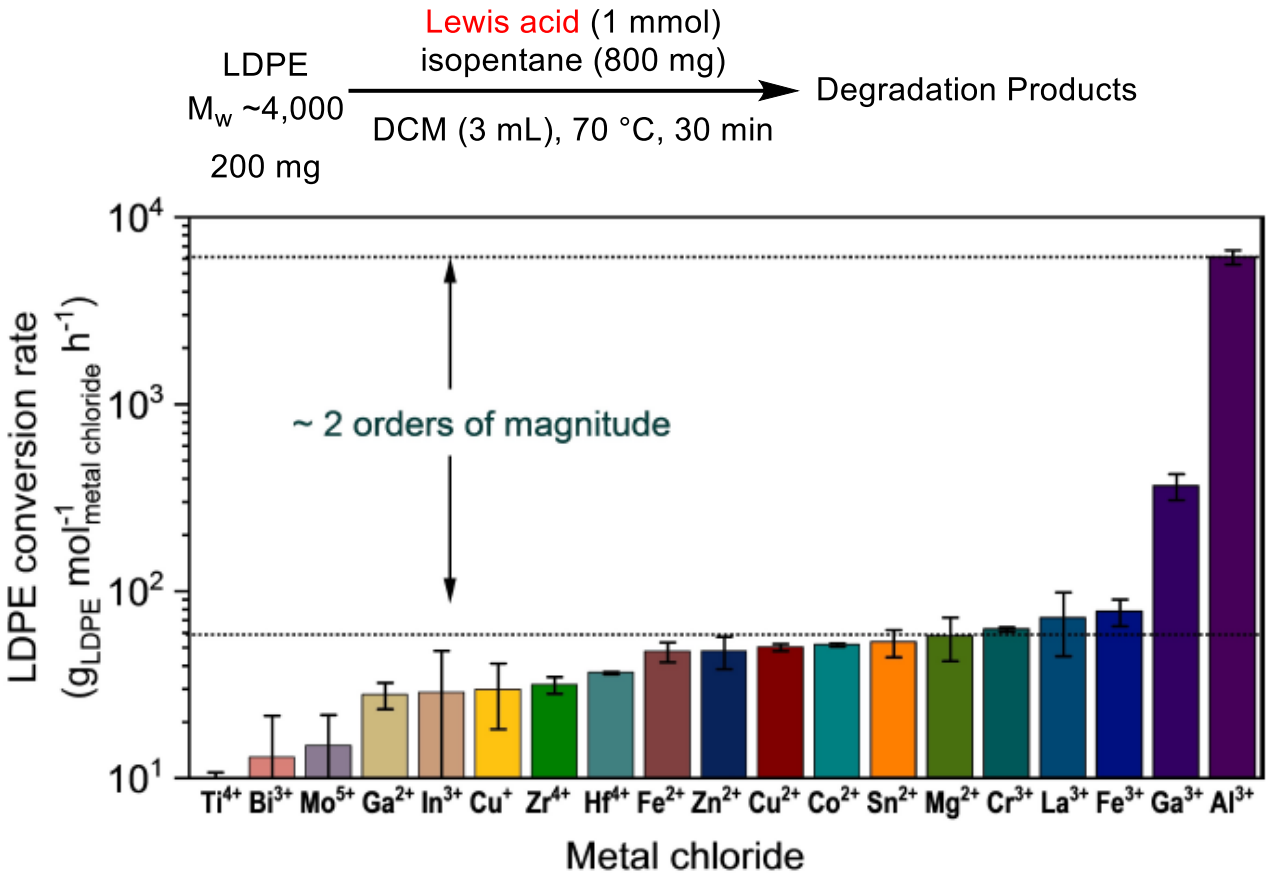
- **循环：**至少**3**次，均能保持LDPE基本**完全转化，**不影响初始降解速率

Carbenium generation:



Lercher, J. A. *et al*. *Angew. Chem. Int. Ed.* **2024**, *63*, e202319580.

