

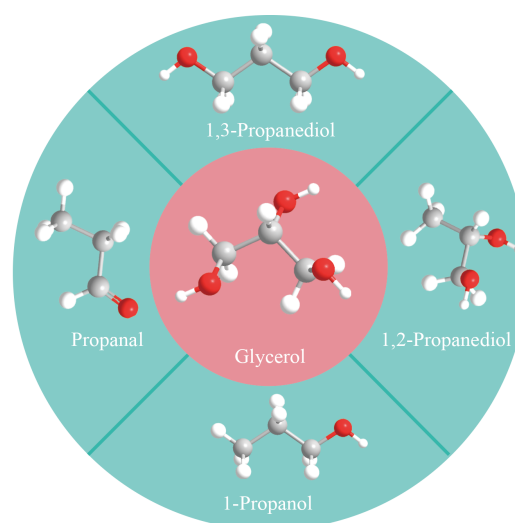
Research advances in the hydrogenolysis of glycerol to C3 oxygenated chemicals

MAO Hongyu, WANG Fei, GONG Honghui*

Henan Key Laboratory of Coal Green Conversion, College of Chemistry and Chemical Engineering, Henan Polytechnic University, Jiaozuo 454003, China

Abstract: The rapid expansion of the biodiesel industry plays a crucial role in achieving carbon neutrality and promoting energy system transformation. However, the oversupply of the by-product glycerol has hindered the sustainable development of biodiesel industry. Therefore, the green conversion of the by-product glycerol is conducive to the sustainable development of the biodiesel industry. Among various valorization routes, the hydrogenolysis of glycerol to C3 oxygenated chemicals is considered one of the most promising pathways. This review first briefly introduces glycerol chemistry and the fundamental reaction mechanism of glycerol hydrogenolysis. Subsequently, recent advances in catalytic systems for the selective hydrogenolysis of glycerol to high-value C3 oxygenated chemicals such as 1,2-propanediol, 1,3-propanediol, 1-propanol and propanal, are comprehensively summarized. Finally, future research directions and development trends in glycerol hydrogenolysis are discussed.

Key words: glycerol; hydrogenolysis; C3 oxygenated chemicals; biomass



Fossil fuels are non-renewable energy resources. Their large-scale exploitation and utilization have led to severe ecological and environmental issues, posing significant challenges to the sustainable development of human society. In this context, developing efficient, clean, low-carbon and renewable energy technologies has become an inevitable choice for transforming the future energy system^[1–3]. Biodiesel, produced from renewable resources such as waste animal and vegetable oils with methanol or ethanol *via* transesterification, serves as a promising alternative to petroleum-based diesel^[4–5]. However, glycerol is generated as the main by-product of the biodiesel production, with approximately 1 ton of crude glycerol produced for every 10 tons of biodiesel. In recent years, the rapid growth of the biodiesel industry has resulted in a substantial surplus of glycerol, exceeding market demand^[6–7].

The conversion of glycerol into high-value chemicals not only promotes the sustainable development of the biodiesel industry, but also contributes to alleviating dependence on fossil resources^[8]. Glycerol can be transformed into a series of fine chemicals through various reactions such as oxidation^[9–12], dehydration^[13–15], esterification^[16–18], etherification^[19–20], reforming^[21–24] and hydrogenolysis^[25–27], as shown in Figure 1. Among them, the hydrogenolysis of glycerol to C3 oxygenated chemicals like 1,2-propanediol (1,2-PDO), 1,3-propanediol (1,3-PDO), 1-propanol (1-PO) and propanal (PA) is one of the most promising pathways for the high-value utilization of glycerol. This is attributed to relatively mild reaction conditions, simple process, and ease of continuous operation of the hydrogenolysis route. Moreover, the products of glycerol hydrogenolysis are high-value-added fine chemicals with broad industrial applications.

Received: 2025-09-30; Revised: 2025-11-12

Foundation items: Supported by National Natural Science Foundation of China (22308089), Henan Provincial Science and Technology Research Project (242102241023).

* Corresponding author. E-mail: gonghonghui@hpu.edu.cn.

DOI: 10.1016/S1872-5813(26)60697-4 CSTR: 32157.14.2097-213X.2026.JFCT.0056

本文的英文电子版由 Elsevier 出版社在 ScienceDirect 上出版 (<http://www.sciencedirect.com/science/journal/18725813>)

