综述与专论

DOI：10.11949/0438-1157.20251015

电子效应精准调控的纳米金催化剂在低碳多元醇选择性氧化研究进展

赵明月[1]，孟凡宇[1]，闫昊[1]，冯翔[1]，刘熠斌[1]，陈小博[1]，杨朝合[1]，陈德[2]

（[1]中国石油大学(华东)重质油全国重点实验室，山东 青岛 266580； [2]挪威科技大学，挪威 特隆赫姆 7491）

摘要： 低碳多元醇(来源于石油、煤或生物质)的选择性氧化是制备乙醇酸、甘油酸等高附加值化学品的关键途径。开发以分子氧为氧化剂的高效绿色催化工艺，对实现多元醇高值化转化及促进高端化工产业链绿色升级具有重要意义，其核心在于开发高性能负载型催化剂。本文系统综述了以电子效应精准调控为核心的纳米金催化剂在伯羟基氧化制羧酸、仲羟基氧化制酮及C—C键断裂制短链酸三大路径的研究进展，重点分析载体工程与双金属协同策略如何通过调变金的电子结构解决羟基选择性活化、过度氧化抑制等关键问题，探讨了电子结构与催化性能之间构效关系及反应机理，并对未来催化剂设计方向与潜在应用前景进行了展望，为绿色催化工艺的开发提供理论依据与技术参考。

关键词： 低碳多元醇；纳米金催化剂；氧化；催化剂载体；电子效应

中图分类号： TQ 426；O 643.3 **文献标志码：** A

文章编号： 0438-1157（2026）05-2322-16

Progress in research of selective oxidation of low carbon polyols over nano-Au catalysts with precise electronic effect regulation

ZHAO Mingyue[1], MENG Fanyu[1], YAN Hao[1], FENG Xiang[1], LIU Yibin[1], CHEN Xiaobo[1],
YANG Chaohe[1], CHEN De[2]

(*[1]State Key Laboratory of Heave Oil Processing, China University of Petroleum (East China), Qingdao* 266580, *Shandong, China*;
[2]Norwegian University of Science and Technology, Tronheim 7491, *Norway*)

Abstract: Selective oxidation of low-carbon polyols (derived from petroleum, coal or biomass) is a key approach for preparing high-value chemicals such as glycolic acid and glyceric acid. The development of efficient and green catalytic processes using molecular oxygen as the oxidant is of great significance for achieving high-value conversion of polyols and promoting the green upgrading of the high-end chemical industry chain. The core lies in the development of high-performance supported catalysts. In this paper, recent advances regarding the nano-gold catalysts with precise electronic effect modulation as the core for conversion of primary hydroxyl groups to carboxylic acids, secondary hydroxyl groups to ketones, and C—C bond cleavage to short-chain acids. It focuses on how support engineering and bimetallic synergistic strategies can address key issues such as selective activation of hydroxyl groups and inhibition of excessive oxidation by modulating the electronic structure of gold. The structure-

---

收稿日期： 2025-09-09 **修回日期：** 2025-10-29

通信作者： 闫昊(1993—)，男，博士，副教授，haoyan@upc.edu.cn；冯翔(1988—)，男，博士，教授，xiangfeng@upc.edu.cn

第一作者： 赵明月(1996—)，女，博士研究生，2965155534@qq.com

基金项目： 国家自然科学基金项目(22108305)；山东省自然科学基金优秀青年基金项目(ZR2023YQ009)；山东省泰山学者专项基金项目(tsqn202408101)；中央高校基本科研业务费专项(25CX06002A)

引用本文： 赵明月, 孟凡宇, 闫昊, 冯翔, 刘熠斌, 陈小博, 杨朝合, 陈德. 电子效应精准调控的纳米金催化剂在低碳多元醇选择性氧化研究进展[J]. 化工学报, 2026, 77(5): 2322-2337

Citation： ZHAO Mingyue, MENG Fanyu, YAN Hao, FENG Xiang, LIU Yibin, CHEN Xiaobo, YANG Chaohe, CHEN De. Progress in research of selective oxidation of low carbon polyols over nano-Au catalysts with precise electronic effect regulation[J]. CIESC Journal, 2026, 77(5): 2322-2337

activity relationships between electronic properties and catalytic performance are discussed, along with associated reaction mechanisms. Future directions for catalyst design and potential applications are also prospected, offering theoretical and practical guidance for the development of sustainable catalytic processes.

Keywords: low carbon polyols; nano-Au catalysts; oxidation; catalyst supports; electronic effect

引言

在当前国家“双碳”战略深入推进、面向新发展阶段谋划的背景下，我国化工行业正加速向高端化、绿色化转型，积极构建绿色低碳循环产业体系。国家发展和改革委员会、工业和信息化部联合发布的《关于推动未来产业创新发展的实施意见》中明确提出，要加快发展生物基材料和高附加值专用化学品，推进碳一原料低碳转化与高值利用[1]。随着煤制乙二醇、轻烃裂解及生物质技术不断发展，乙二醇、丙三醇等低碳多元醇产能持续扩大，出现结构性过剩[2-8]。将这类过剩的多元醇转化为乙醇酸、甘油酸、二羟基丙酮等高附加值含氧化学品，已成为行业重点发展方向[1,9-10]。这些产物可进一步转化为环保聚合物、医用药物、可再生生物塑料和绿色溶剂，广泛应用于国防、医药、日化等领域[11-13]。近年来，水相温和条件下以氧气为氧化剂的多相催化选择性氧化技术，因原子经济性高、过程清洁被视为实现该转化的理想途径。然而，该过程的核心挑战在于开发兼具高活性、高选择性和优异稳定性的非均相催化剂[14-15]。

传统的Pt、Pd等贵金属催化剂在催化低碳多元醇氧化时，易引发C—C键断裂和深度氧化，导致目标酸/酮的选择性偏低[11-19]。与之相比，纳米金催化剂凭借其独特的表面电子结构，可高效活化分子氧生成活性氧物种（OH*或O_2^-），选择性进攻C—H/O—H键；其d轨道对含氧中间体的吸附强度适中，有利于产物脱附，从而抑制过度氧化反应。因此，金催化剂在温和条件下表现出优异的选择性氧化能力，已成功应用于CO氧化、丙烯环氧化等多种反应[20-25]。尽管如此，纳米金催化剂在应对多元醇分子中多个官能团的竞争吸附与活化、复杂产物选择性的精准调控以及活性位点在反应条件下的稳定性等方面，依然面临严峻挑战[26-30]。因此，开发高性能纳米金催化剂，关键在于通过载体界面相互作用和双金属协同效应的精确设计策略调控Au活性位点的电子性质，以实现特定反应路径的高效、高选择性进行。

近年来，多元醇选择性氧化领域的研究日益聚焦于金基催化剂的理性设计及其反应机制的深入解析。研究者们逐渐认识到，通过载体界面工程和双金属协同策略来调变金的电子结构，是引导反应路径向目标产物高效转化的核心[11-19,31]。这一思路将催化剂设计的焦点从传统的几何结构与形貌控制，转向了对活性位点本征电子性质的“自上而下”的精密调控。特别是对于电子效应如何通过特定的载体相互作用与双金属协同机制，来分别解决伯仲羟基选择性活化、抑制过度氧化等关键科学问题，仍需进行系统性的梳理与机理层面的深入探讨。为此，本文旨在围绕电子效应精准调控这一主线，剖析载体工程与双金属协同策略如何通过调变金的电子结构，为解决低碳多元醇选择性氧化中的关键挑战提供新的视角与设计原则。

1 低碳多元醇来源与高值化需求

低碳多元醇（如乙二醇、甘油、丙二醇、丁二醇等C_2~C_4醇）作为基础化工原料，目前已形成显著产能过剩[3-4]。如图1所示，其产能扩张主要源于煤制乙二醇技术[3-4,6]、生物柴油副产甘油路线[32-34]，以及环氧丙烷水解制丙二醇[35-36]、通过炔醛法与顺酐法等工业路径合成丁二醇[37]。此外，通过微生物发酵途径亦可制备上述多元醇，展现了绿色合成的潜力[8,38-39]。然而，该路径目前仍普遍面临菌株产率低、过程经济性差等挑战，实现大规模工业化应用尚需进一步突破[39]。这些多元醇的下游应用高度集中于聚酯纤维制造、日用化学品和通用树脂溶剂等低附加值领域，导致供需结构性失衡与行业利润率持续下滑。因此，在当前背景下，发展高效化学催化技术对现有大量过剩的石油基/煤基多元醇进行高值化转化，具有更为现实和紧迫的工业意义。

突破当前困局的核心路径是将过剩多元醇定向转化为高附加值含氧化学品，例如乙醇酸、甘油酸以及二羟基丙酮等关键酮/酸。此类产物是合成环保聚合物、生物可降解材料及高端医药中间体的核心原料，其市场价值可达原料醇的5~10倍[40-43]。

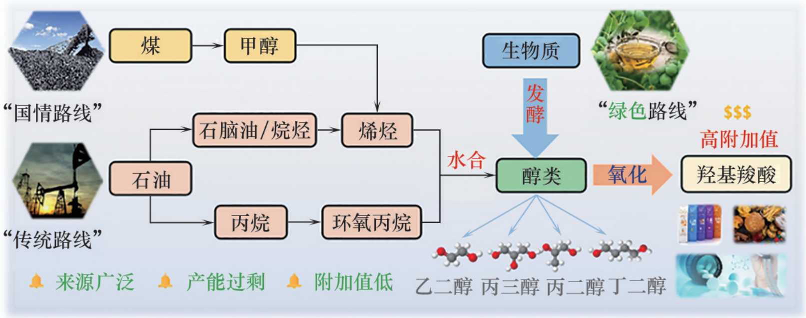

图1 低碳多元醇的生产工艺和氧化产物用途

Fig.1 Production process of low carbon polyols and uses of oxidation products

该过程面临三大催化挑战：精准控制氧化路径选择性，即区分伯羟基生成羧酸、仲羟基生成酮类化合物以及C—C键断裂生成短链酸的定向转化；开发绿色可持续工艺，摆脱对强碱介质的依赖；抑制中间产物的过度氧化反应以提高目标产物收率[44-46]。纳米金催化剂凭借其可调的电子结构、高效的分子氧活化能力以及可实现无碱氧化的催化特性，成为应对上述挑战的重要研究方向，其精准设计与调控机制将在本文中系统阐述。