Lewis酸催化串联裂解-烷基化策略



Lewis酸	LDPE初始降解速率 (g_{LDPE}·mol_{cat}^{-1}·h^{-1})	完全降解时间(min)	表观活化能 (kJ·mol^{-1})	决速步
$AlCl_3$	5000	10	40-44	氢负转移
$GaCl_3$	400	120	16	扩散控制

Lewis酸对反应的影响：

- **酸性：** 无直接关系
- **反离子：** 软的反离子有助于参与氢负离子转移的过渡态形成（如AlI_3≈$AlBr_3$>$AlCl_3$>>AlF_3）
- **溶解动力学：** 在DCM中的有效溶解和扩散
- **反应性：**
  - ✓ 与DCM有效形成能引发反应的电荷转移复合物
  - ✓ 裂解/烷基化的相对速率决定反应选择性和产物分布

Lercher, J. A. *et al*. *Angew. Chem. Int. Ed.* **2024**, *63*, e202319580.

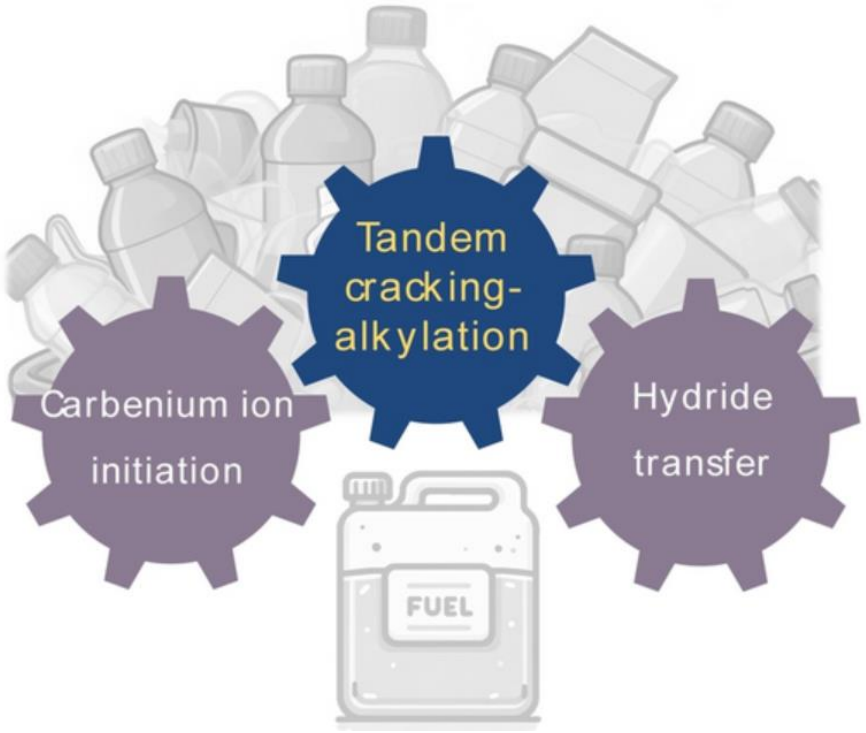
串联裂解-烷基化策略

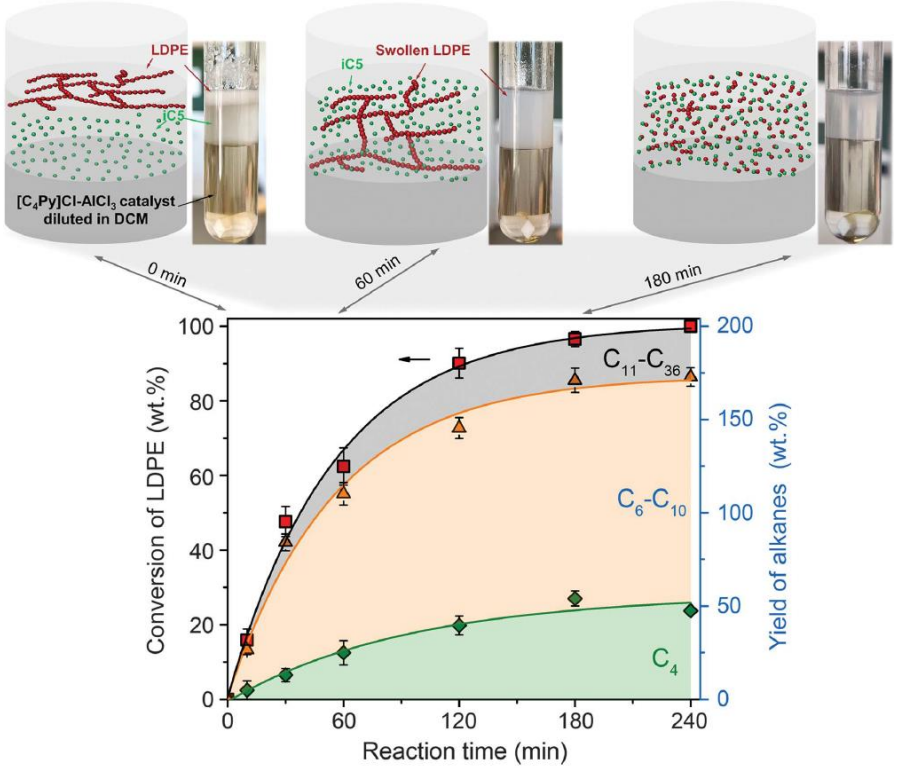
LDPE, M_w ~4,000, 200 mg → Degradation Products
- $[C_4Py]^+[Al_2Cl_7]^-$ (3 mmol), isopentane (800 mg), TBC (5 mg)
- DCM (3 mL), 70 °C, 3 h
- **Full Conversion**

LDPE, M_w ~4,000, 200 mg → Degradation Products
- $AlCl_3$ (1 mmol), isopentane (800 mg)
- DCM (3 mL), 70 °C, 10 min
- **Full Conversion**