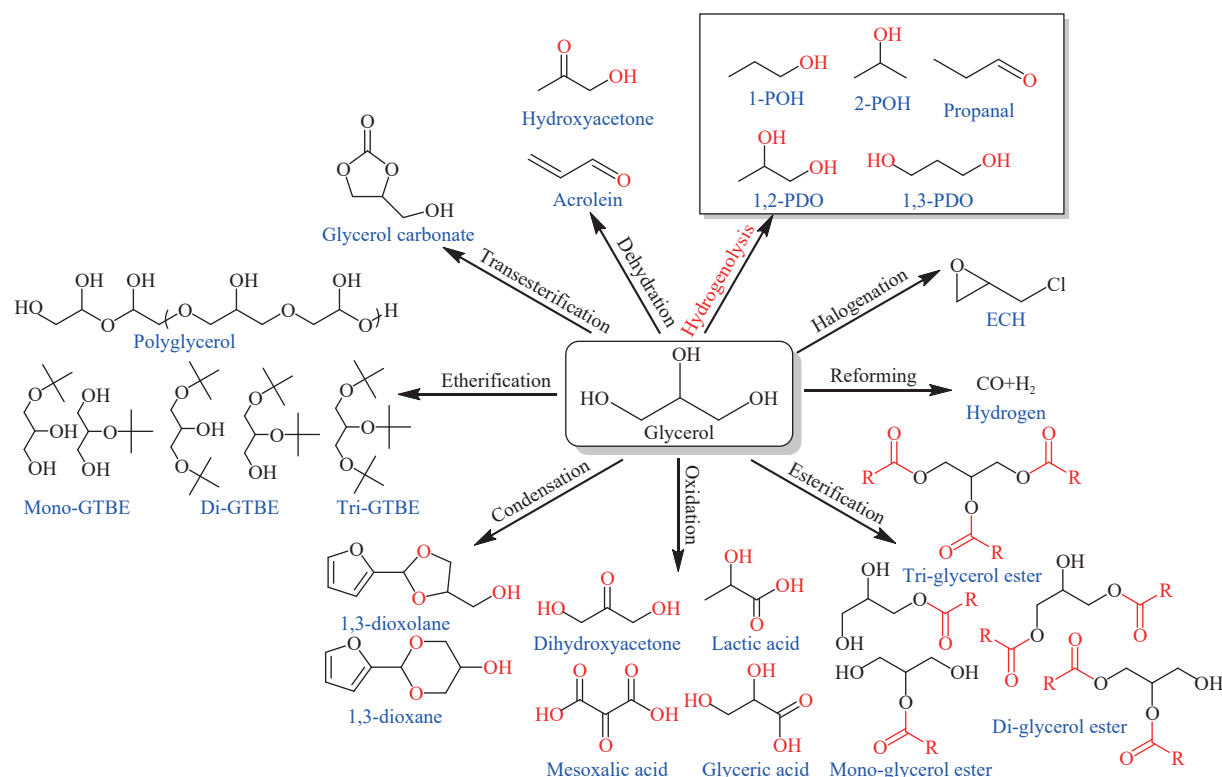


Fig. 1 Catalytic conversion pathway of glycerol

1,2-PDO is an important chemical intermediate widely used in polyester resin, unsaturated polyester, pharmaceuticals, food additives, cosmetics, and other industries^[28]. Conventionally, it is produced *via* the hydrolysis of propylene oxide, a process that relies heavily on petroleum-derived feedstocks and is associated with high energy consumption and environmental concerns^[29]. Consequently, the catalytic hydrogenolysis of biomass-derived glycerol has emerged as a sustainable alternative route for 1,2-PDO production (Figure 2). This approach could realize the high-value utilization of biomass resources and reduce the dependence on fossil resources for the synthesis of 1,2-PDO, holding great strategic significance for constructing a green, low-carbon, and circular economic system.

The hydrogenolysis of glycerol to 1,2-PDO generally involves two key steps: dehydration and hydrogenation. It is widely accepted that the reaction proceeds mainly through two pathways (Figure 3): (1) the “dehydration-hydrogenation” pathway (metal-acid bifunctional catalytic systems) and (2) the “dehydrogenation-dehydration-hydrogenation” pathway (metal-base bifunctional catalytic

systems)^[30]. In the dehydration-hydrogenation pathway, glycerol usually first undergoes dehydration at Lewis acid sites to form the intermediate hydroxyacetone. The hydroxyacetone intermediate is then hydrogenated at metal sites to yield 1,2-PDO. This pathway requires the catalyst to possess both Lewis acid sites and metal active sites. Lewis acid sites activate the primary hydroxyl group (C1–OH) and the adjacent C2–H bond of glycerol, promoting dehydration to form 2,3-dihydroxypropene, which subsequently tautomerizes into the more stable intermediate hydroxyacetone. At the same time, the metal sites activate H₂. Then, the intermediate hydroxyacetone is hydrogenated to 1,2-PDO (Figure 3). Therefore, the synergistic effect between the metal and Lewis acid sites is crucial for the selectivity of 1,2-PDO^[31–32]. Another possible mechanism is the dehydrogenation-dehydration-hydrogenation pathway. With the help of base sites, glycerol first undergoes dehydrogenation on metal sites to form glyceraldehyde or dihydroxypropanone. Both intermediates are then dehydrated to produce hydroxyacrylaldehyde or its tautomer, methylglyoxal.

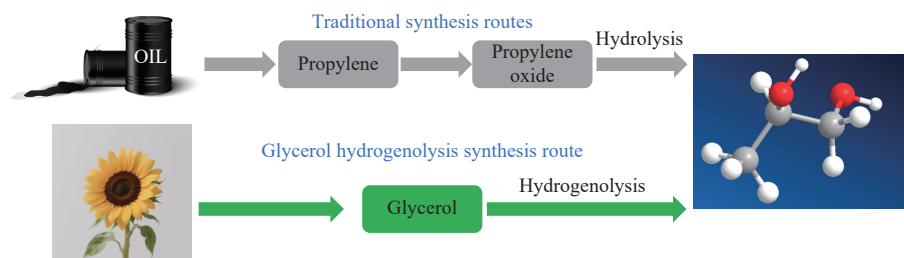


Fig. 2 Synthesis route of 1,2-PDO

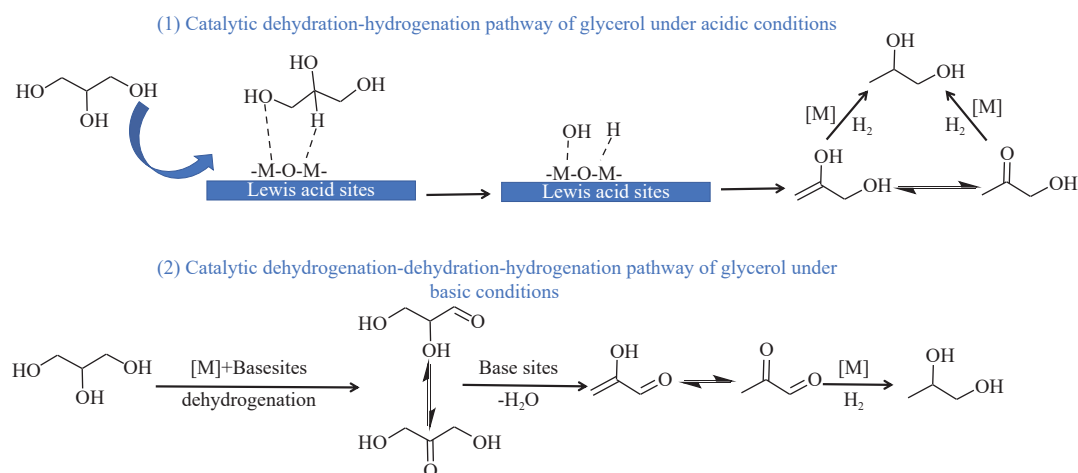


Fig. 3 Reaction mechanism for the hydrogenolysis of glycerol to 1,2-PDO under acidic or basic conditions