2 低碳多元醇选择性氧化机理

多元醇选择性氧化的反应机理虽因底物与催化体系而异，但其核心路径均涉及O—H键断裂、C—H键活化和最终氧化为含氧产物的串联过程。不同路径与反应条件（碱性/无碱）下机制存在本质区别（图2）[47]。伯羟基氧化在碱性条件下由OH^-直接参与脱氢，经烷氧中间体快速转化为醛并进一步氧化为羧酸[48]；而在无碱条件下，反应依赖金属-载体界面处的碱性位与活性氧物种（O*或OOH*）协同促进分步脱氢与氧化，更易实现高选择性调控[48-49]。仲羟基氧化普遍遵循界面介导的协同机制，O_2在活性位点活化形成OOH*，进攻β—C—H实现脱氢生成酮[30]。C—C键断裂路径则多在碱性条件下延续伯羟基氧化过程，醛中间体在OH^-亲核进攻或表面自由基机制下发生断键，但易受羟醛缩合等副反应干扰，导致短链酸选择性偏低、产物分布复杂[50]。尽管金基催化剂在多元醇转化中已取得进展，其界面活性位点与双金属协同机制仍待系统揭示。未来需结合原位表征与理论计算，在原子尺度厘清关键中间体吸附、路径选择与副反应抑制的电子调控规律，为绿色合成提供精准设计策略。

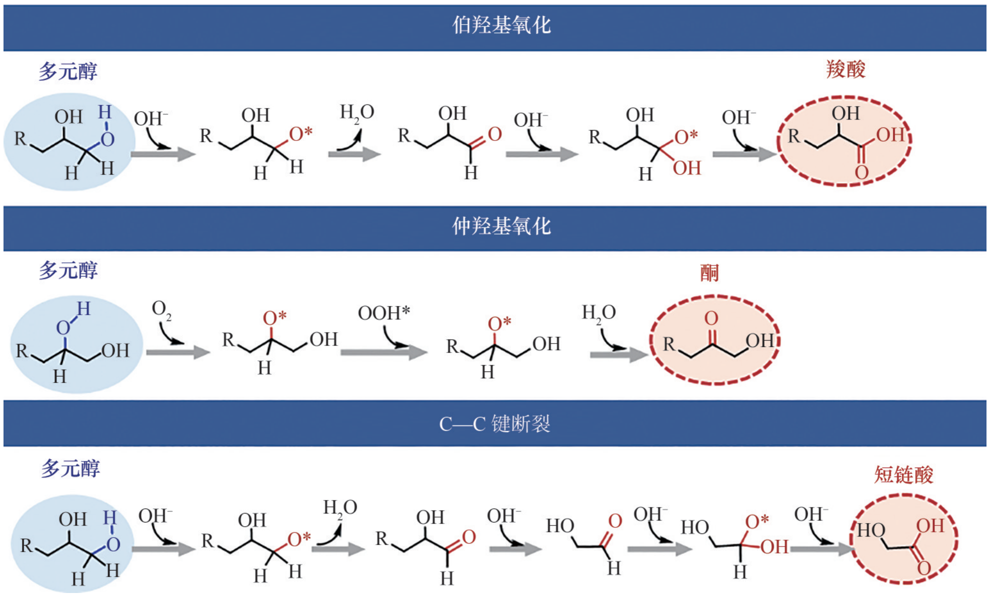

图2 多元醇伯羟基氧化、仲羟基氧化和C—C键断裂氧化的反应机理示意图[47]

Fig.2 Proposed reaction mechanism of primary, secondary hydroxyl and C—C bond cleavage oxidation of polyols[47]

3 伯羟基选择性氧化制羧酸

多元醇的伯羟基选择性氧化作为合成乙醇酸、甘油酸等高附加值羧酸类产物的核心路径，其高效定向转化需依赖多维度协同设计策略，包含利用载体表面酸碱性设计调变O—H键断裂的能垒特征和借助双金属界面电子协同效应抑制深度氧化副反应。这一涵盖载体改性与界面协同的综合性策略，通过重构活性位微环境实现反应路径精准控制，为伯羟基至羧酸的工业转化提供理论基础[19,51-54]。

3.1 载体效应：界面电子结构的精准设计与调控

载体工程通过精准调控载体的表面性质（如酸碱性、形貌结构）及其与金属间的电子相互作用，成为定向优化纳米金催化剂电子结构与催化性能的关键策略（图3和表1）。如图3(a)~(c)所示，

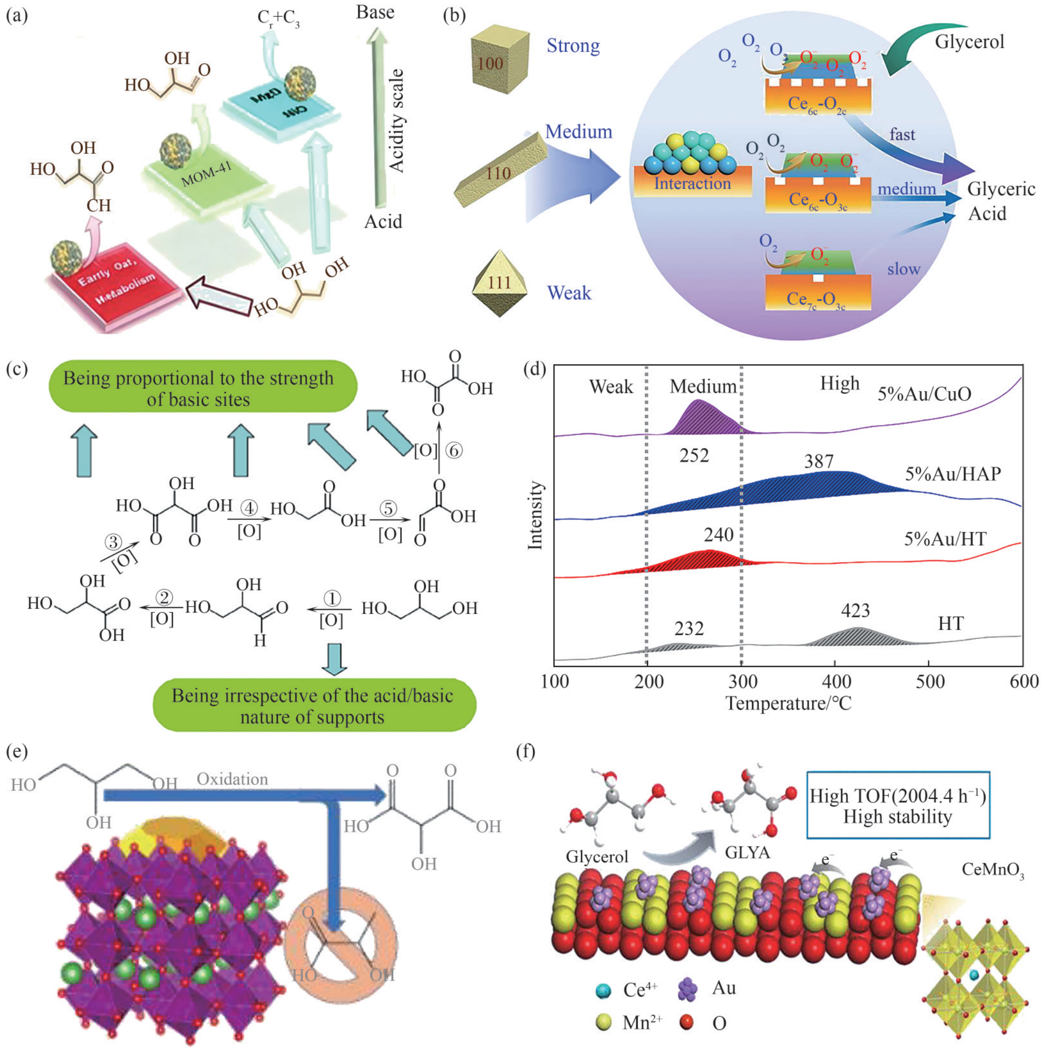

图3 多元醇伯羟基选择性氧化制羧酸相关催化剂载体工程研究：(a)不同酸碱性质载体负载的AuPt催化剂调控甘油氧化产物[55]；(b) Au_1Pt_3/CeO_2催化剂上甘油氧化的可能反应原理图[56]；(c)载体的酸/碱性质与反应速率的关系[57]；(d) 5Au/HT、5Au/HAP、5Au/CuO和水滑石(HT)催化剂的CO_2程序升温脱附(CO_2-TPD)谱图[58]；(e) $LaMnO_3$钙钛矿负载的Au催化剂在甘油氧化制丙醇二酸中的特殊选择性[59]；(f) $CeMnO_3$钙钛矿及Au/$CeMnO_3$催化剂制备过程示意图及催化甘油氧化为甘油酸性能[60]

Fig. 3 Researches on catalyst support engineering related to selective oxidation of primary hydroxyl groups of polyols to carboxylic acids: (a) regulation of glycerol oxidation products by AuPt catalysts loaded on supports with different acid-base properties[55]; (b) possible reaction mechanism of glycerol oxidation on Au_1Pt_3/CeO_2 catalysts[56]; (c) relationship between acid/base properties of supports and reaction rates[57]; (d) CO_2 temperature programmed desorption (CO_2-TPD) spectra of 5Au/HT, 5Au/HAP, 5Au/CuO, and hydrotalcite (HT) catalysts[58]; (e) unique selectivity of Au catalysts supported on $LaMnO_3$ perovskite for glycerol oxidation to tartronic acid[59]; (f) schematic diagram of $CeMnO_3$ perovskite and Au/$CeMnO_3$ catalyst preparation process and performance in catalytic oxidation of glycerol to glyceric acid[60]

表1 多元醇伯羟基选择性氧化中不同载体类型的催化性能总结

Table 1 Summary of catalytic performance of different support types for the selective oxidation of primary hydroxyl groups in polyols

催化剂	温度/℃	时间/h	压力/bar	底物/(mol/L)	碱/(mol/L)	转化率/%	产物选择性/%	TOF/h^{-1}	文献
5Au/HT	60	4	10	甘油:0.1	0.2	89.5	甘油酸:61.2	—	[58]
AuPt/H-SiO_2	80	4	3	甘油:0.3	0	30.0	甘油酸:61.0	—	[55]
Au-Pt/HT	60	4	2	甘油:0.3	0	64.0	甘油酸:69.0	—	[57]
Au-Pt/MgO	60	4	2	甘油:0.3	0	52.0	甘油酸:48.0	—	[57]
Au_1Pt_3/NC	80	2	1	甘油:0.3	0	83.7	甘油酸:60.5	0.26	[56]
Au-Pt/Hβ	100	3	3	甘油:0.3	0	68.0	甘油酸:68.0	—	[61]
Au-Pt/N-TiO_2	100	6	3	甘油:0.3	0	92.1	甘油酸:79.9	—	[62]
Au/$LaMnO_3$	100	24	3	甘油:0.3	1.2	92.0	丙醇二酸:87.0	390	[59]
Au/$CeMnO_3$	90	10	10	甘油:0.4	1.0	71.0	甘油酸:77.0	2004	[60]
Au/$Mg(OH)_2$	60	6	3	1,2-丙二醇:0.68	1.36	94.4	乳酸:89.4	—	[63]