工业化潜力：

- 反应条件温和
- 时空转化率高
- 产物分布窄且附加值高
- 催化体系循环再生方便
- 反应具有一定鲁棒性





Lercher, J. A. *et al*. *Science* **2023**, *379*, 807-811.
Lercher, J. A. *et al*. *Angew. Chem. Int. Ed.* **2024**, *63*, e202319580.
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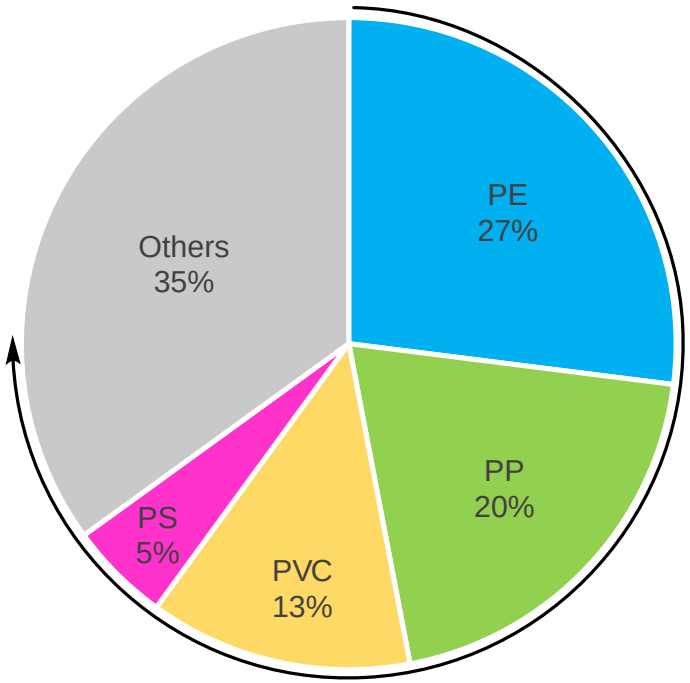
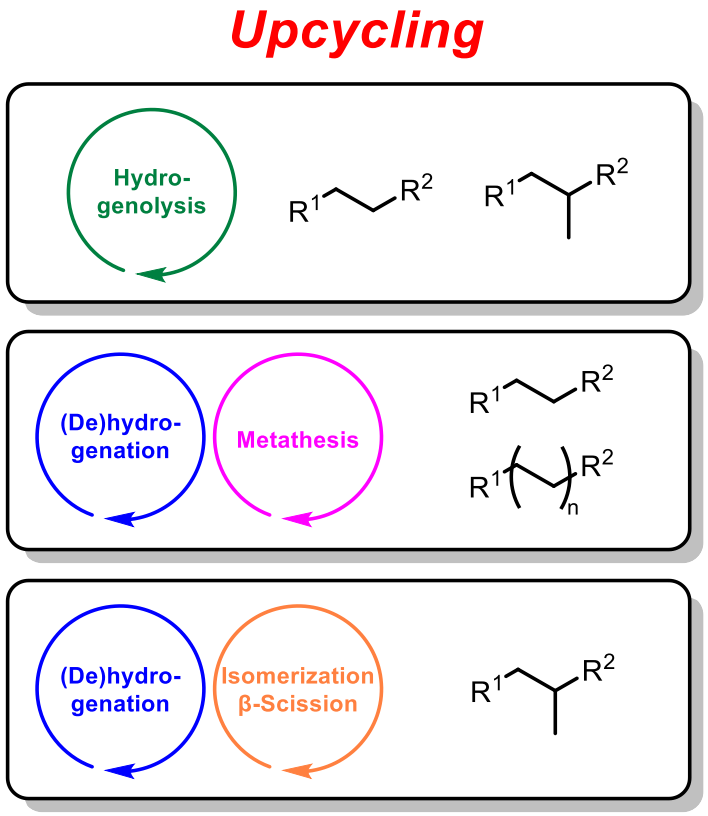
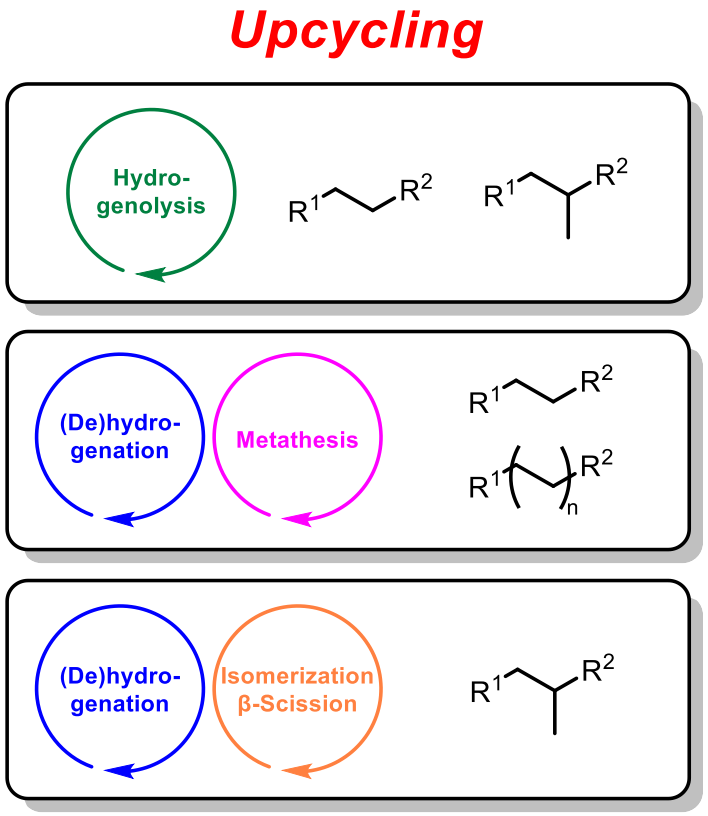