These intermediates are then hydrogenated to 1,2-PDO^[33–35]. Under basic conditions, various parallel and cascade reactions may also occur during the hydrogenolysis of glycerol, including side reactions such as oxidation to lactic acid, over-hydrogenation to propanol, and C–C bond cleavage to ethylene glycol and methanol.

1,3-PDO is one of the most important products of the hydrogenolysis of glycerol. It exhibits excellent chemical reactivity due to the presence of two terminal hydroxyl groups, and is widely used as a feedstock in fields such as polytrimethylene terephthalate (PTT), polyurethane, cosmetics, and medicine (Figure 4)^[36–37]. With the rapid growth of demand for high-performance polyester materials such as PTT, the market demand for 1,3-PDO continues to expand. Traditionally, 1,3-PDO is produced from petroleum-based feedstocks such as acrolein or ethylene oxide. However, traditional synthesis methods suffer from issues like non-renewable feedstocks, harsh reaction conditions, and environmental pollution. Currently, the selective hydrogenolysis of glycerol to 1,3-PDO has attracted widespread attention. This route not only realizes the high-value utilization of renewable glycerol, but also has the advantages of high atom economy and environmental friendliness^[38–39].

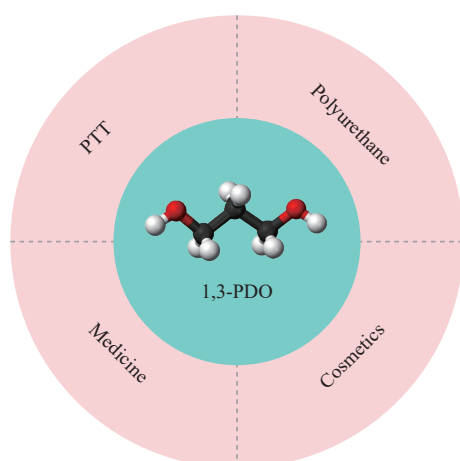
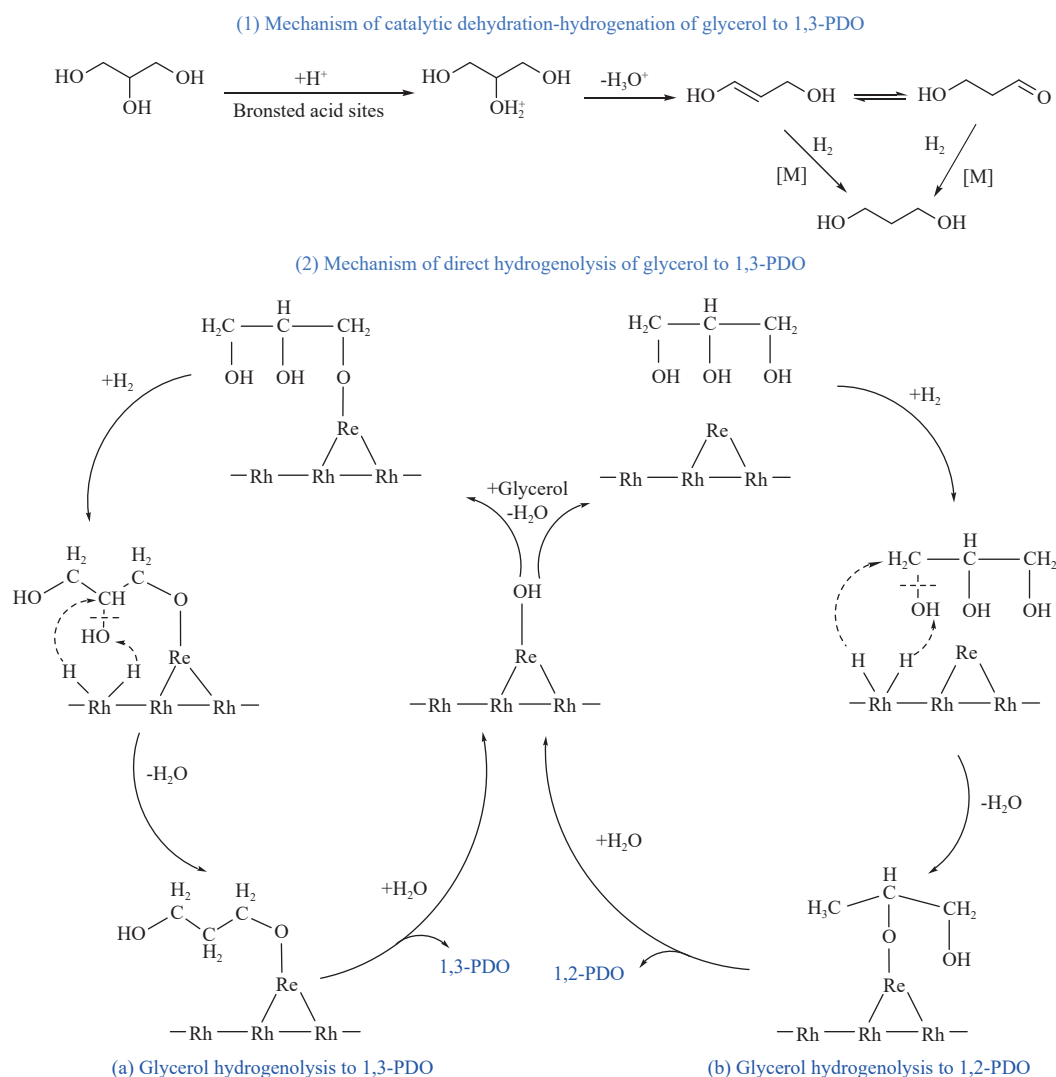