注:1 bar=10^5 Pa。

载体酸碱性的精细调控可直接调变金的电子密度,从而实现对反应路径的精准引导。碱性载体(如水滑石HT)可向Au NPs提供电子形成富电子中心,促进甘油高效转化为甘油酸(5%Au/HT实现89.5%转化率与61.2%选择性),图3(d)的CO_2程序升温脱附(CO_2-TPD)谱图直观对比了不同载体的碱性强度,为碱性调控提供了直接实验证据[58]。弱碱性位点可加速酸产物脱附,有效抑制过度氧化副反应[图3(c)][57]。而酸性载体的可控引入虽可能降低本征活性,但能通过精准调控酸性位密度显著提升C_3产物选择性[61]。同时,碱性强度与产物分布之间存在明显关联:丙醇二酸的选择性随碱性增强而提高,而甘油醛的选择性则随之下降[图3(a)][55]。例如Evans等[59]发现强碱性$LaMnO_3$载体驱动丙醇二酸产率达80%[图3(e)]。载体结构的精细设计进一步强化了电子效应的可调控性,图3(b)的CeO_2纳米立方(NC)因其丰富的氧空位和强电子相互作用,使Au_1Pt_3/CeO_2-NC展现出最高的甘油氧化活性(周转频率TOF:937.8 h^{-1},即单位时间内每个活性位点转化反应物的分子数)[56]。此外,金属-载体强相互作用(SMSI)的有效调控,如图3(f)所示$CeMnO_3$钙钛矿中精心设计的晶格-氧空位双功能位点,可实现与金活性中心的强电子耦合,在保持高活性的同时显著提升稳定性[60]。密度泛函理论(DFT)计算从电子层面揭示了精准调控的化学本质,通过调控载体性质精确控制金的d带中心位置,可定量调节其对含氧中间体的吸附能,从而按需抑制副反应或促进目标路径[62]。计算还能精准解析界面电荷分布,阐明Au与Lewis酸位点的协同机制[61]。综上,载体工程通过对金活性中心电子结构的精准、可控制调变,实现了对多元醇氧化路径的有效引导。

3.2 协同效应:双金属电子相互作用的优化与增强

除了活性较低的单金属催化剂外,研究人员近年来致力于开发具有更高性能的双金属金基催化剂。通过引入Pt、Pd、Cu等第二金属与Au形成合金、核壳或界面复合结构,可实现对金活性位点电子结构的精准调控,从而显著提升催化活性、选择性与稳定性。其性能增强的本质源于双金属间在反应条件下的动态电子相互作用,而非简单的静态电荷转移。该相互作用主要由不同金属对氧的化学亲和力差异所驱动,诱导界面处发生局域化电荷重排,进而优化反应路径。如图4和表2所示,其增效机制主要源于以下几个方面。首先,金属间电荷转移有效调节活性位点的电子结构,优化对氧物种的吸附与活化行为[67]。对氧具有更强亲和力的金属(如Pd、Pt)会优先吸附并活化O_2,诱导电子从Au向第二金属转移,形成缺电子$Au^{\delta+}$物种。如图4(a)、(e)、(g)所示,在Au-Pd体系中,Pd的引入导致电子从Au向缺电子的Pd转移,促进O_2解离吸附[64],还在特定Pd覆盖度下优化了表面电荷密度,甘油氧化活性显著提升(周转频率TOF约6000 h^{-1})[69]。反之,电负性较低的金属(如Cu)则向Au转移电子,形成富电子$Au^{\delta-}$物种,如图4(c)中AuCu-ZnO催化剂因形成富电

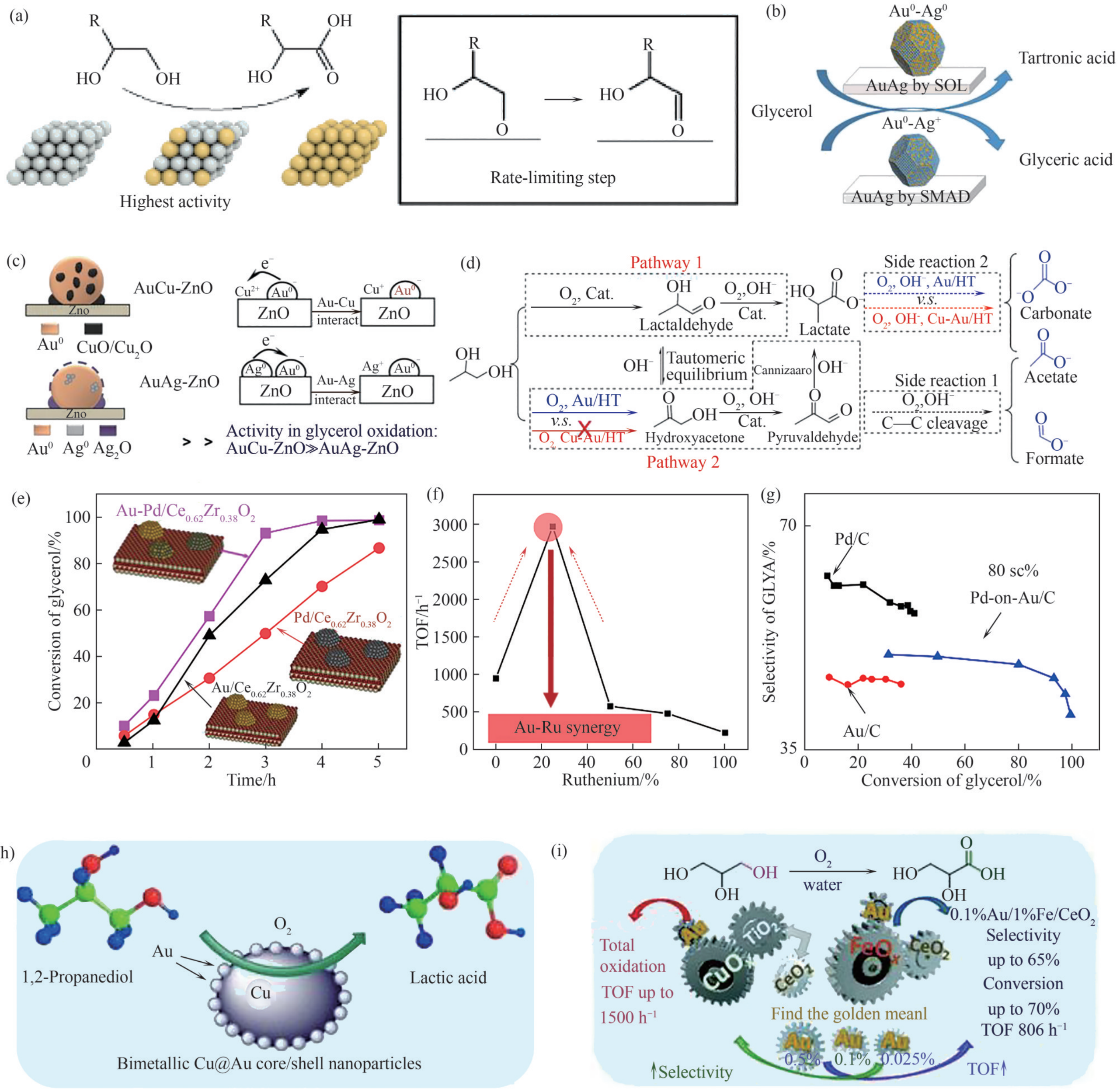

图4 多元醇伯羟基选择性氧化相关催化剂双金属协同研究：(a) Au-Pd/C催化剂上乙二醇氧化反应原理图及速控步骤[64]；(b)溶胶固定(SOL)和溶剂化金属原子沉积(SMAD)制备AuAg/Al$_2$O$_3$催化剂产物分布图[29]；(c) AuAg-ZnO和AuCu-ZnO催化剂性能对比[65]；(d) Au-Cu/HT和Au/HT催化1,2-丙二醇氧化路径[66]；(e) 2.2AuPd/CeZrO$_x$与单金属性能对比图[67]；(f) Au$_1$Ru$_{0.5}$CeZrO$_x$催化剂的Au/Ru比例与活性关系图[68]；(g) Pd-on-Au/C与单金属性能对比图[69]；(h) Cu@Au核/壳纳米颗粒上1,2-丙二醇转化为乳酸[70]；(i) Au/Fe-CeO$_2$与Au/Cu-CeO$_2$性能对比图[28]

Fig. 4 Researches on bimetallic synergy in catalysts related to selective oxidation of primary hydroxyl groups of polyols: (a) schematic diagram of glycol oxidation reaction mechanism and rate determination step on Au-Pd/C catalyst[64]; (b) oxidation product distribution over AuAg/Al$_2$O$_3$ catalysts prepared by sol immobilization (SOL) and solvated metal atom deposition (SMAD) methods[29]; (c) performance comparison between AuAg-ZnO and AuCu-ZnO catalysts[65]; (d) proposed reaction pathways of 1,2-propanediol over Au-Cu/HT and Au/HT catalysts[66]; (e) performance comparison between 2.2AuPd/CeZrO$_x$ catalyst and its monometallic counterparts[67]; (f) relationship between Au/Ru ratio of Au$_1$Ru$_{0.5}$CeZrO$_x$ catalyst and activity[68]; (g) performance comparison between Pd-on-Au/C and monometallic catalysts[69]; (h) conversion of 1,2-propanediol to lactic acid on Cu@Au core/shell nanoparticles[70]; (i) reaction performance comparison between Au/Fe-CeO$_2$ and Au/Cu-CeO$_2$ catalysts[28]

表2　多元醇伯羟基选择性氧化中不同双金属组合的催化性能协同效应总结

Table 2　Summary of catalytic performance and synergistic effects of different bimetallic combinations for selective oxidation of primary hydroxyl groups in polyols

催化剂	温度/℃	时间/h	压力/bar	底物/(mol/L)	碱/(mol/L)	转化率/%	产物选择性/%	TOF/h^{-1}	文献
Au-Pd/C	60	5	10	乙二醇:0.1	1	90.0	乙醇酸:100	600	[64]
0.1Au/Fe-CeO_2	90	4	5	甘油:0.3	0.5	68.0	甘油酸:63.0	0.22	[28]
AuAg/Al_2O_3-SMAD	50	6	3	甘油:0.3	1.2	66.7	甘油酸:52.0	0.28	[29]
AuAg/Al_2O_3-Sol	50	2	3	甘油:0.3	1.2	83.3	甘油酸:44.0	0.83	[29]
2.2AuPd/$CeZrO_x$	60	3	3	甘油:0.3	0.6	93.6	甘油酸:59.8	0.09	[67]
Pd-on-Au/C	60	3	-	甘油:0.1	0.4	99.4	甘油酸:42.3	1.7	[69]
AuCu-ZnO	60	5	6	甘油:1.0	2.0	10.0	甘油酸:77.0	—	[65]
AuAg-ZnO	60	5	6	甘油:1.0	2.0	95.0	甘油酸:59.0	—	[65]
AuPd/C	60	5	10	甘油:0.3	0.6	50.0	甘油酸:84.0	4.6	[71]
$Au_1Ru_{0.5}$/$CeZrO_x$-500	50	2	3	甘油:0.3	0.3	98.0	甘油酸:78.0	0.66	[68]
$Cu_{0.985}Au_{0.015}$	100	4	10	1,2-丙二醇:0.28	0.56	89.3	乳酸:76.1	917	[70]
0.5Cu-Au/HT	80	6	10	1,2-丙二醇:1.3	2.6	98.5	乳酸:88.5	—	[66]
AuPt/H-丝光沸石	100	2	3	甘油:0.3	0	70.0	甘油酸:83.0	—	[72]
Au_1-Pt_3/MgO	23	24	3	甘油:0.3	0	43.0	甘油酸:85.0	—	[73]
AuPt/H-SiO_2	80	4	3	甘油:0.3	0	30.0	甘油酸:61.0	—	[55]
Au-Pt/N-TiO_2	100	6	3	甘油:0.3	0	92.1	甘油酸:79.9	—	[62]
Au_1Pt_3/NC	80	2	1	甘油:0.3	0	83.7	甘油酸:60.5	—	[56]
Au-Pt/HT	60	4	2	甘油:0.3	0	64.0	甘油酸:69.0	—	[57]
Au-Pt/Hβ	100	3	3	甘油:0.3	0	68.0	甘油酸:68.0	—	[61]

