Hans Journal of Chemical Engineering and Technology 化学工程与技术, 2023, 13(2), 69-81
Published Online March 2023 in Hans. https://www.hanspub.org/journal/hjcet
https://doi.org/10.12677/hjcet.2023.132008

丙烷脱氢反应中载体和助剂对Pt基催化剂性能的影响

侯威龙*，王月霞，许铂文，林柯行

浙江师范大学含氟新材料研究所，浙江 金华

收稿日期：2023年2月5日；录用日期：2023年3月4日；发布日期：2023年3月13日

摘 要

丙烷脱氢制丙烯近年来受到学术界广泛关注。Pt基催化剂具有生态环保、催化活性高的优点，但是在高温的反应条件下仍然会发生失活现象，失活原因主要归结于：铂的烧结和积碳的产生。由于目前所使用的催化剂大多数是负载型催化剂，载体和所添加的助剂均会影响催化剂的性能表现。所以，本文较为系统地讨论了Pt基催化剂中载体和助剂对催化剂性能的影响，为今后制备出性能更加优异的Pt基催化剂做一定的参考。

关键词

丙烷脱氢，Pt基催化剂，载体，助剂

Effects of Supports and Promoters on the Performance of Pt-Based Catalysts in Propane Dehydrogenation

Weilong Hou*, Yuexia Wang, Bowen Xu, Kexing Lin

Institute of Advanced Fluorine-Containing Materials, Zhejiang Normal University, Jinhua Zhejiang

Received: Feb. 5th, 2023; accepted: Mar. 4th, 2023; published: Mar. 13th, 2023

Abstract

Propane dehydrogenation to propylene has attracted extensive attention in academia in recent years. Pt-based catalyst has the advantages of ecological protection and high catalytic activity, but deactivation still occurs under high-temperature reaction conditions. The reasons for deactivation are

*通讯作者。

文章引用: 侯威龙, 王月霞, 许铂文, 林柯行. 丙烷脱氢反应中载体和助剂对 Pt 基催化剂性能的影响[J]. 化学工程与技术, 2023, 13(2): 69-81. DOI: 10.12677/hjcet.2023.132008

mainly attributed to the sintering of platinum and the production of carbon deposition. Since most of the catalysts used at present are supported catalysts, supports and promoters will affect the performance of the catalyst. Therefore, this paper systematically discussed the impact of supports and promoters on the performance of the Pt-based catalyst, for the future preparation of more excellent performance of the Pt-based catalyst as a reference.

Keywords

Propane Dehydrogenation, Pt-Based Catalysts, Supports, Promoters

1. 引言

我国拥有丰富的页岩气资源，页岩气中蕴含大量的丙烷。丙烷可以经过催化脱氢制备丙烯，而丙烯是很多重要化学品的母体原料，如聚丙烯、丙烯醛、环氧丙烷等[1]。近年来，丙烷脱氢制备丙烯(Propane Dehydrogenation to Propylene, PDH)受到学术界广泛关注[2] [3] [4] [5]。

丙烷分子的 C-H 键非常稳定，因此断裂 C-H 需要很高的温度，通常温度为 550℃~700℃才可以实现较高的丙烷转化率[6]。由于不使用氧化剂，直接丙烷脱氢反应对丙烯的选择性远高于氧化丙烷脱氢反应[7] [8]。在 PDH 反应过程中，丙烷分子 C-H 键的活化是最重要的步骤，决定了 PDH 催化剂的催化性能[9]。催化反应的五个步骤中，第二步决定了整个 PDH 反应的速率，反应步骤如图 1 所示。然而，产物丙烯分子比丙烷分子更活泼，在 PDH 反应过程中会发生很多副反应，如裂解、深度脱氢和聚合反应，最终导致了丙烯选择性的降低和积碳的生成[1]。因此，一种优良的 PDH 催化剂必须有利于丙烷 C-H 键的断裂而不是 C-C 键的断裂。迄今为止，工业上使用的脱氢催化剂主要是 CrO_x 基催化剂[10] [11] [12]和 Pt 基催化剂。与 CrO_x 基催化剂相比，Pt 基催化剂具有生态友好、稳定性高的优点，已广泛应用于 Oleflex (UOP)工艺中[13] [14] [15] [16]。然而，Pt 基催化剂在使用过程中仍存在活性降低的问题。造成催化剂活性下降的原因可以概括为两类：铂的烧结和积碳的产生。尤其是在 PDH 反应过程中，铂的烧结会导致催化剂不可逆失活。铂的烧结造成铂颗粒尺寸增加，而只有较小尺寸的铂颗粒才能显示出较高的丙烷转化率[17]。原因是粒径较小的铂颗粒暴露出的晶面大部分是 211 晶面，具有更小的脱氢能垒，而大尺寸的铂颗粒暴露出的晶面主要是 111 晶面，对丙烷分子 C-H 键的活化能垒较高[9]。积碳造成催化剂失活的原因是，积碳占据了大部分活性中心，不利于丙烷分子与铂位点的接触。由于大多数催化剂都是负载型催化剂，因此可以从催化剂载体和助剂两方面来讨论其对催化剂性能的影响[18]，如图 2 所示。

2. 载体对 Pt 基催化剂性能的影响

在 Pt 基催化剂中，载体对铂粒子的分散性、稳定性、结构和电子性能方面都有重要作用。2005 年，Rioux 等人研究指出，在 PDH 反应过程中，较高的反应温度会导致 Pt 颗粒尺寸增加，从而对 PDH 反应产生不利影响，如图 3 所示[19]。同时，载体酸性过强，会促进副反应的发生，生成大量积碳，也会导致催化剂活性下降。载体种类繁多，如氧化物或非氧化物载体，包括 Al_2O_3 [20] [21]、CeO_2 [22]、SiO_2 [23] [24]、尖晶石 $MgAl_2O_4$ [25] (或 $ZnAl_2O_4$ [26])、分子筛[27] [28]和碳材料[29]等。因此，合适的催化剂载体必须能够稳定 Pt 物种，抑制副反应的发生。

(1) $C_3H_8 + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_3H_8S$ Adsorption of propane

(2) $C_3H_8S + S \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C_3H_7S + HS$ First C-H activation

(3) $C_3H_7S + S \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} C_3H_6S + HS$ Second C-H activation

(4) $C_3H_6S \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} C_3H_6 + S$ Desorption of propylene

(5) $2HS \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} H_2 + 2S$ Desorption of hydrogen

Figure 1. Reaction pathway of propane dehydrogenation (S stands for a Pt site)
图 1. 丙烷脱氢的反应步骤(S 表示 Pt 位点)

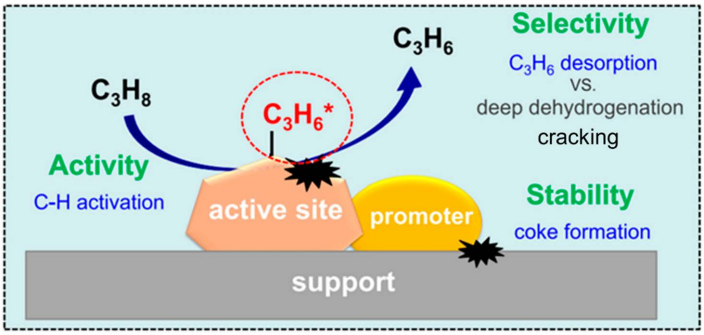

Figure 2. Schematic illustration of different steps during propane dehydrogenation
图 2. 丙烷脱氢反应中不同步骤的示意图