Fig. 4 Application of 1,3-PDO^[36–37]

The synthesis of 1,3-PDO *via* hydrogenolysis of glycerol involves multiple tandem reactions, such as dehydration and hydrogenation. The widely accepted mechanism is the “dehydration-hydrogenation” pathway (Figure 5)^[36]. In the hydrogenolysis of glycerol to 1,3-PDO, glycerol first undergoes selective dehydration at Brønsted acid sites to form 3-hydroxypropionaldehyde, which is subsequently hydrogenated at metal sites to yield 1,3-PDO^[40]. The Brønsted acid site is more favorable for the formation of 3-hydroxypropionaldehyde, which serves as a key intermediate in the synthesis of 1,3-PDO^[41]. The hydrogenation efficiency and product selectivity are strongly influenced by the nature of the metal sites. Metals with moderate hydrogenation ability are beneficial for improving the selectivity of 1,3-PDO. Beyond the aforementioned dehydration-hydrogenation mechanism, researchers have also proposed a “direct hydrogenolysis” pathway, in which glycerol first undergoes chemical adsorption on metal active sites through its hydroxyl groups, forming metal alkoxide intermediates (Figure 5). Subsequently, the active hydrogen atoms selectively attack the C–O bond adjacent to the metal alkoxy bond. This causes C–O bond cleavage and water elimination, ultimately producing 1,3-PDO or 1,2-PDO^[36]. This mechanism provides important insights for controlling the selectivity of glycerol hydrogenolysis. To improve 1,3-PDO selectivity, the key is to promote the preferential adsorption of terminal hydroxyl groups of glycerol on metal active sites. Such selective adsorption can be achieved by precisely tuning the electronic structure and spatial configuration of metal active sites.

1-PO is another important C3 oxygenated chemical widely used in solvents, pharmaceuticals, and agrochemicals. Conventional production routes are petroleum-based and face increasing resource and environmental constraints. Therefore, the development of sustainable processes for 1-PO production from renewable glycerol is of great significance^[42]. However, the hydrogenolysis of glycerol to 1-PO is complex. This process faces significant challenges, including poor selectivity control and catalyst deactivation.

Fig. 5 Reaction mechanism for the hydrogenolysis of glycerol to 1,3-PDO^[36]

The hydrogenolysis of glycerol to 1-PO is kinetically complex and involves multiple competing reactions. Two major pathways (Figure 6) have been proposed: (1) Indirect hydrogenolysis and (2) direct hydrogenolysis. In the indirect route, glycerol is first dehydrated to intermediates such as acrolein or allyl alcohol, which are subsequently hydrogenated to 1-PO. Although this pathway can operate under relatively mild conditions, its multi-step nature may limit overall yield^[43]. In the direct route, glycerol undergoes consecutive hydrodeoxygenation to form 1-PO. This process typically requires higher reaction temperatures and hydrogen pressures, along with specific catalysts to promote the selective cleavage of the C–O bonds of glycerol. Studies indicate that this pathway may involve intermediates such as 1,2-PDO or 1,3-PDO, ultimately yielding the target product 1-PO through further hydrolysis^[44]. Notably, both pathways involve multiple competing reactions, such as over-hydrogenation to propane, dehydration to hydroxyacetone, or C–C bond cleavage to small-molecule alcohols. These side reactions not only reduce target product selectivity but also cause catalyst deactivation.

PA is also a crucial industrial raw material, widely utilized as a chemical intermediate in sectors such as pesticides, plastics, pharmaceuticals, rubber, and polymerization inhibitors^[45]. Additionally, PA is frequently employed as a feedstock for the production of bulk chemicals like propionic acid and *n*-propanol. Currently, more than 90% of PA is produced *via* ethylene hydroformylation using homogeneous rhodium-phosphine catalysts, relying on non-renewable fossil resources^[46]. The hydrogenolysis of renewable glycerol to PA offers a sustainable alternative route. This process generally involves sequential dehydration, hydrogenation, and isomerization steps. Generally, glycerol first undergoes dehydration at Brønsted acid sites to form acrolein, which is subsequently selectively hydrogenated at metal sites to produce PA (Figure 7)^[47]. The selectivity toward PA strongly depends on the acid-base properties of the catalyst and the nature of the metal active sites. For instance, metal-acid bifunctional catalysts with moderate-to-strong Brønsted acidity and appropriate hydrogenation activity tend to exhibit high PA selectivity.

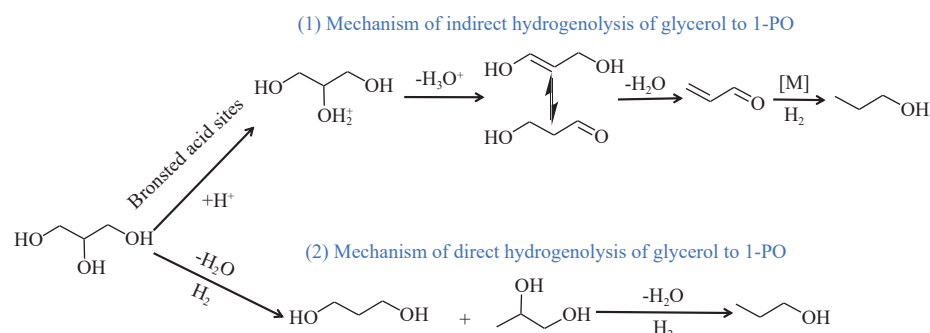
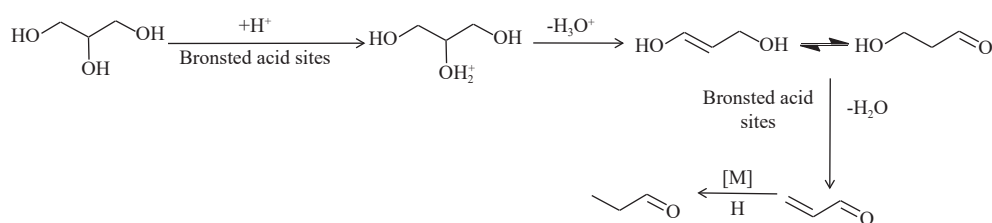