子的$(Au^0)^{\eta-}$低负电中心，其催化活性显著优于单金属及其他双金属组合[65]。其次，双金属位点通过电子协同实现多步反应的串联推进与副反应抑制，例如Au-Pd体系中的Pd位可促进H_2O_2分解，而诱导产生的$Au^{\delta+}$物种弱化中间体吸附，抑制过度氧化[71]。而$Au_1Ru_{0.5}$/$CeZrO_x$催化剂上Au/Ru比例与催化活性呈火山型关系，表明Ru-Au界面处的氧空位协同活化C—H键，实现了高达806 h^{-1}的TOF[图4(f)][68]。Au-Cu/HT催化剂则在无碱条件下通过界面协同实现乳酸高选择性合成[图4(d)][66]。此外，第二金属的引入通过强电子耦合提升催化剂耐久性，如图4(b)所示，经焙烧去除封端剂后的AuAg/Al_2O_3催化剂活性位点完全暴露，丙醇二酸选择性提升至45.5%[29]；核壳结构Cu@Au中内部的Cu核通过电子稳定作用保护Au壳层，降低反应能垒[图4(h)][70]，以及Au/Fe-CeO_2催化剂中Fe与Au的电子相互作用赋予高稳定性[图4(i)][28]。总之，通过精准调控双金属电子效应与界面结构，可系统优化反应路径、抑制深度氧化。对电子相互作用本质的深入理解，特别是认识到其在氧化氛围下的诱导性和动态性，是实现低碳多元醇绿色、高值化转化的关键理论基础。

4　仲羟基选择性氧化制酮类化合物

多元醇仲羟基的选择性氧化是合成二羟基丙酮等高附加值酮类的关键途径，其核心挑战在于优先活化反应能垒较高的仲羟基，并抑制伯羟基竞争氧化及过度氧化等副反应[74-76]。近年来，基于电子效应调控的纳米金催化剂为该过程的选择性提升提供了新思路。通过载体工程与双金属协同等策略，可精准调控活性位点的电子结构与界面微环境，增强对仲羟基的特异性活化与转化效率，推动该绿色合成路径的实际应用。

4.1　载体效应：界面电子结构的精准设计与调控

为实现多元醇仲羟基定向氧化为酮类化合物，载体工程通过精准调控金的电子结构成为关键策略。其本质是通过改变载体的物理化学性质（如酸碱性、晶面、形貌等），调变金活性中心的电荷分布与轨道态密度，从而控制其对反应中间体的吸附行为和催化路径的选择性（图5和表3）。首先，酸性载体可诱导金物种呈现缺电子态，优化中间体在活性位

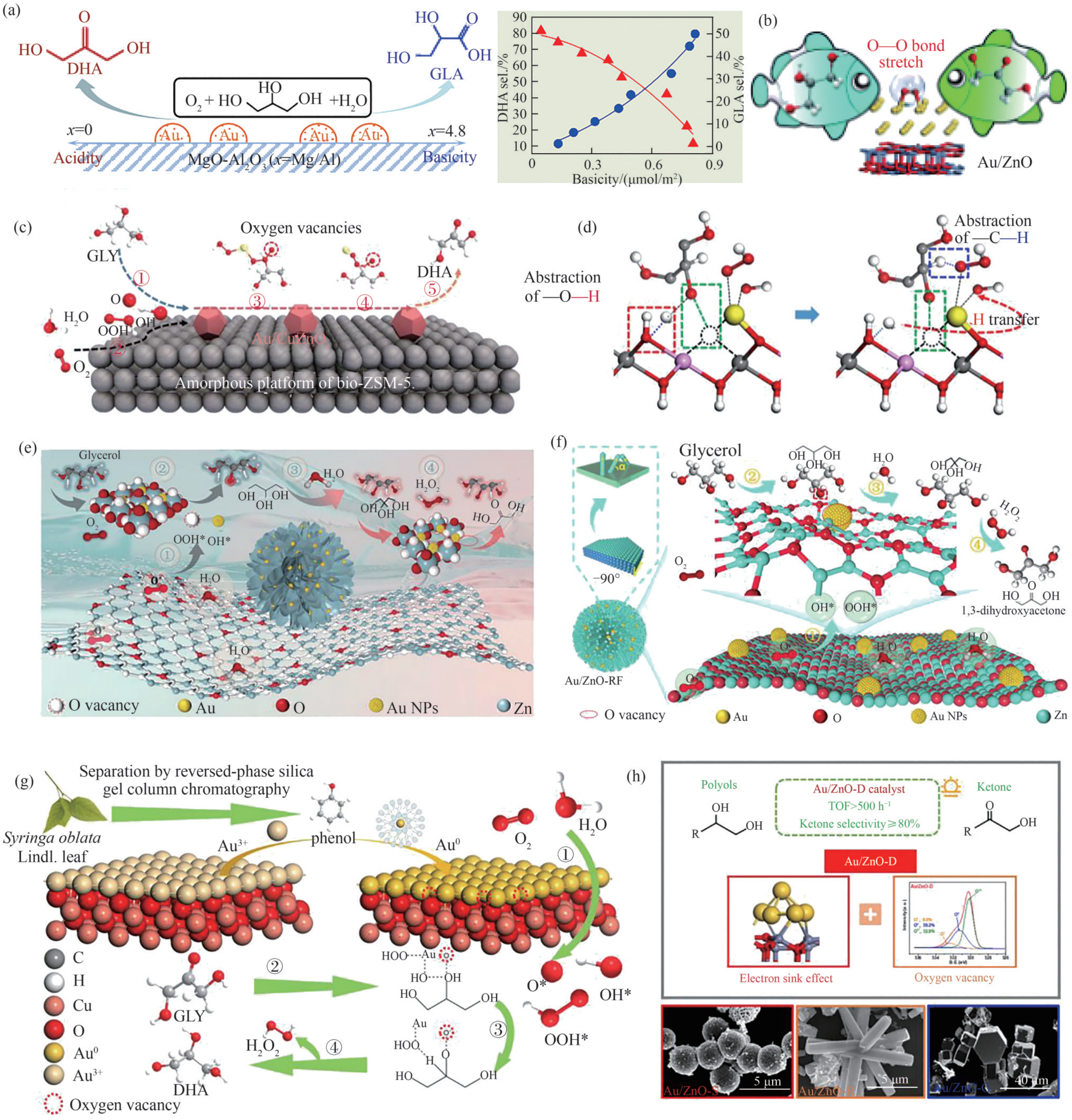

图5　多元醇仲羟基选择性氧化催化剂载体工程研究：(a) Au/MgO-Al_2O_3载体酸度提高和碱度降低来提高二羟基丙酮选择性[77]；(b)O_2在Au/ZnO(001)上吸附模型[26]；(c) Au/CuZnO_x@bio-ZSM-5催化剂制备图及甘油催化机理[78]；(d)在甘油选择性氧化生成二羟基丙酮过程中羟基空位与Zn^{II}-O-Au^{3+}位点的额外协同作用[79]；(e) Au/ZnO-花形催化剂合成图和甘油选择性氧化机理[80]；(f)不同形貌Au/ZnO-Z催化剂制备图和仲羟基氧化机理[81]；(g)由丁香叶提取物S3制备的Au/CuO用于甘油氧化的机理图[76]；(h) Au/ZnO-球、棒、盘上甘油氧化制二羟基丙酮性能[82]

Fig. 5　Researches on catalyst support engineering related to selective oxidation of secondary hydroxyl groups of polyols: (a) enhanced acidity and reduced basicity of Au/MgO-Al_2O_3 support to improve dihydroxyacetone selectivity[77]; (b) adsorption model of O_2 on Au/ZnO (001)[26]; (c) preparation of Au/CuZnO_x@bio-ZSM-5 catalyst and oxidation mechanism[78]; (d) additional synergistic effect between hydroxyl vacancies and Zn^{II}-O-Au^{3+}sites during oxidation of glycerol to dihydroxyacetone[79]; (e) synthesis of Au/ZnO-flower catalyst and oxidation mechanism of glycerol[80]; (f) preparation for Au/ZnO-Z nanocatalysts with different morphologies and mechanism of secondary alcohol oxidation[81]; (g) reaction mechanism diagram of Au/CuO prepared from S3 clove leaf extract for oxidation of glycerol[76]; (h) performance of glycerol selective oxidation to dihydroxyacetone over Au/ZnO-sphere, rod, and disk catalysts [82]

表3 多元醇仲羟基选择性氧化中不同载体类型的催化性能总结

Table 3 Summary of catalytic performance of different support types for selective oxidation of secondary hydroxyl groups in polyols

催化剂	温度/℃	时间/h	压力/bar	底物/(mol/L)	碱/(mol/L)	转化率/%	产物选择性/%	TOF/h^{-1}	文献
Au/Al_2O_3	80	3	10	甘油:0.1	0	11.9	DHA:81.7	43.0	[77]
Au/MgO-Al_2O_3(0.1)	80	0.5	10	甘油:0.1	0	16.4	DHA:74.1	358.0	[77]
Au/CuMgAl-HTs	60	4	3	甘油:0.3	0	42.0	DHA:64.0	292.0	[83]
Au/CuO	60	4	5	甘油:0.1	0	36.6	DHA:81.6	92.0	[84]
Au/Cu-NPC-15%-H	60	4	5	甘油:0.1	0	65.6	DHA:92.1	177.7	[84]
Au/$Cu_{0.95}Zr_{0.05}O_{1.05}$	50	4	2	甘油:0.1	0	72.8	DHA:96.2	32.1	[85]
Au/CuO-SnO_2-3:1	80	2	10	甘油:0.1	0	100.0	DHA:94.7	874.8	[86]
0.98Au/$Zn_{2.15}Ga_{1.0}$-LDHs	60	4	5	甘油:0.1	0	73.1	DHA:63.6	267.3	[79]
0.98Au/$Mg_{2.10}Al_{1.0}$-LDHs	60	4	5	甘油:0.1	0	71.2	DHA:57.0	245.3	[79]
S3-Au/CuO	100	2	10	甘油:0.1	0	86.6	DHA:82.0	430.3	[76]
Au/ZnO-NF	100	1	10	甘油:0.1	0	92.9	DHA:69.5	—	[80]
Au/$CuZnO_x$@bio-ZSM-5	80	2	10	甘油:0.1	0	93.0	DHA:86.3	—	[78]
Au/$CuZnO_x$	80	2	10	甘油:0.1	0	88.0	DHA:83.0	—	[78]
Au/ZnO-RF	100	1	1	甘油:0.1	0	91.1	DHA:76.2	—	[81]
Au/ZnO-D	60	4	10	甘油:0.1	0	58.0	DHA:68.5	521	[82]
Au/CuAlO-3	80	2	10	甘油:0.1	0	76.7	DHA:97.3	80.4	[87]