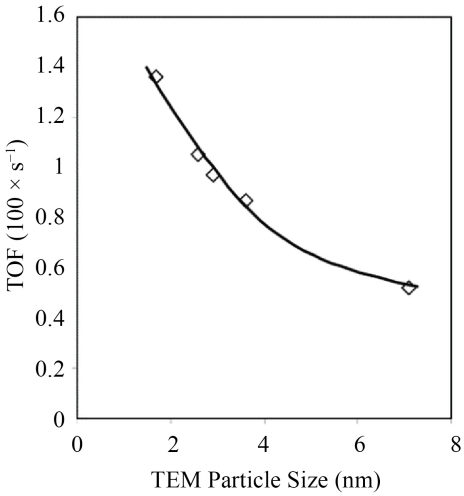

Figure 3. Effects of different sizes of Pt particles on propane dehydrogenation
图 3. 不同尺寸的 Pt 颗粒对丙烷脱氢反应的影响

2.1. Al_2O_3 载体对催化剂性能的影响

Al_2O_3 因其热稳定性好、孔隙丰富、价格低廉、机械强度高等优点，成为 Pt 基催化剂的主要载体。2014 年，Zhang 等人研究了不同载体(ZSM-5、γ-Al_2O_3、mes-Al_2O_3 和 SBA-15)在 PDH 反应中对 Pt-Sn 催

化剂性能的影响[30]。结果表明，负载在 γ-Al_2O_3 和 mes-Al_2O_3 上的 Pt-Sn 催化剂对 PDH 反应具有较高的催化活性和选择性。然而，SBA-15 和 ZSM-5 为载体负载的 Pt-Sn 催化剂的活性和选择性都很低。这是因为 SBA-15 和 Pt-Sn 之间存在弱相互作用，ZSM-5 的强酸性会导致裂解和深度脱氢副反应的发生。Al_2O_3 表现出的强酸性，也会导致深度脱氢、裂解等副反应的发生，产生大量的积碳。为了降低 Al_2O_3 的酸性，需要引入一种非酸性金属氧化物。2014 年，Jiang 发表论文指出，Al_2O_3 载体中加入 TiO_2 可以提高 Pt 基催化剂的稳定性[31]。TiO_2 的引入可以增加 Pt 的电子云密度，促进丙烯的解吸，提高催化剂的稳定性。此外，还可以在 Al_2O_3 载体中引入 MgO 物种。2016 年 Shan 等人发现 $MgAl_2O_4$ 负载的 Pt-Sn 催化剂对 PDH 反应表现出较高的催化活性和长期稳定性，这是因为载体的多级结构和弱酸性[32]。Pt 基催化剂的结构、酸度、表面性质和电子性能的变化均会影响催化剂的活性和稳定性。特别是载体酸度的降低有利于产物丙烯的解吸，从而提高了催化剂的稳定性和抗积碳能力。随后，又有研究证实[33]，载体的弱酸位点密度越高，越有利于催化反应的进行，如图 4 所示。此外，其他非酸性氧化物(如 CeO_2、ZrO_2 和 SiO_2)也被引入到 Al_2O_3 载体中，这些氧化物加入后，Pt 基催化剂的活性、稳定性和抗积碳能力得到了增强。这是因为 Pt 与载体之间的相互作用力增加，改善了 Pt 基催化剂的分散性，降低了酸性，调节了 Pt 基催化剂的电子性质[34] [35] [36] [37]。

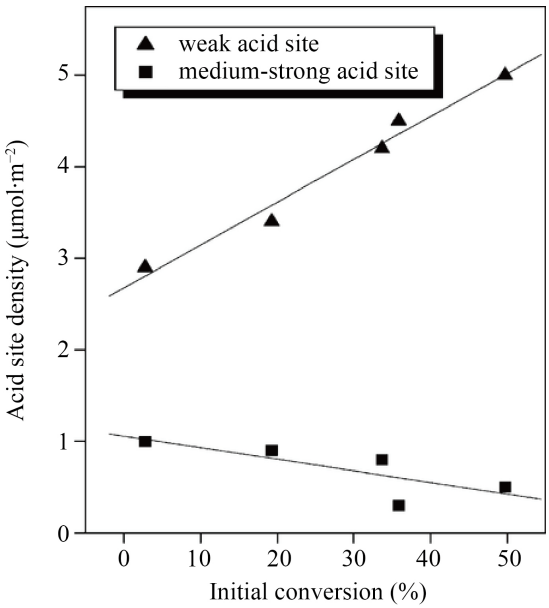

Figure 4. Effect of acid density of different strengths on initial conversion of propane dehydrogenation
图 4. 不同强度酸的密度对丙烷脱氢初始转化率的影响

2.2. 分子筛载体对催化剂性能的影响

分子筛由于其规则的孔道结构，高比表面积和可调节的酸性，被称为 Pt 基催化剂最有应用前景的载体。2010 年，Nawaz 等人报道了 Pt-Sn 负载在 SAPO-34 上制备的催化剂对 PDH 反应具有较高的催化活性[38]。然而，煅烧温度会影响 Pt 基催化剂的性能。高温焙烧后，SAPO-34 的结构发生改变，导致催化活性降低。此外，ZSM-5 分子筛表现出较高的热稳定性，可作为 Pt 基催化剂的载体。2015 年，Zhang 等人报道了 Zn 修饰的 ZSM-5 载体负载 Pt 制备的催化剂具有较高的催化活性和稳定性[39]。然而，ZSM-5 载体的强酸性会导致严重的裂解反应发生，生成大量积碳。2017 年，Li 等人合成了不同粒径的 TS-1 分

子筛，并将其作为 Pt-Sn 催化剂的载体[40]。结果表明，粒径越小的 TS-1 分子筛负载 Pt-Sn 催化剂的催化性能越好。作为对比，研究者同时合成了相同尺寸的 ZSM-5 载体，与 Pt-Sn/TS-1 催化剂相比，前者作为载体制备的催化剂对丙烯的选择性和反应的稳定性都非常低，如图 5 所示。这是由于 TS-1 粒径较小，酸性弱，有利于传质，促进了丙烯解吸。然而，Pt-Sn 与 TS-1 之间存在弱相互作用，Pt-Sn/TS-1 催化剂的再生稳定性很低。2018 年，陆续有文章报道了一些催化剂，在 PDH 反应中表现出优异的催化性能。这些催化剂是将 Pt 直接负载在分子筛上[41] [42]。然而，分子筛作为 Pt 基催化剂载体在 PDH 反应中的应用仍然面临很大的挑战，因为分子筛的酸性较强，会导致裂解和深度脱氢等副反应的发生[43]。此外，Pt 与分子筛之间的弱相互作用会导致 Pt 颗粒在 PDH 反应过程中尺寸增加[44] [45]。随后又有报道指出，Pt 可以嵌入具有特殊三维孔道的分子筛中[46] [47] [48]，如 Pt@KA 和 Pt@ZSM-5，这样制备的催化剂具有一些独特的理化性质。2020 年 Sun 等人发文指出，PtZn 搭配使用，形成限域团簇，如图 6 所示[49]。