Fig. 6 Reaction mechanism for the hydrogenolysis of glycerol to 1-PO

Fig. 7 Reaction pathway for the hydrogenolysis of glycerol to PA^[47]

The production of C3 oxygenated chemicals (e.g., 1,3-PDO, 1,2-PDO, 1-PO and PA) *via* glycerol hydrogenolysis offers significant economic and environmental advantages. These processes could promote the efficient utilization of biomass resources, contributing to the construction of a green and low-carbon energy system.

This review systematically summarizes recent advances in the catalytic hydrogenolysis of glycerol to C3 oxygenated chemicals. It focuses on key issues including catalytic systems design, reaction mechanism, and process optimization. Through in-depth analysis of reaction pathways and the structure-activity relationships of catalyst, this work aims to provide a theoretical basis for developing catalytic systems for the hydrogenolysis of glycerol with high catalytic activity and selectivity. It also provides insights for process optimization and industrial implementation, thereby accelerating the high-value conversion of glycerol into C3 oxygenated chemicals.

1 Application of catalytic hydrogenolysis of glycerol

1.1 Hydrogenolysis of glycerol to 1,2-PDO

As an important pathway for the valorization of biomass resources, glycerol hydrogenolysis to 1,2-PDO has attracted considerable research interest. Currently, various catalytic systems have been developed for this reaction. They can be broadly classified into two categories: noble metal and non-noble metal catalysts.

1.1.1 Noble metal catalysts

Noble metal catalysts (e.g. Ir, Pt, Ru, Pd, et al.) have been

extensively employed in the hydrogenolysis of glycerol to 1,2-PDO due to their excellent hydrogenolysis activity^[48–50]. However, during the catalytic hydrogenolysis of glycerol, noble metals tend to not only activate the C–O bonds of glycerol but also promote undesired C–C bond cleavage (e.g. Ru/C catalysts). This effect leads to the formation of by-products such as ethylene glycol, methanol, ethane and methane, which significantly reduces the selectivity of the target product 1,2-PDO. This limitation has prompted researchers to regulate the performance of noble metal catalysts *via* catalyst modification. Shao et al.^[51] successfully regulated the Lewis acidity of activated carbon (AC)-supported RuO_x catalysts by utilizing the electron coupling effect induced by Pt doping. The catalyst achieved highly efficient conversion of glycerol to 1,2-PDO *via in situ* hydrogenolysis. Characterization results indicated that the introduction of Pt reconstructs the ligand oxygen in the RuO_x sites, forming a unique Ru–O–Pt structure. The formation of the Ru–O–Pt species promoted the electron transfer from Ru to Pt. This effect allows controllable regulation of the electronic structure of Ru and enhances the Lewis acidity of RuO_x. DFT calculations demonstrated that the synergistic effect of RuPt nanoparticles induces the reconstruction of the 4d orbitals of Ru. This effect results in more electrons distributed near the Fermi level, thereby accelerating the cleavage of C–O and C–H bonds of glycerol. Experimental results show that the conversion of glycerol on the surface of Ru₂Pt₂/AC catalyst followed the “dehydration-hydrogenation” pathway. Here, the dehydration of glycerol at the acidic RuO_x sites is the rate-determining step. First, the hydroxyl groups of glycerol coordinate with the RuO_x sites, catalyzing the activation of the primary hydroxyl group (C1–OH bond) and the secondary C–H bond (C2–H) of glycerol to form 2,3-dihydroxypropene. 2,3-Dihydroxypropene subsequently tautomerizes into hydroxyacetone. Concurrently, another

glycerol molecule undergoes reforming reaction catalyzed by RuO_x sites, generating active hydrogen adsorbed on the catalyst surface *via* the water-gas shift reaction. These *in situ* generated active hydrogen then participate in the hydrogenation of hydroxyacetone, ultimately yielding 1,2-PDO. Further studies reveal that when the Pt/Ru atomic ratio is controlled within the range of 0.24–0.78, Pt could be effectively embedded into the framework of RuO_x clusters. The corresponding catalyst could achieve a breakthrough improvement in the hydrogenolysis of glycerol without external H_2 . The turnover frequency (TOF) reached 827 h^{-1} at 200°C , which is 9 times higher than that of the monometallic Ru catalyst. The 1,2-PDO selectivity is approximately 51%. In 2021, Valle et al. reported a Pt catalyst supported on Al_2O_3 ($\text{Pt}/\text{Al}_2\text{O}_3$). At 240°C and 2.5 MPa H_2 , the conversion of glycerol is up to 38.5%, and the selectivity of 1,2-PDO is 45%^[52]. To further improve the catalytic performance of Pt-based catalysts in the hydrogenolysis of glycerol to 1,2-PDO, Zhang et al. successfully prepared a WO_x -supported Pt-Mn bimetallic catalyst ($\text{Mn}/\text{Pt}/\text{WO}_x$) by regulating prereduction temperature of the catalyst. They systematically study the regulation mechanism of reduction temperature on the selectivity of the hydrogenolysis of glycerol^[53]. The results indicated that the prereduction temperature of the $\text{Mn}/\text{Pt}/\text{WO}_x$ catalyst had a significant impact on the product distribution. The $\text{Mn}/\text{Pt}/\text{WO}_x$ catalyst reduced at a low temperature (240°C) contained WO_x species on its surface, which provide medium-to-strong acid sites. The existence of the medium-to-strong acid sites directs glycerol hydrogenolysis preferentially toward 1-PO with a yield of up to 88.0%. In contrast, the $\text{Mn}/\text{Pt}/\text{WO}_x$ catalyst reduced at a high temperature generates MnWO_4 species on its surface. Compared with WO_x species, the MnWO_4 species formed by high-temperature reduction had fewer acidic sites but more basic sites. This change in acid-base properties is conducive to the base-assisted glycerol dehydrogenation reaction, which promotes the formation of 1,2-PDO with a high yield of 93.0%.