总结：聚烯烃催化高值化降解



反应类别	非贵金属催化剂	核心机理	能量补偿来源	共反应物
氢解	负载型金属（Zr、Ta）氢化物	σ键复分解 烷基裂解转移	烷烃氢解放热	H_2
烷烃复分解	负载型金属（Ta）氢化物	烯烃中间体生成、复分解、氢化	烯烃复分解反应 整体热效应不明显	未充分探索 （小分子烷烃？）
裂解-串联反应	$[C_4Py]^+[Al_2Cl_7]^-$ $AlCl_3$等Lewis酸	碳正离子产生、迁移、异构化、β-裂解	烷基化反应等串联的放热反应	异戊烷等 共反应试剂

Lercher, J. A. *et al*. *Science* **2023**, *379*, 807-811.
Scott, S. L.; *et al*. *Chem. Rev.* **2024**, *124*, 9457-9579.

展望：聚烯烃高值化的未解难题与光明前景

基础研究亟待解决的问题
（微观，反应本质）

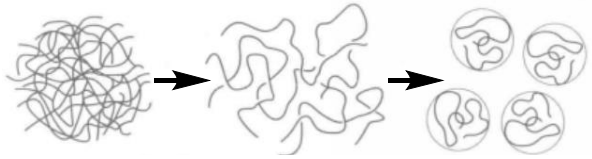
工业化面临的问题
（宏观，技术手段）

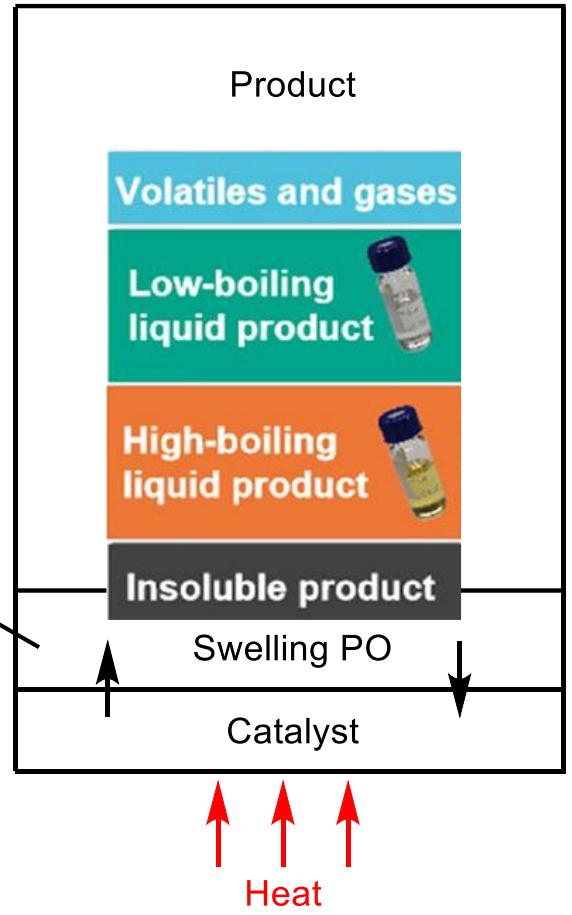
工艺改进？

产物分离应用？

反应器设计？

聚合物链溶解溶胀动力学？





聚合物链在催化中心附近的行为？

混合塑料废弃物？

催化剂分离与循环？

反应的热量传递与质量传递？

Zhang, L.; *et al*. *ChemSusChem.* **2021**, *14*, 4137-4151.
Scott, S. L.; *et al*. *Chem. Rev.* **2024**, *124*, 9457-9579.
Plastics Europe. *Plastics-The Facts 2022*, Plastics Europe: Brussels, **2022**.

谢谢大家！

敬请批评指正！