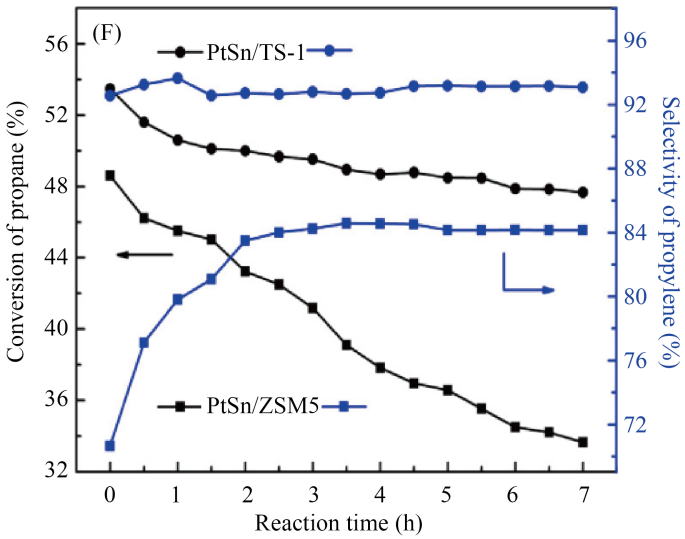

Figure 5. PDH catalytic performance of different acid strength supports
图 5. 不同酸强度载体的 PDH 催化性能表现

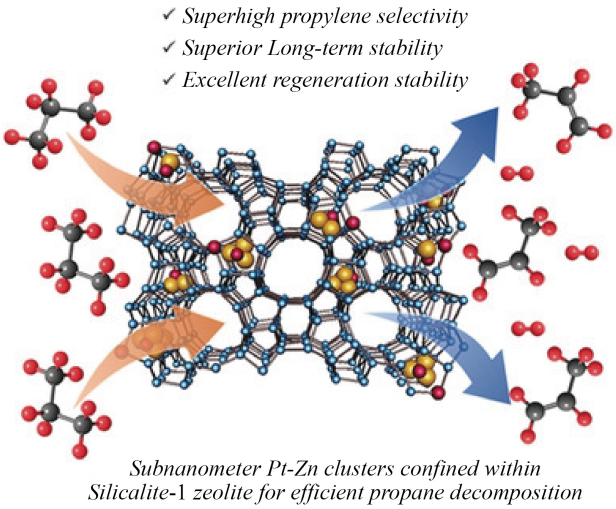

Figure 6. Pt-Zn is confined to the pore of zeolite
图 6. Pt-Zn 被限域在分子筛孔道内

这样可以进一步提升催化剂的催化活性和稳定性，如图 7 所示。此外，一些介孔材料，如 SBA-15 [50] 和 MCM-41 [27] [51]也常被用作催化剂载体，可以使活性相更加分散，具备更多的活性位点，抑制积碳的生成。

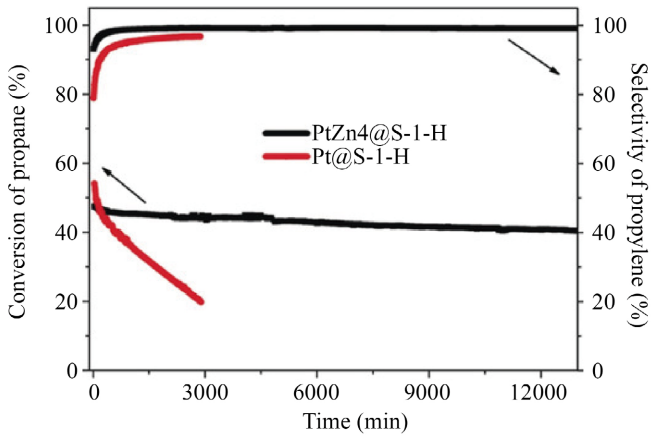

Figure 7. Comparison of catalytic performance of different catalysts
图 7. 不同催化剂的催化性能对比

3. 助剂的加入对 Pt 基催化剂性能的影响

2015 年，有研究指出，纯粹的 Pt 催化剂在 PDH 反应中表现出非常低的活性[9] [52]。商业化的 Pt 基催化剂是 Pt-Sn/Al_2O_3，而不是 Pt/Al_2O_3。将 Pt 与其他金属(M)结合形成合金或 Pt-M 复合材料是提高 PDH 反应活性和选择性以及降低 Pt 负载量的有效方法。之后的几年间有多篇文章报道了各种助剂，如 Sn [29] [53]、Zn [46] [54]、Cu [55]、Fe [56]、Co [57]、Mn [58]、In [59] [60]、Ga [61]、V [62]和 Ti [63]等，现将目前常见的助剂展示如下，如图 8 所示[64]。均得到相似的结论，助剂的加入可以极大地改善 Pt 基催化剂的分散性、结构和电子性能，从而提高催化剂的活性、选择性、稳定性和抗积碳能力[37] [38] [39]。

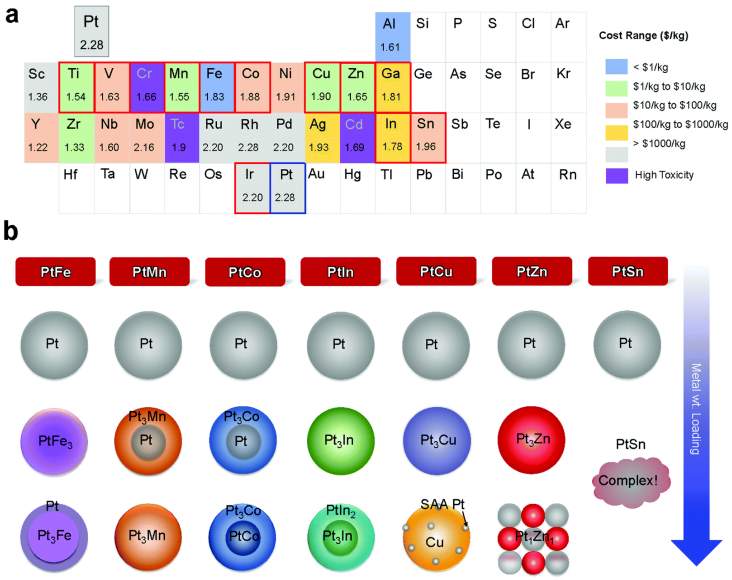

Figure 8. Common promoters used with Pt
图 8. 常见的与 Pt 搭配使用的助剂

3.1. 助剂 Sn 对催化剂性能的影响

到目前为止，使用最广泛的助剂是 Sn。在 H_2 预处理过程中，会形成 Pt-Sn 合金[65]。Pt-Sn 双金属催化剂表现出良好的选择性和稳定性，受到了最广泛的关注。对于 Sn 的作用，从 2007 年开始，陆续有研究者提出了“几何效应”和“电子效应”的概念[25] [66] [67]。一方面，研究人员认为，Sn 的加入有助于将较大的 Pt 颗粒分隔成较小的团簇，减少了形成积炭的反应位点，因为这是一种结构敏感的副反应。[29] [30] [68]。另一方面，研究人员认为 Sn 和 Pt 原子之间存在较强的电子转移，使得 Pt 原子呈现富电子状态，促进了丙烯的解吸，产生的积碳也可以从 Pt 位点转移到载体上。2012 年，Yang 等人发现 Sn 的加入有助于拓宽 Pt 的 d 能带，从而相应地降低了 Pt 表面上的 d 带能量[53]。PtSn 催化剂降低了丙烯解吸的能垒，提高了丙烯脱氢的活化能，从而提高了催化剂的稳定性和丙烯选择性。也有研究者称，Sn 物种可以在催化剂再生程序中维持 Pt 的高分散[20]。图 9 的 DFT 理论计算表明，丙烯在铂颗粒上容易发生深度脱氢反应，然而 Pt-Sn 合金形成后，丙烯在 Pt-Sn 合金上的脱氢能垒远大于丙烯在 Pt 颗粒上的脱氢能垒，从而提高了催化剂的选择性、稳定性和抗积碳能力[69]。在制备好的 Pt-Sn 催化剂中存在 Pt_3Sn、Pt_2Sn_3、Pt_n 和 $PtSn_4$ 等多种物相。特别是 Pt/Sn 的比值和 Sn 的位置对 Pt 基催化剂的性能有很大的影响。2014 年，Zhu 等人开发了一种表面有机金属法，用于合成表面富集 Sn 的 Pt-Sn 纳米颗粒，这些纳米颗粒以 $MgAl_2O_4$ 为载体，用于 PDH 催化反应[70]。这些催化剂表现出较高的催化活性和长期稳定性。这是由于高浓度的非活性物种 Sn 在铂纳米颗粒表面，会形成许多孤立的活性 Pt 位点。随着 Sn/Pt 比值从 0 增加到 2，Pt-Sn/$MgAl_2O_4$ 催化剂的活性和抗积碳能力得到了明显提高，如图 10 所示。此外，还合成了一些负载型 Pt-Sn 催化剂，如 Pt-Sn/Al_2O_3 [71] [72] [73]、PtSn/Al_2O_3/SBA-15 [36] [37] [74]、PtSnNa@SUZ-4 [75] [76] 和 Pt-Sn/SiO_2 [23]，Sn 的加入可以大大提高 Pt 基催化剂的催化活性、稳定性和抗积碳能力。