Dynamic metal-support interaction (DMSI) plays a key role in charge transfer, active site reconstruction and interfacial recombination between metals and oxide supports under redox conditions. However, when the reforming reaction is coupled with hydrogenolysis, precise regulation the redox balance—which is strongly influenced by dynamic interactions—remains highly challenging. Shu et al.^[54] achieved efficient coupling of aqueous-phase glycerol reforming and hydrogenolysis by regulating the DMSI effect between sub-nanoscale Pt clusters and iron oxide supports. The redox reaction process of glycerol reforming coupled with hydrogenolysis can be effectively balanced (Figure 8)^[54] by precisely regulating the surface reconstruction and cyclic conversion of active sites ($\text{Pt}^{\delta-}\text{-O}_v\text{-Fe}^{2+} \leftrightarrow \text{Pt}^{\delta+}\text{-O-Fe}^{3+}$). The specific process is as follows: Under the synergistic regulation of strong metal-support interaction (SMSI) and electronic metal-support interaction (EMSI), abundant $\text{Pt}^{\delta-}\text{-O}_v\text{-Fe}^{2+}$ active sites are formed on the catalyst. Subsequently, adsorbed water molecules

dissociated at defect sites, inducing the formation of $\text{Pt}^{\delta+}\text{-O-Fe}^{3+}$ active sites *via* DMSI. Glycerol molecules adsorbed on $\text{Pt}^{\delta+}\text{-O-Fe}^{3+}$ sites undergo complete oxidation, generating CO and H_2 , CO is converted to CO_2 at the oxidation sites, simultaneously enabling the regeneration of $\text{Pt}^{\delta-}\text{-O}_v\text{-Fe}^{2+}$ active sites. Notably, the hydrogenolysis of glycerol to 1,2-PDO mainly proceeds through two pathways: on one hand, the oxidative dehydration reaction of glycerol occurring on $\text{Pt}^{\delta+}\text{-O-Fe}^{3+}$ sites generates thermodynamically unstable intermediates, which are converted to more stable hydroxyacetone through intramolecular isomerization; then, under the reduction of CO or H_2 , the oxidation sites are converted to reduction sites, and finally the hydrogenation of hydroxyacetone to 1,2-PDO is completed on $\text{Pt}^{\delta-}\text{-O}_v\text{-Fe}^{2+}$ sites. On the other hand, glycerol is first converted to glyceraldehyde through oxidative dehydrogenation reaction, and this intermediate further undergoes oxidative dehydration reaction on $\text{Pt}^{\delta+}\text{-O-Fe}^{3+}$ sites to form the key intermediate methylglyoxal. Through the reduction of CO or H_2 , $\text{Pt}^{\delta+}\text{-O-Fe}^{3+}$ sites are reversibly converted to $\text{Pt}^{\delta-}\text{-O}_v\text{-Fe}^{2+}$ sites. Subsequently, methylglyoxal is further hydrogenated to 1,2-PDO. Experimental results demonstrated that the 2.5Pt/ FeO_x catalyst exhibited excellent performance in the aqueous-phase reforming and hydrogenolysis of glycerol. The conversion of glycerol is 94.7%, the liquid phase selectivity of 1,2-PDO is 78.4%, and the yield of 1,2-PDO is 36.3%.

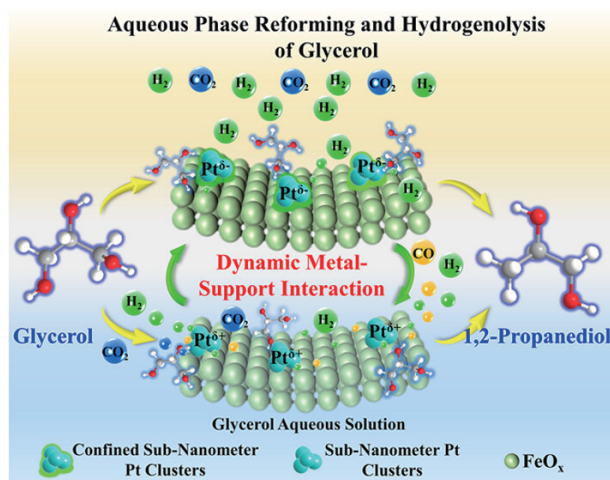


Fig. 8 Preparation of 1,2-PDO by coupling aqueous-phase reforming and hydrogenolysis of glycerol catalyzed by 2.5Pt/ FeO_x ^[54]

(with permission from ACS Publications)

In glycerol hydrogenolysis to 1,2-PDO, noble metal catalysts exhibit not only high hydrogenolysis activity but also excellent hydrothermal stability. They maintain high catalytic efficiency under harsh reaction conditions. Based on these advantages, researchers have developed many efficient noble metal catalytic systems. Besides the representative catalysts mentioned above, many catalytic systems with outstanding performance have also been reported in the literature. Examples include MOF-808- SO_4 -Pd^[55] and bimetallic PtSn^[56], IrFe^[57], CuPd^[58], CuPt^[59] and

RuCu^[60] catalysts. The above catalytic systems show their own advantages in improving 1,2-PDO selectivity and inhibiting C–C bond cleavage through different active component combinations and support regulation, which provides an important reference for the optimal design of catalysts for the hydrogenolysis of glycerol.