点的吸附强度，进而提高酮类产物选择性，如图5(a)所示，提高Au/MgO-Al_2O_3载体酸性可将二羟基丙酮（DHA）选择性提升至74.1%[77]。适度碱性载体则通过向金转移电子形成富电子中心，促进C—H键活化，如图5(g)所示，Au/CuO催化剂中碱性微环境有利于质子转移[76]。此外，复合界面设计[如Au/$CuZnO_x$@bio-ZSM-5，图5(c)][78]和晶面工程[如特定形貌ZnO负载的Au催化剂，图5(e)、(f)、(h)][80-82]能够进一步调控金属-载体电子相互作用，增强界面电荷转移，实现高活性与高选择性。理论计算与实验研究[图5(b)、(d)]表明，界面处Zn^{II}-O-Au^{3+}等[79]结构的构建以及晶面依赖的氧活化行为，共同强化了金电子结构对反应路径的引导作用[26]。综上，载体工程通过酸碱调控、界面构建与晶面设计等手段，实现对金电子结构的精准调变，从而推动仲羟基高效转化为酮类化合物。未来研究应更注重在电子尺度关联载体属性与金的催化行为，为理性设计高性能催化剂提供依据。

4.2 协同效应：双金属电子相互作用的优化与增强

双金属协同效应通过精准调控界面活性位的电子结构，成为提升仲羟基氧化制酮选择性与活性的关键策略（图6和表4）。该调控本质在于通过第二金属或载体诱导金位点发生定向电子转移，优化其d带中心及电荷分布，从而实现对反应路径的精确引导。如图6(b)所示，Au-Cu/ZnO中Cu诱导形成富电子Au位点，协同氧空位活化C—H键，实现83.4% DHA选择性[18]。图6(a)中Bi改性AuPt/AC通过电子修饰抑制过度氧化，将DHA选择性稳定在63%~65%[88]。构型调控进一步影响电子协同效率，合金结构AuPd凭借优化的金属间电子相互作用，其甘油TOF（754.8 h^{-1}）显著高于核壳与Janus结构[图6(c)][89]。此外，载体与金属的协同设计可增强界面电子传递，如图6(d)中AuPd/ZnO-CuO借助氧空位调变金的电子态，实现65% DHA产率及687 h^{-1}的TOF值[90]。该策略在C_3~C_4多元醇体系中亦展现普适性，AuPt/C催化剂在1,2-丙二醇、1,2-丁二醇、1,3-丁二醇和2,3-丁二醇选择氧化中相应酮产物的选择性分别为52%、42%、39%和84%，进一步证实双金属电子效应对反应路径的通用调控能力[91]。上述成果表明，通过精准设计双金属界面以调控金的电子结构，可有效抑制副反应、稳定活性中心，为酮类化合物的绿色合成提供电子级解决方案。

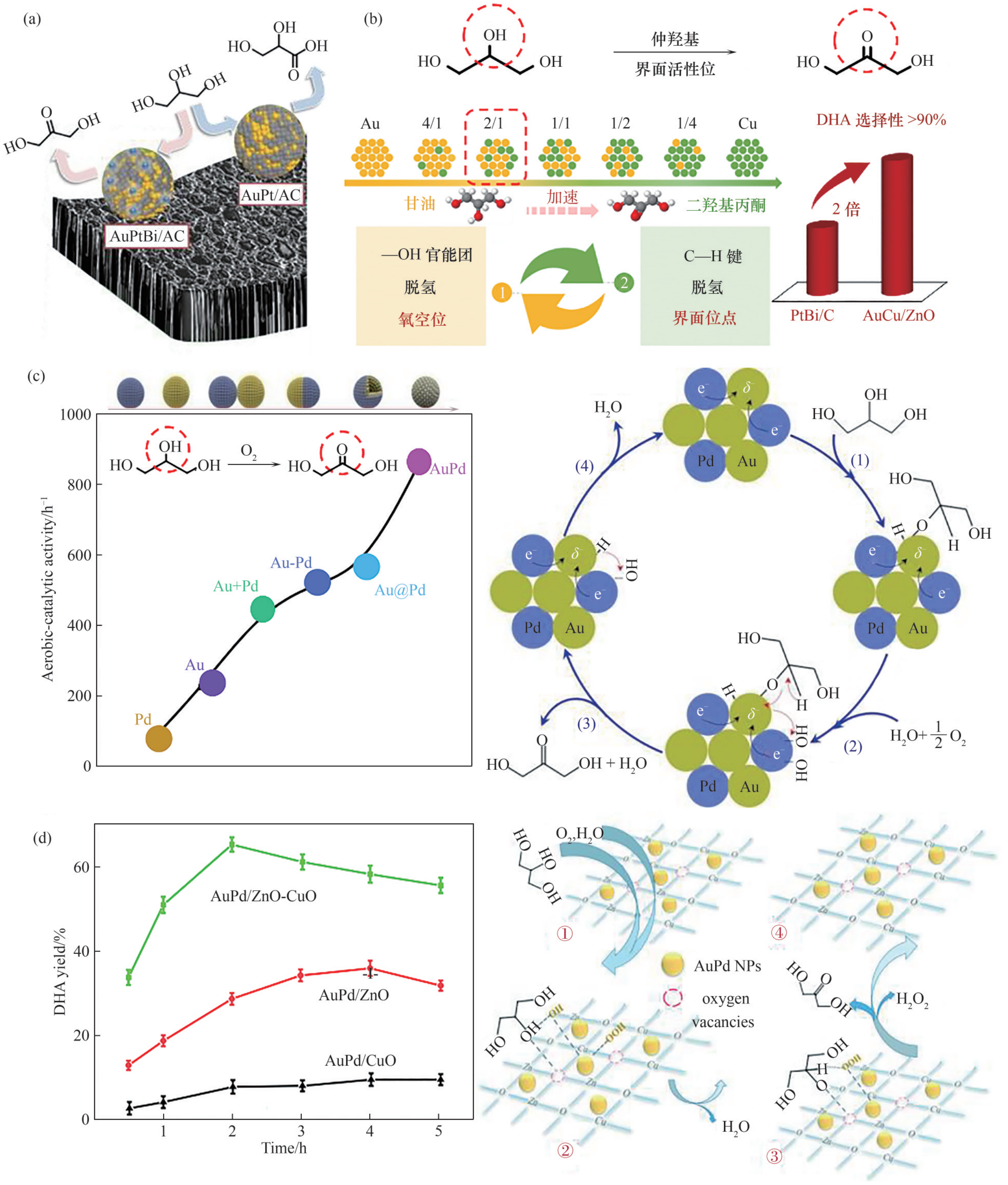

图6 多元醇仲羟基选择性氧化相关催化剂双金属协同研究：(a)铋改性AuPt/AC催化甘油氧化生成二羟基丙酮[88]；(b)不同比例AuCu/ZnO催化剂甘油氧化性能[18]；(c) AuPd合金、Au@Pd核壳、Au-Pd Janus颗粒和不同构型Au+Pd混合催化剂选择性氧化甘油制DHA性能与机理[89]；(d) AuPd/ZnO-CuO界面上甘油仲羟基氧化性能与机理[90]

Fig. 6 Researches on bimetallic synergy in catalysts related to selective oxidation of secondary hydroxyl groups of polyols: (a) bismuth-modified AuPt/AC catalyst for glycerol oxidation to dihydroxyacetone[88]; (b) performance of glycerol oxidation over AuCu/ZnO with different ratios[18]; (c) catalytic performance and mechanism for glycerol oxidation to DHA over supported AuPd alloy, Au@Pd core-shell, Au-Pd Janus particles, and differently configured Au+Pd mixed catalysts[89]; (d) performance and mechanism of glycerol secondary hydroxyl oxidation at AuPd/ZnO-CuO interface[90]

表4 多元醇仲羟基选择性氧化中不同双金属组合的催化性能协同效应总结

Table 4 Summary of catalytic performance and synergistic effects of different bimetallic combinations for the selective oxidation of secondary hydroxyl groups in polyols

催化剂	温度/℃	时间/h	压力/bar	底物/(mol/L)	碱/(mol/L)	转化率/%	产物选择性/%	TOF/h^{-1}	文献
AuCu/ZnO	60	5	10	甘油:0.105	0	90.6	DHA:83.4	402.5	[18]
0.1Bi-AuPt/AC	80	2	3	甘油:0.3	0	80.0	DHA:63.0	585.0	[88]
AuPd/ZnO	110	12	10	甘油:0.1	0	87.0	DHA:70.1	754.8	[89]
AuPd/ZnO-CuO	80	2	1	甘油:0.05	0	75.0	DHA:86.0	687.1	[90]
Au$_{0.5}$-Pt$_{0.5}$/MgO	40	4	3	1,2-丙二醇:0.6	0	40.0	α-羟基丙酮:65.0	400.0	[91]
Au$_{0.5}$-Pt$_{0.5}$/C	100	24	10	1,2-丙二醇:0.6	0	67.0	α-羟基丙酮:52.0	112.0	[91]
Au$_{0.5}$-Pt$_{0.5}$/C	100	24	3	1,2-丁二醇:0.6	0	75.0	1-羟基-2-丁酮:42.0	—	[92]
Au$_{0.5}$-Pt$_{0.5}$/C	100	24	3	1,3-丁二醇:0.6	0	67.0	4-羟基-2-丁酮:39.0	—	[92]
Au$_{0.5}$-Pt$_{0.5}$/C	100	24	3	2,3-丁二醇:0.6	0	62.0	3-羟基-2-丁酮:84.0	—	[92]

5 C—C键断裂制短链酸

C—C键断裂路径可实现多元醇向短链羧酸的转化，但其发展面临选择性低、反应机理不明确及强碱依赖等核心挑战[93-95]。研究表明，通过双金属与载体调控电子效应可部分提升性能（图7和表5）。如图7(a)所示，使用大丽花提取物制备的Fe$_3$O$_4$@TiO$_2$-Au纳米催化剂用于甘油选择性氧化中，不仅凭借磁性可回收特性强化了传质与分离效能（6个循环后催化活性稳定在约98%），其独特的Au-TiO$_2$界面电子相互作用也在碱性条件下使乙醇酸选择性提升至68.5%[93]。双金属电子协同方面，图7（b）中的Ag-Au/CeO$_2$催化剂通过金属间电荷重分布使乙醇酸选择性达46.2%[94]；而Au-Pt/C通过Pt调变Au的电子结构，进一步将选择性提升至54.2%[97]。当前体系仍受限于碱性介质依赖，因此开发高活性和高选择性的催化剂以实现无碱条件下多元醇C—C键断裂制短链酸更具挑战性[98]。如Au/水滑石利用Au^{0}与载体碱性位点的电子协同，实现了53%的乙醇酸选择性[图7(c)][96]，但仍存在过度氧化等问题。目前该领域研究仍处于起步阶段，未来需通过精准调控金的电子结构，深入揭示C—C键断裂的机理，推动高效无碱催化体系的开发。