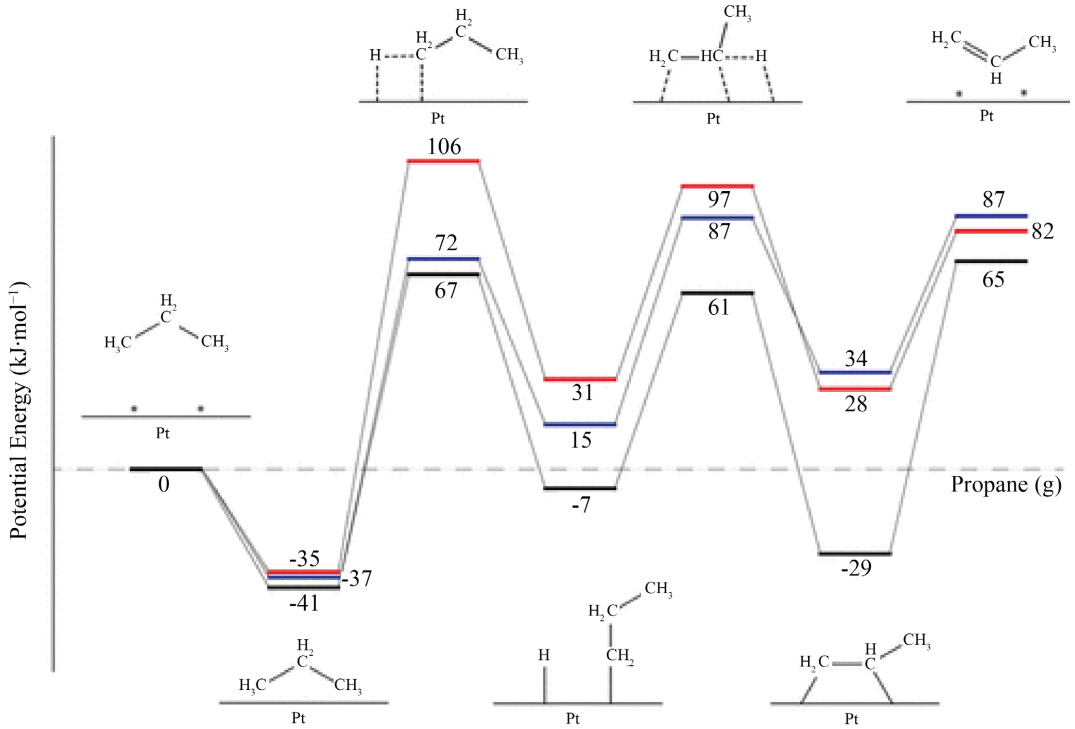

Figure 9. Energy profiles for propane dehydrogenation to propylene on Pt (111) (black), Pt_3Sn (111) (blue), and Pt_2Sn (111) (red) surfaces, as obtained by DFT calculations

图 9. 使用 DFT 计算 Pt (111) (黑色)、Pt_3Sn (111) (蓝色)和 Pt_2Sn (111) (红色)表面上丙烷脱氢制丙烯的能量分布

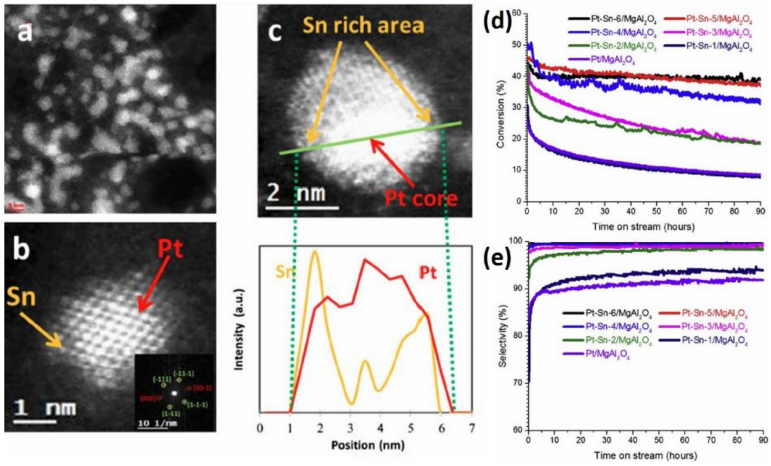

Figure 10. (a) TEM, (b) HAADF-STEM, (c) EELS line scans of Pt-Sn particles, (d) Propane conversions and (e) propylene selectivities of different Pt-Sn/$MgAl_2O_4$ catalysts
图 10. (a) TEM，(b) HAADF-STEM，(c) Pt-Sn 粒子的 EELS 线扫描，(d) 不同 Pt-Sn/$MgAl_2O_4$ 催化剂的丙烷转化率和(e) 丙烯选择性

3.2. 助剂 Zn 对催化剂性能的影响

Zn 是另一种常见的用于制备 Pt 基催化剂的助剂。添加 Zn 后，Pt 催化剂的表面结构和电子性能都发生了较大的变化。2015 年，Zhang 等人报道了含 Zn 的 ZSM-5 负载 Pt 之后的催化剂在 PDH 反应中表现出更高的催化活性和稳定性[39]。2016 年，有报道指出，Zn 的加入可以毒化 ZSM-5 分子筛的强酸位点[77]，同时改善 Pt 物种的分散，避免发生裂解、深度脱氢、结焦积碳等副反应。2018 年，Camacho 发文指出，H_2 预处理过程中会形成 Pt-Zn 合金，有利于提高催化剂活性和稳定性[78]。与此同时，Cybulskis 等人报道了 Zn 物种可以影响 Pt 物种的结构和电子性质[54]。特别指出，催化剂表面形成具有均匀间隔的 Pt_1Zn_1 金属间合金可以抑制结构敏感反应的速率。同时，Zn 的加入降低了表面 Pt 填充态的能量，削弱了 5d 轨道与吸附分子之间的成键。这说明，Zn 具有明显的给电子效应，如图 11 所示。Belskaya 等人报道了 Zn