1.1.2 Non-noble metal catalysts

Although noble metal catalysts (e.g., Ir, Pt, Ru, Pd) exhibit excellent catalytic activity in the hydrogenolysis of glycerol to 1,2-PDO, their high cost severely restricts large-scale application. To address this issue, researchers have turned attention to non-noble metal catalysts (e.g., Cu, Ni, Co). Non-noble metal catalysts are not only inexpensive but can also achieve good 1,2-PDO selectivity through simple modification^[61–63]. Among them, Cu-based catalysts have become one of the most practical non-noble metal catalytic systems in glycerol hydrogenolysis due to their low cost and high 1,2-PDO selectivity^[64–66]. In 2022, Omar et al. prepared a novel Cu/ZnO/ZnAl₂O₄/PAAH (PAAH = polyacrylic acid) hybrid nanomaterial *via* a sol-gel process. The catalyst was applied to glycerol hydrogenolysis for 1,2-PDO production^[64]. Characterization results indicated that the synergistic effect between Al component and PAAH promoted the formation of active metallic copper (Cu⁰) nanoparticles with uniform particle size (4–13 nm) and good dispersion. Pyridine adsorption FT-IR analysis confirmed that the catalyst has Lewis acidity. In addition, the increase in Lewis acid sites could promote the activation and dehydration of the primary hydroxyl group (C1–OH) and C2–H bond of glycerol to generate the intermediate hydroxyacetone. The intermediate hydroxyacetone can be

subsequently hydrogenated to 1,2-PDO on well-dispersed Cu⁰ nanoparticles. The optimized Cu-based catalyst achieved 96% glycerol conversion and 83% 1,2-PDO selectivity (Table 1). To further improve the catalytic performance of the Cu-based catalysts, Liu et al.^[65] prepared a ZnO-doped copper carbide (Cu_xC) catalyst. The addition of ZnO improves the dispersion of copper species and enhances the Lewis acidity of the catalyst, which is beneficial for catalyzing the dehydration of glycerol to hydroxyacetone intermediate. The hydroxyacetone intermediate can be subsequently hydrogenated to 1,2-PDO. In addition, this study found that the hydrogenation activity of Cu_xC is significantly higher than that of metallic Cu⁰, which is conducive to improving the catalytic activity of the hydrogenolysis of glycerol in a fixed-bed reactor. The Cu_xC composite catalyst (Cu/Zn = 8) exhibited 100% glycerol conversion and 92.3% 1,2-PDO selectivity at 240 °C, 2.0 MPa H₂ and WHSV = 3 h^{–1}. In 2022, Kumar et al.^[66] further investigated the catalytic activity of Cu-derived oxide catalysts in the hydrogenolysis of glycerol and investigate the effect of different Cu/Al molar ratios on 1,2-PDO selectivity. It is found that glycerol conversion/1,2-PDO selectivity depend on the metal sites dispersion and Lewis acidity of the Cu-based catalyst. With increasing of Cu/Al molar ratio in the catalyst, the surface acidity and the dispersion of metallic Cu⁰ are significantly improved. The enhanced acidity is beneficial for catalyzing the dehydration of glycerol to hydroxyacetone, while the improved dispersion of metallic Cu⁰ nanoparticles is conducive to promoting the hydrogenation of intermediate hydroxyacetone to the target product 1,2-PDO. 3CuAl exhibited 83.5% glycerol conversion and 84.2% 1,2-PDO selectivity (20% glycerol aqueous solution, 210 °C, 4.0 MPa H₂).

Table 1 Comparison of catalytic properties over different catalysts for the hydrogenolysis of glycerol to 1,2-PDO

Entry	Catalyst	<i>t</i> /°C	<i>p</i> /MPa	Conversion/%	Selectivity/%	Ref.
					1,2-PDO	
1	Ru ₂ Pt ₃ /AC	200	–	67.8	51.0	[51]
2	Pt/Al ₂ O ₃	240	2.5	38.5	45.0	[52]
3	Mn/Pt/WO _x	240	6.0	100	93.0	[53]
4	2.5Pt/FeO _x	240	–	94.7	38.3	[54]
5	MOF-808-SO ₄ -Pd	200	4.0	23.9	93.9	[55]
6	Cu/ZnO/ZnAl ₂ O ₄ /PAAH	200	3.0	96.0	83.0	[64]
7	Cu _x C-Cu-ZnO	240	2.0	100	92.3	[65]
8	3CuAl	210	4.0	83.5	84.2	[66]
9	30Co-Al ₂ O ₃	230	3.5	53.7	76.0	[67]
10	Co ₂ -Ca ₄ -Al ₃	210	4.0	100	90.5	[68]
11	CA (1)-Ni ₃ P	220	–	74.6	43.2	[69]
12	3Ni1Sn-ZIF_R500	220	4.0	99.0	95.2	[70]

The unique *d*-electronic structure of metallic cobalt (Co⁰) endows it with excellent H₂ adsorption and dissociation capabilities. Accordingly, Co-based catalysts have been widely investigated for glycerol hydrogenolysis to 1,2-PDO. Cai et al.^[67] evaluated the performance of Co-Al₂O₃ catalysts for the hydrogenolysis of glycerol to 1,2-PDO in

batch and flow reactors. The 30Co-Al₂O₃ catalyst exhibits high catalytic activity and good stability in the continuous reactor, achieving a glycerol conversion of 53.7% and a 1,2-PDO selectivity of 76%. The good catalytic performance is mainly attributed to the high acid density and Co dispersion of 30Co-Al₂O₃. To further improve the catalytic

performance of the Co-based catalysts in glycerol hydrogenolysis, Gong et al.^[68] reported a hydrotalcite-derived $\text{Co}_2\text{-Ca}_4\text{-Al}_3$ catalyst, which achieves 100% glycerol conversion and 90.5% 1,2-PDO selectivity in hydrogenolysis of glycerol (Table 1).