6 总结与展望

本文系统综述了电子效应调控策略在纳米金催化低碳多元醇选择性氧化中的研究进展。围绕伯羟基制羧酸、仲羟基制酮及C—C键断裂制短链酸三大路径，重点探讨了如何通过载体工程与双金属协同策略调变金的电子结构，以应对羟基选择性活化、过度氧化抑制等关键挑战，进而优化界面微环境并提升产物选择性。主要结论包括：载体工程通过金属-载体相互作用调控电子密度，是实现伯羟基定向氧化的基础；双金属合金化通过电子协同与功能位点分工突破活性-选择性权衡瓶颈；界面电子与氧空位协同是促进仲羟基选择性脱氢的关键；C—C键断裂路径则亟待从电子层面阐明其活化与选择性控制机制。

为实现纳米金催化剂从传统“经验试错”到现代“理性设计”的革命性转变，未来研究必须致力于在电子尺度上实现真正的精准调控。这一目标的实现需依托三大核心路径的突破：首要任务是创制结构精准的模型催化体系，通过发展单/双原子催化剂构建具有明确原子构型与配位环境的活性中心，为揭示本征构效关系提供理想平台；关键环节是发展动态原位表征技术，利用时空分辨谱学手段实时追踪反应过程中界面电荷转移、中间体吸附/脱附等动态过程，从实验上直接揭示电子结构的演化规律；最终方向是建立理论预测平台，通过融合第一性原理计算与机器学习，构建“电子描述符-催化性能”的智能映射模型，实现从目标性能出发逆向设计催化剂电子结构的范式变革。通过贯通“精准结构创制→动态过程解析→性能预测设计”的全创新链条，必将实现从微观电子结构到宏观催化性能的精准调控，推动金基催化剂迈向真正的定向设计与按需定制。

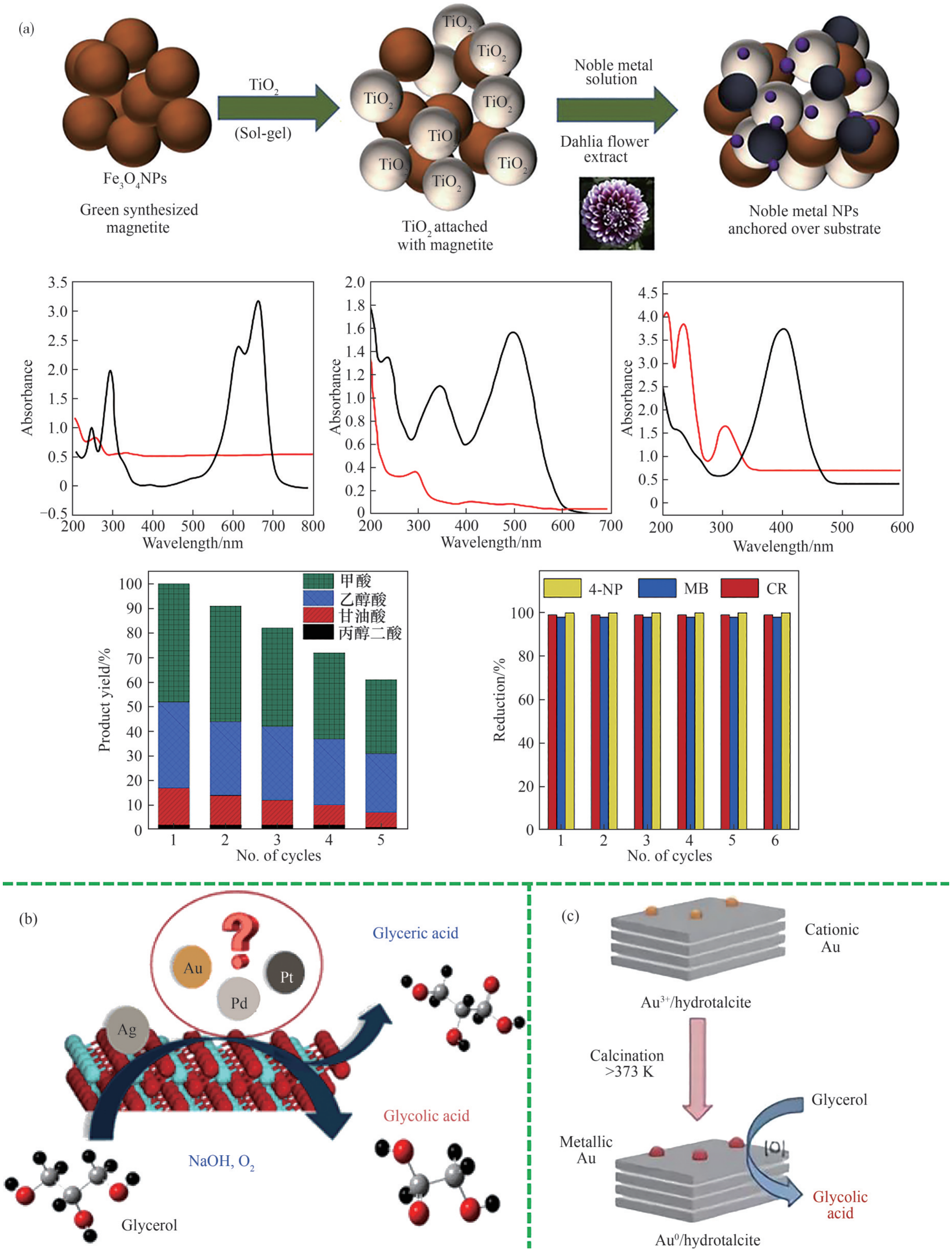

图7 多元醇C—C键断裂相关催化剂研究：(a)可磁分离Au-Pt@TiO_2纳米复合材料的绿色合成及用于甘油选择性氧化和回收测试[93]；(b)贵金属M (M=Au, Pd或Pt)促进银基甘油液相氧化催化剂[94]；(c)经高温焙烧处理后的水滑石负载催化活性金纳米颗粒无碱选择性氧化甘油成乙醇酸[96]

Fig. 7 Researches on catalysts for C—C bond cleavage of polyols: (a) green synthesis of magnetically separable Au-Pt@TiO_2 nanocomposites for selective oxidation of glycerol and recycling performance[93]; (b) noble metal M (M = Au, Pd or Pt) promoted silver-based catalysts for liquid-phase oxidation of glycerol[94]; (c) selective oxidation of glycerol to glycolic acid over hydrotalcite-supported gold nanoparticles activated by high-temperature calcination[96]

表5 多元醇C—C键断裂相关催化剂性能总结

Table 5 Summary of catalytic performance of catalysts for C—C bond cleavage of polyols

催化剂	温度/℃	时间/h	压力/bar	底物/(mol/L)	碱/(mol/L)	转化率/%	产物选择性/%	TOF/h^{-1}	文献
Au-Pt/C	50	0.5	3	甘油:0.3	1.2	90.0	乙醇酸:54.2	1258	[97]
Au-Pt/C-$NaBH_4$	50	0.5	3	甘油:0.3	1.2	75.8	乙醇酸:59.9	758	[98]
Au-Pt/C-H_2	50	0.5	3	甘油:0.3	1.2	98.3	乙醇酸:46.9	878	[98]
Fe_3O_4@TiO_2-Au	60	4	4	甘油:0.3	1.2	16.5	乙醇酸:68.5	—	[93]
Ag-Au/CeO_2	60	5	4	甘油:0.3	1.2	43.8	乙醇酸:46.2	115	[94]
Au/HT	20	72	1	甘油:0.1	0	97.3	乙醇酸:73.8	—	[96]
Au-Pt/C	50	0.5	3	甘油:0.3	1.2	90.0	乙醇酸:54.2	1258	[97]

参考文献

[1] 王雪鹏. 草酸二甲酯加氢制备乙二醇催化剂稳定性研究[D]. 金华: 浙江师范大学, 2020.
Wang X P. Study on stability of catalyst for hydrogenation of dimethyl oxalate to ethylene glycol[D]. Jinhua: Zhejiang Normal University, 2020.

[2] Taniguchi I, Yoshida S, Hiraga K, et al. Biodegradation of PET: current status and application aspects[J]. ACS Catalysis, 2019, **9**(5): 4089-4105.

[3] Yue H R, Zhao Y J, Ma X B, et al. Ethylene glycol: properties, synthesis, and applications[J]. Chemical Society Reviews, 2012, **41**(11): 4218-4244.

[4] Xia R, Chen Y Q, Chang Y X, et al. Electrosynthesis of ethylene glycol from ethylene coupled with CO_2 capture[J]. Nature Catalysis, 2025, **8**(8): 833-842.

[5] Sun Y L, Chai G L. Direct synthesis of ethylene glycol from syngas[J]. ChemistrySelect, 2022, **7**(6): e202103642.

[6] Fan L, Zhao Y L, Chen L, et al. Selective production of ethylene glycol at high rate *via* cascade catalysis[J]. Nature Catalysis, 2023, **6**(7): 585-595.

[7] Zhu Z Y, Li W W, Wang D, et al. Constructing a new pathway for ethylene glycol biosynthesis and its coenzyme reuse mechanism[J]. Fermentation, 2024, **10**(11): 558.

[8] 竺方欢, 岑雪聪, 陈振. 微生物合成二元醇研究进展[J]. 合成生物学, 2024, **5**(6): 1367-1385.
Zhu F H, Cen X C, Chen Z. Research progress of diols production by microbes[J]. Synthetic Biology Journal, 2024, **5**(6): 1367-1385.

[9] 季旭. 磷酸转酮酶定向进化及3-羟基丙酸生产应用[D]. 北京: 北京化工大学, 2021.
Ji X. Directed evolution of phosphoketolase and applications of 3-hydroxypropionic acid production[D]. Beijing: Beijing University of Chemical Technology, 2021.

[10] 吴云. 不同预处理方式对生物基多元醇制备的影响[D]. 马鞍山: 安徽工业大学, 2019.
Wu Y. Effect of different pretreatment methods on preparation of bio-based polyols[D]. Ma'anshan: Anhui University of Technology, 2019.

[11] Yan H, Yao S, Liang W, et al. Ni-Co oxide catalysts with lattice distortions for enhanced oxidation of glycerol to glyceric acid[J]. Journal of Catalysis, 2020, **381**: 248-260.