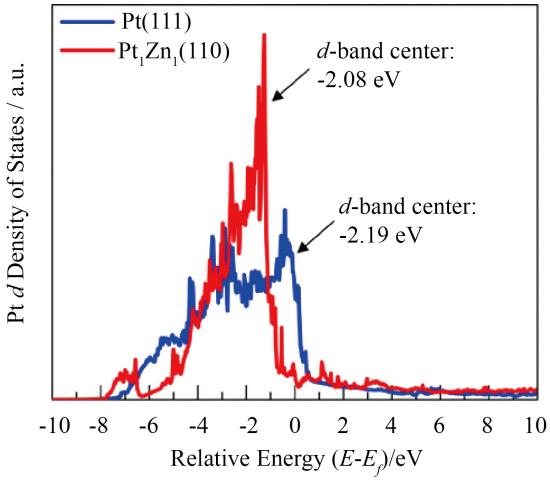

Figure 11. Projected Density of States (DOS) for d orbitals of Pt (111) and Pt_1Zn_1 (110). The vertical axis represents the electron density, and the horizontal axis corresponds to the energy relative to the Fermi energy (E_f)
图 11. Pt (111)和 Pt_1Zn_1 (110) d 轨道的预计态密度(DOS)。纵轴表示电子密度，横轴对应相对于费米能(Ef)的能量

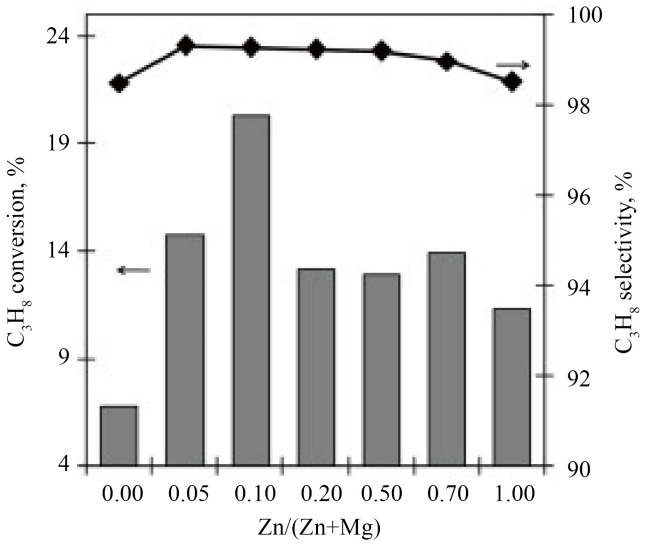

Figure 12. Propane conversion and selectivity of propylene formation for 0.3% Pt/Mg (Zn)AlO_x samples versus the fraction of Zn
图 12. 0.3% Pt/Mg (Zn)AlO_x样品的丙烷转化率和丙烯选择性随 Zn 含量的变化

的加入会对相应的混合氧化物的结构参数、结构特征和酸碱性能产生影响，这可以改变 Pt/Mg(Zn)AlO_x 催化剂的催化性能[78]，如图 12 所示。载体之间相互作用的结构和强度与 Zn 含量有很大的关系。Zn 的加入降低了活性金属 Pt 的粒径，提高了 Pt 颗粒的稳定性，从而保证了催化剂具有较高的催化活性和丙烯选择性。2019 年，Chen 和同事报道了高硅型 HZSM-5 负载的 Pt-Zn 催化剂在 PDH 反应中表现出较高的催化活性和良好的稳定性[79]。HZSM-5 分子筛中骨架 Zn 物种的存在可以改善 Pt 颗粒的分散性和稳定性，提高 Pt 基催化剂的催化活性。

4. 总结与展望

载体和助剂是影响 Pt 基催化剂性能的两个主要因素。对于负载型 Pt 基催化剂而言，合适的载体和助剂可以提升铂的分散度，降低酸性，抑制副反应的发生，增强催化剂的稳定性。除此之外，合适的反应条件也是一个重要的因素[80]。因此，在特定的反应条件下，设计最合适的催化剂，会是一项十分重要的任务。

参考文献

[1] Sattler, J.J., Ruiz-Martinez, J., Santillan-Jimenez, E., *et al*. (2014) Catalytic Dehydrogenation of Light Alkanes on Metals and Metal Oxides. *Chemical Reviews*, **20**, 10613-10653. https://doi.org/10.1021/cr5002436

[2] Wan, H., Gong, N. and Liu, L. (2022) Solid Catalysts for the Dehydrogenation of Long-Chain Alkanes: Lessons from the Dehydrogenation of Light Alkanes and Homogeneous Molecular Catalysis. *Science China Chemistry*, **11**, 2163-2176. https://doi.org/10.1007/s11426-022-1415-x

[3] Yang, F., Zhang, J., Shi, Z., *et al*. (2022) Advanced Design and Development of Catalysts in Propane Dehydrogenation. *Nanoscale*, **28**, 9963-9988. https://doi.org/10.1039/D2NR02208G

[4] 甘洪宇, 冯燕. 杂原子掺杂生物质碳催化丙烷直接脱氢制丙烯[J]. 无机材料学报, 2022, 37(10): 1058-1064.

[5] Rodaum, C., Chaipornchalerm, P., Nunthakitgoson, W., *et al*. (2022) Highly Efficient Propane Dehydrogenation Promoted by Reverse Water-Gas Shift Reaction on Pt-Zn Alloy Surfaces. *Fuel*, **325**, Article ID: 124833. https://doi.org/10.1016/j.fuel.2022.124833

[6] Sattler, J.J., Gonzalez-Jimenez, I.D., Mens, A.M., *et al*. (2013) Operando UV-Vis Spectroscopy of a Catalytic Solid in

a Pilot-Scale Reactor: Deactivation of a CrO(x)/Al_2O_3 Propane Dehydrogenation Catalyst. *Chemical Communications*, **15**, 1518-1520. https://doi.org/10.1039/c2cc38978a

[7] Sattler, J.J., Gonzalez-Jimenez, I.D., Luo, L., *et al*. (2014) Platinum-Promoted Ga/Al_2O_3 as Highly Active, Selective, and Stable Catalyst for the Dehydrogenation of Propane. *Angewandte Chemie*, **35**, 9251-9256. https://doi.org/10.1002/anie.201404460

[8] Carter, J.H., Bere, T., Pitchers, J.R., *et al*. (2021) Direct and Oxidative Dehydrogenation of Propane: From Catalyst Design to Industrial Application. *Green Chemistry*, **24**, 9747-9799. https://doi.org/10.1039/D1GC03700E

[9] Zhu, J., Yang, M.-L., Yu, Y., *et al*. (2015) Size-Dependent Reaction Mechanism and Kinetics for Propane Dehydrogenation over Pt Catalysts. *ACS Catalysis*, **11**, 6310-6319. https://doi.org/10.1021/acscatal.5b01423

[10] Liu, J., Liu, Y., Ni, Y., *et al*. (2020) Enhanced Propane Dehydrogenation to Propylene over Zinc-Promoted Chromium Catalysts. *Catalysis Science & Technology*, **6**, 1739-1746. https://doi.org/10.1039/C9CY01921A

[11] Shao, H., Wang, X., Gu, X., *et al*. (2021) Improved Catalytic Performance of CrO_x Catalysts Supported on Foamed Sn-Modified Alumina for Propane Dehydrogenation. *Microporous and Mesoporous Materials*, **311**, Article ID: 110684. https://doi.org/10.1016/j.micromeso.2020.110684

[12] Hu, Z.-P., Wang, Y., Yang, D., *et al*. (2020) CrO Supported on High-Silica HZSM-5 for Propane Dehydrogenation. *Journal of Energy Chemistry*, **47**, 225-233. https://doi.org/10.1016/j.jechem.2019.12.010

[13] Sokolov, S., Stoyanova, M., Rodemerck, U., *et al*. (2012) Comparative Study of Propane Dehydrogenation over V-, Cr-, and Pt-Based Catalysts: Time on-Stream Behavior and Origins of Deactivation. *Journal of Catalysis*, **293**, 67-75. https://doi.org/10.1016/j.jcat.2012.06.005

[14] Wang, J., Chang, X., Chen, S., *et al*. (2021) On the Role of Sn Segregation of Pt-Sn Catalysts for Propane Dehydrogenation. *ACS Catalysis*, **8**, 4401-4410. https://doi.org/10.1021/acscatal.1c00639

[15] Motagamwala, A.H., Almallahi, R., Wortman, J., *et al*. (2021) Stable and Selective Catalysts for Propane Dehydrogenation Operating at Thermodynamic Limit. *Science*, **373**, 217-222. https://doi.org/10.1126/science.abg7894

[16] Xu, Z., Yue, Y., Bao, X., *et al*. (2019) Propane Dehydrogenation over Pt Clusters Localized at the Sn Single-Site in Zeolite Framework. *ACS Catalysis*, **1**, 818-828. https://doi.org/10.1021/acscatal.9b03527

[17] Zhang, W., Wang, H., Jiang, J., *et al*. (2020) Size Dependence of Pt Catalysts for Propane Dehydrogenation: From Atomically Dispersed to Nanoparticles. *ACS Catalysis*, **21**, 12932-12942. https://doi.org/10.1021/acscatal.0c03286

[18] Martino, M., Meloni, E., Festa, G., *et al*. (2021) Propylene Synthesis: Recent Advances in the Use of Pt-Based Catalysts for Propane Dehydrogenation Reaction. *Catalysts*, **9**, Article 1070. https://doi.org/10.3390/catal11091070

[19] Rioux, R.M., Song, H., Hoefelmeyer, J.D., *et al*. (2005) High-Surface-Area Catalyst Design: Synthesis, Characterization, and Reaction Studies of Platinum Nanoparticles in Mesoporous SBA-15 Silica. *Journal of Physical Chemistry B*, **109**, 2192-2202. https://doi.org/10.1021/jp048867x

[20] Pham, H.N., Sattler, J.J., Weckhuysen, B.M., *et al*. (2016) Role of Sn in the Regeneration of Pt/gamma-Al_2O_3 Light Alkane Dehydrogenation Catalysts. *ACS Catalysis*, **4**, 2257-2264. https://doi.org/10.1021/acscatal.5b02917

[21] Shi, L., Deng, G.M., Li, W.C., *et al*. (2015) Al_2O_3 Nanosheets Rich in Pentacoordinate Al^{3+} Ions Stabilize Pt-Sn Clusters for Propane Dehydrogenation. *Angewandte Chemie*, **47**, 13994-13998. https://doi.org/10.1002/anie.201507119

[22] Frogley, B.J. and Wright, L.J. (2017) Cover Picture: A Metallaanthracene and Derived Metallaanthraquinone (Angew. Chem. Int. Ed. 1/2017). *Angewandte Chemie International Edition*, **56**, 1. https://doi.org/10.1002/anie.201610955

[23] Deng, L., Miura, H., Shishido, T., *et al*. (2018) Elucidating Strong Metal-Support Interactions in Pt-Sn/SiO_2 Catalyst and Its Consequences for Dehydrogenation of Lower Alkanes. *Journal of Catalysis*, **365**, 277-291. https://doi.org/10.1016/j.jcat.2018.06.028

[24] Zhu, Y., Kong, X., Yin, J., *et al*. (2017) Covalent-Bonding to Irreducible SiO_2 Leads to High-Loading and Atomically Dispersed Metal Catalysts. *Journal of Catalysis*, **353**, 315-324. https://doi.org/10.1016/j.jcat.2017.07.030

[25] Virnovskaia, A., Morandi, S. and Rytter, E. (2007) Characterization of Pt, Sn/Mg(Al)O Catalysts for Light Alkane Dehydrogenation by FT-IR Spectroscopy and Catalytic Measurements. *Journal of Physical Chemistry C*, **111**, 14732-14742. https://doi.org/10.1021/jp074686u

[26] Wu, J., Mallikarjun Sharada, S., Ho, C., *et al*. (2015) Ethane and Propane Dehydrogenation over PtIr/Mg(Al)O. *Applied Catalysis A*: *General*, **506**, 25-32. https://doi.org/10.1016/j.apcata.2015.08.029

[27] Silvestre-Albero, J., Serrano-Ruiz, J.C., Sepúlveda-Escribano, A., *et al*. (2008) Zn-Modified MCM-41 as Support for Pt Catalysts. *Applied Catalysis A*: *General*, **351**, 16-23. https://doi.org/10.1016/j.apcata.2008.08.021

[28] Santhosh Kumar, M., Chen, D., Walmsley, J.C., *et al*. (2008) Dehydrogenation of Propane over Pt-SBA-15: Effect of Pt Particle Size. *Catalysis Communications*, **5**, 747-750. https://doi.org/10.1016/j.catcom.2007.08.015

[29] Zhang, J., Deng, Y., Cai, X., *et al*. (2019) Tin-Assisted Fully Exposed Platinum Clusters Stabilized on Defect-Rich Gra-

phene for Dehydrogenation Reaction. *ACS Catalysis*, **7**, 5998-6005. https://doi.org/10.1021/acscatal.9b00601

[30] Zhang, Y., Zhou, Y., Shi, J., *et al.* (2014) Comparative Study of Bimetallic Pt-Sn Catalysts Supported on Different Supports for Propane Dehydrogenation. *Journal of Molecular Catalysis A*: *Chemical*, **381**, 138-147. https://doi.org/10.1016/j.molcata.2013.10.007

[31] Jiang, F., Zeng, L., Li, S., *et al*. (2014) Propane Dehydrogenation over Pt/TiO_2-Al_2O_3 Catalysts. *ACS Catalysis*, **5**, 438-447. https://doi.org/10.1021/cs501279v

[32] Shan, Y.-L., Wang, T., Sui, Z.-J., *et al*. (2016) Hierarchical $MgAl_2O_4$ Supported Pt-Sn as a Highly Thermostable Catalyst for Propane Dehydrogenation. *Catalysis Communications*, **84**, 85-88. https://doi.org/10.1016/j.catcom.2016.06.005

[33] Ren, Y., Wang, J., Hua, W., *et al*. (2012) Ga_2O_3/HZSM-48 for Dehydrogenation of Propane: Effect of Acidity and Pore Geometry of Support. *Journal of Industrial and Engineering Chemistry*, **18**, 731-736. https://doi.org/10.1016/j.jiec.2011.11.134

[34] Wang, T., Jiang, F., Liu, G., *et al*. (2016) Effects of Ga Doping on Pt/CeO_2-Al_2O_3 Catalysts for Propane Dehydrogenation. *AIChE Journal*, **12**, 4365-4376. https://doi.org/10.1002/aic.15339

[35] Long, L.-L., Xia, K., Lang, W.-Z., *et al*. (2017) The Comparison and Optimization of Zirconia, Alumina, and Zirconia-Alumina Supported PtSnIn Trimetallic Catalysts for Propane Dehydrogenation Reaction. *Journal of Industrial and Engineering Chemistry*, **51**, 271-280. https://doi.org/10.1016/j.jiec.2017.03.012