[12] Yan H, Yao S, Yin B, et al. Synergistic effects of bimetallic PtRu/MCM-41 nanocatalysts for glycerol oxidation in base-free medium: structure and electronic coupling dependent activity[J]. Applied Catalysis B: Environmental, 2019, **259**: 118070.

[13] Yan H, Qin H, Feng X, et al. Synergistic Pt/MgO/SBA-15 nanocatalysts for glycerol oxidation in base-free medium: catalyst design and mechanistic study[J]. Journal of Catalysis, 2019, **370**: 434-446.

[14] Yan H, Yao S, Zhao S M, et al. Insight into the basic strength-dependent catalytic performance in aqueous phase oxidation of glycerol to glyceric acid[J]. Chemical Engineering Science, 2021, **230**: 116191.

[15] Yan H, Yao S, Wang J Y, et al. Engineering Pt-Mn_2O_3 interface to boost selective oxidation of ethylene glycol to glycolic acid[J]. Applied Catalysis B: Environmental, 2021, **284**: 119803.

[16] Yan H, Shen Q, Sun Y H, et al. Tailoring facets of α-Mn_2O_3 microcrystalline catalysts for enhanced selective oxidation of glycerol to glycolic acid[J]. ACS Catalysis, 2021, **11**(11): 6371-6383.

[17] Yan H, Zhao M Y, Feng X, et al. PO_4^{3-} coordinated robust single-atom platinum catalyst for selective polyol oxidation[J]. Angewandte Chemie International Edition, 2022, **61**(21): e202116059.

[18] Zhao M Y, Yan H, Lu R L, et al. Insight into the selective oxidation mechanism of glycerol to 1, 3-dihydroxyacetone over AuCu - ZnO interface[J]. AIChE Journal, 2022, **68**(11): e17833.

[19] Yan H, Li J, Rao Z Q, et al. Fully exposed Pt_n cluster catalysts enable cascade oxidation of polyol to dicarboxylic acid[J]. Nature Communications, 2025, **16**: 7030.

[20] Song Z N, Yan H, Yuan J C, et al. Engineering a coordinatively unsaturated Au-O-Ti^{3+} structure toward unprecedented H_2 efficiency for low-temperature propene epoxidation with H_2 and O_2[J]. Engineering, 2023, **9**(6): 144-156.

[21] Zhang Y S, Liu J X, Qian K, et al. Structure sensitivity of Au-TiO_2 strong metal-support interactions[J]. Angewandte Chemie International Edition, 2021, **60**(21): 12074-12081.

[22] Guo Z L, Jing G H, Tolba S A, et al. Design and construction of an O-Au-O coordination environment in Au single atom-doped Ti^{4+} defected TiO_2 for an enhanced oxidative ability of lattice oxygen for Hg^0 oxidation[J]. Chemical Engineering Journal, 2023, 451: 138895..

[23] Wang L, Xu W D, Yuan Z R, et al. Tannic acid assisted construction of Au-Ti integrated catalyst regulating the local environment of framework Ti toward propylene epoxidation under H_2/O_2[J]. Molecular Catalysis, 2023, **545**: 113206.

[24] Li Y C, Li X S, Zhu B, et al. Boosting low-temperature water gas shift reaction over Au/TiO_2 nanocatalyst activated by oxygen plasma[J]. Chemical Engineering Journal, 2022, **430**: 133013.

[25] Yao S Y, Zhang X, Zhou W, et al. Atomic-layered Au clusters on α-MoC as catalysts for the low-temperature water-gas shift reaction[J]. Science, 2017, **357**(6349): 389-393.

[26] Meng Y, Zou S H, Zhou Y H, et al. Activating molecular oxygen by Au/ZnO to selectively oxidize glycerol to dihydroxyacetone[J]. Catalysis Science & Technology, 2018, **8**(10): 2524-2528.

[27] 陶伟. Au/HAP、CuPd、CuPdAu纳米金属催化剂催化氧化1, 2-丙二醇制备乳酸研究[D]. 镇江: 江苏大学, 2021.
Tao W. Study on the catalytic oxidation of 1, 2-propan diol tolactic acid over Au/HAP, CuPd and CuPdAu nano-metal catalysts[D]. Zhenjiang: Jiangsu University, 2021.

[28] Redina E A, Kapustin G I, Tkachenko O P, et al. Effect of ultra-low amount of gold in oxide-supported bimetallic Au-Fe and Au-Cu catalysts on liquid-phase aerobic glycerol oxidation in water [J]. Catalysis Science & Technology, 2021, **11**(17): 5881-5897.

[29] Jouve A, Nagy G, Somodi F, et al. Gold-silver catalysts: effect of catalyst structure on the selectivity of glycerol oxidation[J]. Journal of Catalysis, 2018, **368**: 324-335.

[30] Pan Y N, Wu G D, He Y F, et al. Identification of the Au/ZnO interface as the specific active site for the selective oxidation of the secondary alcohol group in glycerol[J]. Journal of Catalysis, 2019, **369**: 222-232.

[31] Yan H, Qin H S, Liang W, et al. Enhanced performance of bimetallic PtCo/MCM-41 catalysts for glycerol oxidation in base-free medium[J]. Catalysis Science & Technology, 2019, **9**(18): 4909-4919.

[32] Xiong L Q, Yu Z N, Cao H C, et al. Converting glycerol into valuable trioses by $Cu^{\delta+}$-single-atom-decorated WO_3 under visible light[J]. Angewandte Chemie International Edition, 2024, **63**(12): e202318461.

[33] 于志奕, 方俊彦, 陈文尧, 等. Pt-Bi界面结构调控及其催化甘油选择性氧化反应性能[J]. 化工学报, 2024, **75**(10): 3568-3578.
Yu Z Y, Fang J Y, Chen W Y, et al. Regulation of Pt-Bi interfaces for selective catalytic oxidation of glycerol[J]. CIESC Journal, 2024, **75**(10): 3568-3578.

[34] de Nazaré de Oliveira A, Melchiorre M, Farias da Costa A A, et al. Glycerol: a green solvent for synthetic chemistry[J]. Sustainable Chemistry and Pharmacy, 2024, **41**: 101656.

[35] Ke J W, Chi M F, Zhao J K, et al. Dynamically reversible interconversion of molecular catalysts for efficient electrooxidation of propylene into propylene glycol[J]. Journal of the American Chemical Society, 2023, **145**(16): 9104-9111.

[36] Liu X C, Wang T, Zhang Z M, et al. Reaction mechanism and selectivity tuning of propene oxidation at the electrochemical interface[J]. Journal of the American Chemical Society, 2022, **144** (45): 20895-20902.

[37] 李庆远, 王超, 许世佩, 等. PBS前体1, 4-丁二醇合成的反应工艺和催化剂研究进展[J]. 化工进展, 2022, **41**(11): 5771-5782.
Li Q Y, Wang C, Xu S P, et al. Research progress on reaction process and catalysts for PBS precursor of 1, 4-butanediol synthesis[J]. Chemical Industry and Engineering Progress, 2022, **41**(11): 5771-5782.

[38] Zhu Y, Yang J M, Mei F, et al. Bio-based 1, 4-butanediol and tetrahydrofuran synthesis: perspective[J]. Green Chemistry, 2022, **24**(17): 6450-6466.

[39] Liu Y F, Wang W, Zeng A P. Biosynthesizing structurally diverse diols *via* a general route combining oxidative and reductive formations of OH-groups[J]. Nature Communications, 2022, **13**: 1595.

[40] Torbina V V, Nedoseykina N S, Ivanchikova I D, et al. Propylene glycol oxidation with hydrogen peroxide over Zr-containing metal-organic framework UiO-66[J]. Catalysis Today, 2019, **333**: 47-53.

[41] Lin H, Xu J Y, Sun W L, et al. Efficient 1-hydroxy-2-butanone production from 1, 2-butanediol by whole cells of engineered E. coli[J]. Catalysts, 2021, **11**(10): 1184.

[42] Wang H Y, Zhu C H, Liu Q Y, et al. Selective conversion of cellulose to hydroxyacetone and 1-hydroxy-2-butanone with Sn-Ni bimetallic catalysts[J]. ChemSusChem, 2019, **12**(10): 2154-2160.

[43] Cai T, Sun H B, Qiao J, et al. Cell-free chemoenzymatic starch synthesis from carbon dioxide[J]. Science, 2021, **373**(6562): 1523-1527.

[44] Zhan T, Liu W B, Teng J J, et al. Selective oxidation of glycerol to tartronic acid over Pt/N-doped mesoporous carbon with extra framework magnesium catalysts under base-free conditions[J]. Chemical Communications, 2019, **55**(18): 2620-2623.

[45] Zhang H, Zhang R Z, Zhang W D, et al. Base-free selective oxidation of 5-hydroxymethylfurfural over Pt nanoparticles on surface Nb-enriched Co-Nb oxide[J]. Applied Catalysis B: Environmental, 2023, **330**: 122670.

[46] Dou J, Zhang B W, Liu H, et al. Carbon supported Pt_9Sn_1 nanoparticles as an efficient nanocatalyst for glycerol oxidation[J]. Applied Catalysis B: Environmental, 2016, **180**: 78-85.

[47] Kaminski P, Ziolek M, van Bokhoven J A. Mesoporous cerium-zirconium oxides modified with gold and copper-synthesis, characterization and performance in selective oxidation of glycerol [J]. RSC Advances, 2017, **7**(13): 7801-7819.

[48] Davis S E, Ide M S, Davis R J. Selective oxidation of alcohols and aldehydes over supported metal nanoparticles[J]. Green Chemistry, 2013, **15**(1): 17-45.

[49] Han Z Y, Xie R F, Song Y H, et al. Efficient and stable platinum nanocatalysts supported over Ca-doped $ZnAl_2O_4$ spinels for base-free selective oxidation of glycerol to glyceric acid[J]. Molecular Catalysis, 2019, **477**: 110559.

[50] Xu S G, Xiao Y, Zhang W Y, et al. Relay catalysis of copper-magnesium catalyst on efficient valorization of glycerol to glycolic acid[J]. Chemical Engineering Journal, 2022, **428**: 132555.

[51] Xiao Y H, Wang M R, Liu D, et al. Selective photoelectrochemical oxidation of glycerol to glyceric acid on (002) facets exposed WO_3 nanosheets[J]. Angewandte Chemie International Edition, 2024, **63** (11): e202319685.

[52] Pakrieva E, Kolobova E, German D, et al. Glycerol oxidation over supported gold catalysts: the combined effect of Au particle size and basicity of support[J]. Processes, 2020, **8**(9): 1016.

[53] Martínez Q H, Neira J A, Amaya Á A, et al. Selective oxidation of glycerol mediated by surface plasmon of gold nanoparticles deposited on titanium dioxide nanowires[J]. Chemosphere, 2024, **364**: 142995.

[54] Villa A, Dimitratos N, Chan-Thaw C E, et al. Glycerol oxidation using gold-containing catalysts[J]. Accounts of Chemical Research, 2015, **48**(5): 1403-1412.