[36] Huang, L., Xu, B., Yang, L., *et al*. (2008) Propane Dehydrogenation over the PtSn Catalyst Supported on Alumina-Modified SBA-15. *Catalysis Communications*, **15**, 2593-2597. https://doi.org/10.1016/j.catcom.2008.07.015

[37] Fan, X., Li, J., Zhao, Z., *et al*. (2015) Dehydrogenation of Propane over PtSnAl/SBA-15 Catalysts: Al Addition Effect and Coke Formation Analysis. *Catalysis Science & Technology*, **5**, 339-350. https://doi.org/10.1039/C4CY00951G

[38] Nawaz, Z., Tang, X., Chu, Y., *et al*. (2010) Influence of Calcination Temperature and Reaction Atmosphere on the Catalytic Properties of Pt-Sn/SAPO-34 for Propane Dehydrogenation. *Chinese Journal of Catalysis*, **5**, 552-556. https://doi.org/10.1016/S1872-2067(09)60071-1

[39] Zhang, Y., Zhou, Y., Huang, L., *et al*. (2015) Structure and Catalytic Properties of the Zn-Modified ZSM-5 Supported Platinum Catalyst for Propane Dehydrogenation. *Chemical Engineering Journal*, **270**, 352-361. https://doi.org/10.1016/j.cej.2015.01.008

[40] Li, J., Li, J., Zhao, Z., *et al*. (2017) Size Effect of TS-1 Supports on the Catalytic Performance of PtSn/TS-1 Catalysts for Propane Dehydrogenation. *Journal of Catalysis*, **352**, 361-370. https://doi.org/10.1016/j.jcat.2017.05.024

[41] Lezcano-González, I., Cong, P., Campbell, E., *et al*. (2022) Structure-Activity Relationships in Highly Active Platinum-Tin MFI-Type Zeolite Catalysts for Propane Dehydrogenation. *ChemCatChem*, **7**, e202101828. https://doi.org/10.1002/cctc.202101828

[42] Ponomaryov, A.B., Smirnov, A.V., Pisarenko, E.V., *et al*. (2022) Enhanced Pt Dispersion and Catalytic Properties of NaCl-Promoted Pt/MFI Zeolite Catalysts for Propane Dehydrogenation. *Microporous and Mesoporous Materials*, **339**, Article ID: 112010. https://doi.org/10.1016/j.micromeso.2022.112010

[43] Nakaya, Y. and Furukawa, S. (2022) Tailoring Single-Atom Platinum for Selective and Stable Catalysts in Propane Dehydrogenation. *ChemPlusChem*, **4**, e202100560. https://doi.org/10.1002/cplu.202100560

[44] Qi, L., Zhang, Y., Babucci, M., *et al*. (2022) Dehydrogenation of Propane and n-Butane Catalyzed by Isolated $PtZn_4$ Sites Supported on Self-Pillared Zeolite Pentasil Nanosheets. *ACS Catalysis*, **18**, 11177-11189. https://doi.org/10.1021/acscatal.2c01631

[45] Qi, L., Babucci, M., Zhang, Y., *et al*. (2021) Propane Dehydrogenation Catalyzed by Isolated Pt Atoms in Identical with SiOZn-OH Nests in Dealuminated Zeolite Beta. *Journal of the American Chemical Society*, **50**, 21364-21378. https://doi.org/10.1021/jacs.1c10261

[46] Iida, T., Zanchet, D., Ohara, K., *et al*. (2018) Concerted Bimetallic Nanocluster Synthesis and Encapsulation via Induced Zeolite Framework Demetallation for Shape and Substrate Selective Heterogeneous Catalysis. *Angewandte Chemie*, **22**, 6454-6458. https://doi.org/10.1002/anie.201800557

[47] Ma, S. and Liu, Z.P. (2022) Zeolite-Confined Subnanometric PtSn Mimicking Mortise-and-Tenon Joinery for Catalytic Propane Dehydrogenation. *Nature Communications*, **13**, Article No. 2716. https://doi.org/10.1038/s41467-022-30522-1

[48] Wang, Y., Hu, Z.-P., Lv, X., *et al*. (2020) Ultrasmall PtZn Bimetallic Nanoclusters Encapsulated in Silicalite-1 Zeolite with Superior Performance for Propane Dehydrogenation. *Journal of Catalysis*, **385**, 61-69. https://doi.org/10.1016/j.jcat.2020.02.019

[49] Sun, Q., Wang, N., Fan, Q., *et al*. (2020) Subnanometer Bimetallic Platinum-Zinc Clusters in Zeolites for Propane Dehydrogenation. *Angewandte Chemie*, **44**, 19450-19459. https://doi.org/10.1002/anie.202003349

[50] Santhosh Kumar, M., Chen, D., Holmen, A., *et al*. (2009) Dehydrogenation of Propane over Pt-SBA-15 and Pt-Sn-SBA-15: Effect of Sn on the Dispersion of Pt and Catalytic Behavior. *Catalysis Today*, **142**, 17-23.

https://doi.org/10.1016/j.cattod.2009.01.002

[51] Xu, J., Shi, C., Zhang, S., *et al*. (2022) Framework Zr StabilizedPtSn/Zr-MCM-41 as a Promising Catalyst for Non-Oxidative Ethane Dehydrogenation. *Chinese Journal of Chemistry*, **8**, 918-924. https://doi.org/10.1002/cjoc.202100657

[52] Shan, Y.-L., Zhu, Y.-A., Sui, Z.-J., *et al*. (2015) Insights into the Effects of Steam on Propane Dehydrogenation over a Pt/Al_2O_3 Catalyst. *Catalysis Science & Technology*, **8**, 3991-4000. https://doi.org/10.1039/C5CY00230C

[53] Yang, M.-L., Zhu, Y.-A., Zhou, X.-G., *et al*. (2012) First-Principles Calculations of Propane Dehydrogenation over PtSn Catalysts. *ACS Catalysis*, **6**, 1247-1258. https://doi.org/10.1021/cs300031d

[54] Cybulskis, V.J., Bukowski, B.C., Tseng, H.-T., *et al*. (2017) Zinc Promotion of Platinum for Catalytic Light Alkane Dehydrogenation: Insights into Geometric and Electronic Effects. *ACS Catalysis*, **6**, 4173-4181. https://doi.org/10.1021/acscatal.6b03603

[55] Han, Z., Li, S., Jiang, F., *et al*. (2014) Propane Dehydrogenation over Pt-Cu Bimetallic Catalysts: The Nature of Coke Deposition and the Role of Copper. *Nanoscale*, **17**, 10000-10008. https://doi.org/10.1039/C4NR02143F

[56] Cai, W.T., Mu, R.T. and Zha, S.J. (2018) Subsurface Catalysis-Mediated Selectivity of Dehydrogenation Reaction. *Science Advance*, **4**, 5418-5426. https://doi.org/10.1126/sciadv.aar5418

[57] Cesar, L.G., Yang, C., Lu, Z., *et al*. (2019) Identification of a Pt_3Co Surface Intermetallic Alloy in Pt-Co Propane Dehydrogenation Catalysts. *ACS Catalysis*, **6**, 5231-5244. https://doi.org/10.1021/acscatal.9b00549

[58] Wu, Z., Bukowski, B.C., Li, Z., *et al*. (2018) Changes in Catalytic and Adsorptive Properties of 2 nm Pt(3)Mn Nanoparticles by Subsurface Atoms. *Journal of the American Chemical Society*, **44**, 14870-14877. https://doi.org/10.1021/jacs.8b08162

[59] Wegener, E.C., Wu, Z., Tseng, H.-T., *et al*. (2018) Structure and Reactivity of Pt-In Intermetallic Alloy Nanoparticles: Highly Selective Catalysts for Ethane Dehydrogenation. *Catalysis Today*, **299**, 146-153. https://doi.org/10.1016/j.cattod.2017.03.054

[60] Xia, K., Lang, W.-Z., Li, P.-P., *et al*. (2016) The Properties and Catalytic Performance of PtIn/Mg(Al)O Catalysts for the Propane Dehydrogenation Reaction: Effects of pH Value in Preparing Mg(Al)O Supports by the Co-Precipitation Method. *Journal of Catalysis*, **338**, 104-114. https://doi.org/10.1016/j.jcat.2016.02.028

[61] Nakaya, Y., Hirayama, J., Yamazoe, S., *et al*. (2020) Single-Atom Pt in Intermetallics as an Ultrastable and Selective Catalyst for Propane Dehydrogenation. *Nature communications*, **11**, Article No. 2838. https://doi.org/10.1038/s41467-020-16693-9

[62] Purdy, S.C., Ghanekar, P., Mitchell, G., *et al*. (2020) Origin of Electronic Modification of Platinum in a Pt3V Alloy and Its Consequences for Propane Dehydrogenation Catalysis. *ACS Applied Energy Materials*, **3**, 1410-1422. https://doi.org/10.1021/acsaem.9b01373

[63] Li, Z., Yu, L., Milligan, C., *et al*. (2018) Two-Dimensional Transition Metal Carbides as Supports for Tuning the Chemistry of Catalytic Nanoparticles. *Nature Communications*, **9**, Article No. 5258. https://doi.org/10.1038/s41467-018-07502-5

[64] Chen, S., Chang, X., Sun, G., *et al*. (2021) Propane Dehydrogenation: Catalyst Development, New Chemistry, and Emerging Technologies. *Chemical SOCIETY reviews*, **5**, 3315-3354. https://doi.org/10.1039/D0CS00814A

[65] Iglesias-Juez, A., Beale, A.M., Maaijen, K., *et al*. (2010) A Combined *in Situ* Time-Resolved UV-Vis, Raman and High-Energy Resolution X-Ray Absorption Spectroscopy Study on the Deactivation Behavior of Pt and PtSn Propane Dehydrogenation Catalysts under Industrial Reaction Conditions. *Journal of Catalysis*, **276**, 268-279. https://doi.org/10.1016/j.jcat.2010.09.018

[66] Gorczyca, A., Raybaud, P., Moizan, V., *et al*. (2019) Atomistic Models for Highly-Dispersed PtSn/γ-Al_2O_3 Catalysts: Ductility and Dilution Affect the Affinity for Hydrogen. *ChemCatChem*, **16**, 3941-3951. https://doi.org/10.1002/cctc.201900429

[67] Hauser, A. W., Gomes, J., Bajdich, M., *et al*. (2013) Subnanometer-Sized Pt/Sn Alloy Cluster Catalysts for the Dehydrogenation of Linear Alkanes. *Physical Chemistry Chemical Physics*, **47**, 20727-20734. https://doi.org/10.1039/c3cp53796j

[68] Zhu, Y., An, Z. and He, J. (2016) Single-Atom and Small-Cluster Pt Induced by Sn(IV) Sites Confined in an LDH Lattice for Catalytic Reforming. *Journal of Catalysis*, **341**, 44-54. https://doi.org/10.1016/j.jcat.2016.06.004

[69] Nykänen, L. and Honkala, K. (2013) Selectivity in Propene Dehydrogenation on Pt and Pt_3Sn Surfaces from First Principles. *ACS Catalysis*, **12**, 3026-3030. https://doi.org/10.1021/cs400566y

[70] Zhu, H., Anjum, D.H., Wang, Q., *et al*. (2014) Sn Surface-Enriched Pt-Sn Bimetallic Nanoparticles as a Selective and Stable Catalyst for Propane Dehydrogenation. *Journal of Catalysis*, **320**, 52-62. https://doi.org/10.1016/j.jcat.2014.09.013

[71] Zangeneh, F.T., Mehrazma, S. and Sahebdelfar, S. (2013) The Influence of Solvent on the Performance of Pt-Sn/θ-Al_2O_3

Propane Dehydrogenation Catalyst Prepared by Co-Impregnation Method. *Fuel Processing Technology*, **109**, 118-123. https://doi.org/10.1016/j.fuproc.2012.09.046

[72] Sun, C., Luo, J., Cao, M., *et al*. (2018) A Comparative Study on Different Regeneration Processes of Pt-Sn/γ-Al_2O_3 Catalysts for Propane Dehydrogenation. *Journal of Energy Chemistry*, **27**, 311-318. https://doi.org/10.1016/j.jechem.2017.09.035

[73] Zangeneh, F.T., Taeb, A., Gholivand, K., *et al*. (2015) The Effect of Mixed HCl-KCl Competitive Adsorbate on Pt Adsorption and Catalytic Properties of Pt-Sn/Al_2O_3 Catalysts in Propane Dehydrogenation. *Applied Surface Science*, **357**, 172-178. https://doi.org/10.1016/j.apsusc.2015.08.235

[74] Li, B., Xu, Z., Chu, W., *et al*. (2017) Ordered Mesoporous Sn-SBA-15 as Support for Pt Catalyst with Enhanced Performance in Propane Dehydrogenation. *Chinese Journal of Catalysis*, **4**, 726-735. https://doi.org/10.1016/S1872-2067(17)62805-5

[75] Zhou, H., Gong, J., Xu, B., *et al*. (2016) PtSnNa@SUZ-4-Catalyzed Propane Dehydrogenation. *Applied Catalysis A*: *General*, **527**, 30-35. https://doi.org/10.1016/j.apcata.2016.08.017

[76] Zhou, H., Gong, J., Xu, B., *et al*. (2017) PtSnNa/SUZ-4: An Efficient Catalyst for Propane Dehydrogenation. *Chinese Journal of Catalysis*, **3**, 529-536. https://doi.org/10.1016/S1872-2067(17)62750-5

[77] Belskaya, O.B., Stepanova, L.N., Gulyaeva, T.I., *et al*. (2016) Zinc Influence on the Formation and Properties of Pt/Mg(Zn)AlO Catalysts Synthesized from Layered Hydroxides. *Journal of Catalysis*, **341**, 13-23. https://doi.org/10.1016/j.jcat.2016.06.006

[78] Camacho-Bunquin, J., Ferrandon, M.S., Sohn, H., *et al*. (2018) Atomically Precise Strategy to a PtZn Alloy Nanocluster Catalyst for the Deep Dehydrogenation of n-Butane to 1,3-Butadiene. *ACS Catalysis*, **11**, 10058-10063. https://doi.org/10.1021/acscatal.8b02794

[79] Chen, C., Sun, M., Hu, Z., *et al*. (2019) New Insight into the Enhanced Catalytic Performance of ZnPt/HZSM-5 Catalysts for Direct Dehydrogenation of Propane to Propylene. *Catalysis Science & Technology*, **8**, 1979-1988. https://doi.org/10.1039/C9CY00237E

[80] Liu, H., Liu, Y., Zhang, X., *et al*. (2023) Effect of Different Properties of Silicon-Based Support on Propane Dehydrogenation Performance of PtZn Bimetallic Catalyst. *Fuel*, **332**, Article ID: 125858. https://doi.org/10.1016/j.fuel.2022.125858