[55] Villa A, Campisi S, Mohammed K M H, et al. Tailoring the selectivity of glycerol oxidation by tuning the acid-base properties of Au catalysts[J]. Catalysis Science & Technology, 2015, **5**(2):

1126-1132.

[56] Zhang X Y, Yang P F, Liu Y N, et al. Support morphology effect on the selective oxidation of glycerol over AuPt/CeO_2 catalysts[J]. Journal of Catalysis, 2020, **385**: 146-159.

[57] Xu C L, Du Y Q, Li C, et al. Insight into effect of acid/base nature of supports on selectivity of glycerol oxidation over supported Au-Pt bimetallic catalysts[J]. Applied Catalysis B: Environmental, 2015, **164**: 334-343.

[58] Shen L Q, Chen X Y, Chen X J, et al. The support influence of Au-based catalysts in glycerin selective oxidation to glyceric acid [J]. Journal of Chemical Technology & Biotechnology, 2023, **98**(1): 179-187.

[59] Evans C D, Bartley J K, Taylor S H, et al. Perovskite supported catalysts for the selective oxidation of glycerol to tartronic acid[J]. Catalysis Letters, 2023, **153**(7): 2026-2035.

[60] Jiang K H, Li Z Y, Zhang Z H, et al. Stable and active Au catalyst supported on $CeMnO_3$ perovskite for selective oxidation of glycerol [J]. Inorganic Chemistry, 2023, **62**(21): 8145-8157.

[61] Purushothaman R K P, van Haveren J, Mayoral A, et al. Exploratory catalyst screening studies on the base free conversion of glycerol to lactic acid and glyceric acid in water using bimetallic Au-Pt nanoparticles on acidic zeolites[J]. Topics in Catalysis, 2014, **57**(17): 1445-1453.

[62] Cherni D, Moussa N, Nsib M F, et al. Base-free glycerol oxidation over N-TiO_2 supported Au-Pt catalysts[J]. Reaction Kinetics, Mechanisms and Catalysis, 2019, **128**(2): 979-990.

[63] Ma H, Nie X, Cai J Y, et al. Au/$Mg(OH)_2$: highly efficient for selective oxidation of 1, 2-propanediol to lactic acid with molecular oxygen[J]. Science China Chemistry, 2010, **53**(7): 1497-1501.

[64] Griffin M B, Rodriguez A A, Montemore M M, et al. The selective oxidation of ethylene glycol and 1, 2-propanediol on Au, Pd, and Au-Pd bimetallic catalysts[J]. Journal of Catalysis, 2013, **307**: 111-120.

[65] Kaskow I, Decyk P, Sobczak I. The effect of copper and silver on the properties of Au-ZnO catalyst and its activity in glycerol oxidation[J]. Applied Surface Science, 2018, **444**: 197-207.

[66] Tian J, Liu H, Li P, et al. Selective oxidation of 1,2-propanediol to lactic acid over Cu-modified Au/hydrotalcite catalysts[J]. New Journal of Chemistry, 2020, **44**(38): 16311-16319.

[67] Olmos C M, Chinchilla L E, Rodrigues E G, et al. Synergistic effect of bimetallic Au-Pd supported on ceria-zirconia mixed oxide catalysts for selective oxidation of glycerol[J]. Applied Catalysis B: Environmental, 2016, **197**: 222-235.

[68] Chinchilla L E, Olmos C M, Villa A, et al. Ru-modified Au catalysts supported on ceria-zirconia for the selective oxidation of glycerol[J]. Catalysis Today, 2015, **253**: 178-189.

[69] Zhao Z, Arentz J, Pretzer L A, et al. Volcano-shape glycerol oxidation activity of palladium-decorated gold nanoparticles[J]. Chemical Science, 2014, **5**(10): 3715-3728.

[70] Xue W P, Yin H B, Lu Z P, et al. Catalytic oxidation of 1, 2-propanediol over bimetallic Cu@Au core/shell nanoparticles[J]. Catalysis Letters, 2016, **146**(6): 1139-1152.

[71] Ketchie W C, Murayama M, Davis R J. Selective oxidation of glycerol over carbon-supported AuPd catalysts[J]. Journal of Catalysis, 2007, **250**(2): 264-273.

[72] Villa A, Veith G, Prati L. Selective oxidation of glycerol under acidic conditions using gold catalysts[J]. Angewandte Chemie International Edition, 2010, **49**(26): 4499-4502.

[73] Brett G L, He Q, Hammond C, et al. Selective oxidation of glycerol by highly active bimetallic catalysts at ambient temperature under base-free conditions[J]. Angewandte Chemie International Edition, 2011, **50**(43): 10136-10139.

[74] Hirasawa S, Watanabe H, Kizuka T, et al. Performance, structure and mechanism of Pd-Ag alloy catalyst for selective oxidation of glycerol to dihydroxyacetone[J]. Journal of Catalysis, 2013, **300**: 205-216.

[75] Liu S S, Sun K Q, Xu B Q. Specific selectivity of Au-catalyzed oxidation of glycerol and other C_3-polyols in water without the presence of a base[J]. ACS Catalysis, 2014, **4**(7): 2226-2230.

[76] Cui L, Wang F, Zhang X L, et al. Plant-mediated biosynthesized Au/CuO catalysts for efficient glycerol oxidation to 1, 3-dihydroxyacetone: effect of biomass component on catalytic activity[J]. New Journal of Chemistry, 2024, **48**(45): 19206-19219.

[77] Yuan Z F, Gao Z K, Xu B Q. Acid-base property of the supporting material controls the selectivity of Au catalyst for glycerol oxidation in base-free water[J]. Chinese Journal of Catalysis, 2015, **36**(9): 1543-1551.

[78] Yuan Z, Wang Y M, Xie W D, et al. Manipulating the interfacial integration mode of a bio-templated porous ZSM-5 platform with an Au/$CuZnO_x$ catalyst for enhanced efficiency and recycling stability in glycerol conversion to 1, 3-dihydroxyacetone[J]. Nanoscale, 2025, **17**(9): 5259-5269.

[79] An Z, Ma H H, Han H B, et al. Insights into the multiple synergies of supports in the selective oxidation of glycerol to dihydroxyacetone: layered double hydroxide supported Au[J]. ACS Catalysis, 2020, **10**(21): 12437-12453.

[80] Xiong Z L, Zhang X L, Huang J L, et al. Flower-shaped zinc oxide nanostructures loaded with Au nanoparticles for efficient and highly stable production of dihydroxyacetone from glycerol oxidation[J]. Advanced Sustainable Systems, 2025, **9**(4): 2400947.

[81] Zhang X L, Liu H, Ke Y H, et al. Biomimetic flower-petal-architected Zn-based nanocatalysts for selective oxidation of glycerol to 1, 3-dihydroxyacetone[J]. ACS Applied Nano Materials, 2025, **8**(28): 14052-14064.

[82] Yan H, Zhao M Y, Cao Y Q, et al. Crystal-facet-dependent, electron sink effect for the enhanced selective oxidation of polyols at the secondary hydroxyl position[J]. Journal of Catalysis, 2024, **431**: 115401.

[83] Yin Y R, Tang T, Xu C L. Au/CuMgAl-hydrotalcite catalysts promoted by Cu^+ and basic sites for selective oxidation of glycerol to dihydroxyacetone[J]. Gold Bulletin, 2017, **50**(4): 319-326.

[84] Tan H, Yao C J, Zhan T, et al. Selective oxidation of glycerol to dihydroxyacetone over N-doped porous carbon stabilized Cu_xO supported Au catalysts[J]. Molecular Catalysis, 2020, **498**: 111243.

[85] Wang Y X, Pu Y F, Yuan D P, et al. Selective oxidation of glycerol to dihydroxyacetone over Au/$Cu_xZr_{1-x}O_y$ catalysts in base-free conditions[J]. ACS Applied Materials & Interfaces, 2019, **11**(47): 44058-44068

[86] Ke Y H, Qin H Y, Wang X, et al. Facile conversion of glycerol to 1, 3-dihydroxyacetone by using mesoporous CuO-SnO_2 composite oxide supported Au catalysts[J]. Journal of Porous Materials, 2023, **30**(3): 723-737.

[87] Ke Y H, Wang X, Qin H Y, et al. Cu-Al composite oxides: a

highly efficient support for the selective oxidation of glycerol to 1, 3-dihydroxyacetone[J]. New Journal of Chemistry, 2020, **44**(42): 18173-18184.

[88] Villa A, Campisi S, Chan-Thaw C E, et al. Bismuth modified Au-Pt bimetallic catalysts for dihydroxyacetone production[J]. Catalysis Today, 2015, **249**: 103-108.

[89] Feng Y M, Bi Y P, Wang Y F, et al. Enhanced glycerol oxidation toward dihydroxyacetone over gold/palladium binary nanocatalysts by structure control[J]. Chemistry-A European Journal, 2025, **31**(23): e202500601

[90] Zhao G Q, Wu G D, Liu Y N, et al. Preparation of AuPd/ZnO-CuO for the directional oxidation of glycerol to DHA[J]. Catalysis Science & Technology, 2020, **10**(18): 6223-6234.

[91] Ryabenkova Y, Miedziak P J, Dummer N F, et al. The selective oxidation of 1, 2-propanediol by supported gold-based nanoparticulate catalysts[J]. Topics in Catalysis, 2012, **55**(19): 1283-1288.

[92] Ryabenkova Y, Miedziak P J, Knight D W, et al. Heterogeneously catalyzed oxidation of butanediols in base free aqueous media[J]. Tetrahedron, 2014, **70**(36): 6055-6058.

[93] Sarangapany S, Mohanty K. Facile green synthesis of magnetically separable Au-Pt@TiO_2 nanocomposite for efficient catalytic reduction of organic pollutants and selective oxidation of glycerol [J]. Journal of Alloys and Compounds, 2020, **830**: 154636.

[94] Zaid S, Skrzyńska E, Addad A, et al. Development of silver based catalysts promoted by noble metal M (M=Au, Pd or Pt) for glycerol oxidation in liquid phase[J]. Topics in Catalysis, 2017, **60**(15): 1072-1081.

[95] Yan H, Liu B W, Zhou X, et al. Enhancing polyol/sugar cascade oxidation to formic acid with defect rich MnO_2 catalysts[J]. Nature Communications, 2023, **14**: 4509.

[96] Takagaki A, Tsuji A, Nishimura S, et al. Genesis of catalytically active gold nanoparticles supported on hydrotalcite for base-free selective oxidation of glycerol in water with molecular oxygen[J]. Chemistry Letters, 2011, **40**(2): 150-152.

[97] Bianchi C L, Canton P, Dimitratos N, et al. Selective oxidation of glycerol with oxygen using mono and bimetallic catalysts based on Au, Pd and Pt metals[J]. Catalysis Today, 2005, **102**: 203-212.

[98] Dimitratos N, Messi C, Porta F, et al. Investigation on the behaviour of Pt(0)/carbon and Pt(0), Au(0)/carbon catalysts employed in the oxidation of glycerol with molecular oxygen in water[J]. Journal of Molecular Catalysis A: Chemical, 2006, **256**(1/2): 21-28.