This catalyst also shows good cycling stability in batch reactions. Activity tests and characterization results indicate that Co^0 species present in the catalyst were identified as the primary active sites for hydrogenolysis of glycerol. The strong interaction between Co(II) and Ca(II) oxides led to the formation of $\text{CaO-CoAl}_2\text{O}_4$ mixed metal oxides. This structure not only generates more electron-deficient Co(II) sites but also forms a large number of moderate-strength basic sites, promoting the dehydrogenation of glycerol and thus significantly improving the catalytic activity and 1,2-PDO selectivity (Figure 9)^[68]. Notably, CaCO_3 phase on the $\text{Co}_2\text{-Ca}_4\text{-Al}_3$ catalyst surface could effectively prevent the leaching of medium basic sites and metal active sites by coating the $\text{CaO-CoAl}_2\text{O}_4$ mixed metal oxides, which is the key reason for the excellent stability of the $\text{Co}_2\text{-Ca}_4\text{-Al}_3$ catalyst under aqueous reaction conditions.

Compared with Cu- and Co-based systems, Ni-based catalysts have been less extensively investigated for glycerol hydrogenolysis to 1,2-PDO. The main reason is that there is usually a strong metal-support interaction between Ni species and the support. These effects make the Ni species difficult to reduce (usually requiring high reduction temperatures ($>500^\circ\text{C}$)), thereby limiting the formation of active Ni^0 sites. Additionally, the electronic structure of Ni could easily induce the cleavage of C-C bonds in glycerol, resulting in low selectivity of the target product 1,2-PDO (most reports show 1,2-PDO selectivity $< 70\%$). In recent years, it has been found that the selectivity of Ni-based catalysts for 1,2-PDO can be improved by adding promoters. Hu et al.^[69] prepared Ni_3P catalysts *via* citric acid (CA) modification. The catalytic activity of Ni_3P catalysts were tested in the coupled reaction of aqueous-phase glycerol reforming and hydrogenolysis to 1,2-PDO. The $\text{CA(1)-Ni}_3\text{P}$ catalyst exhibits 74.6% glycerol conversion and 43.2% 1,2-PDO selectivity at 220°C , 0.5 MPa N_2 and 8 h. The study found that adding CA significantly improved the dispersion of Ni_3P species and

increased specific surface area of the catalyst, thereby showing higher catalytic activity. In addition, Nimbalkar et al. successfully prepared a mixed-metal zeolitic imidazolate framework (MM-ZIF) precursor using one-pot synthesis strategy^[70]. By controlling calcination and reduction processes, they obtain a ZnO-supported highly dispersed Ni-Sn nanoalloy catalyst. In-depth characterization studies show that introducing Sn effectively regulated the electronic structure of Ni and inhibit C-C bond cleavage side reaction. Under optimized reaction conditions, this catalytic system exhibits excellent catalytic performance for glycerol hydrogenolysis and achieves 95.2% 1,2-PDO selectivity (Table 1).

1.2 Hydrogenolysis of glycerol to 1,3-PDO

The hydrogenolysis of surplus glycerol into high-value chemicals exhibits significant economic and environmental benefits. Among these products, 1,3-PDO is considered the most promising. It can serve as a crucial precursor for the production of PTT and polyurethane. However, due to steric hindrance and thermodynamic factors, selective cleavage of the secondary hydroxyl group (C2-OH) of glycerol to 1,3-PDO still faces great challenges^[71]. In recent years, to enhance the selective hydrogenolysis of glycerol to 1,3-PDO, researchers have developed a variety of catalytic systems. Among these, Pt-WO_x and Ir-ReO_x catalytic systems are the most representative^[72].

1.2.1 Pt-WO_x catalytic systems

The Pt-WO_x catalytic system has attracted much attention from academia and industry owing to its cost advantage and excellent catalytic performance in glycerol hydrogenolysis to 1,3-PDO. It possesses the following outstanding features: (1) Excellent stability under aqueous reaction conditions; (2) High 1,3-PDO selectivity can be achieved by precisely regulating the ratio of Brønsted/Lewis acid sites on the WO_x support; (3) The unique strong metal-support interaction effect could effectively inhibit sintering and deactivation of Pt nanoparticles^[73–74].

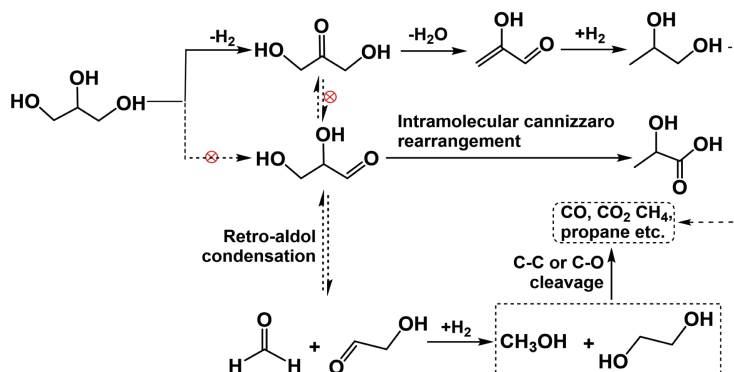


Fig. 9 Reaction pathway for the hydrogenolysis of glycerol to 1,2-PDO on $\text{Co}_2\text{-Ca}_4\text{-Al}_3$ ^[68] (with permission from ACS Publications)

These features enable Pt-WO_x catalysts to meet cost control requirements of industrial applications, and could also achieve a balance between catalytic activity and selectivity. These characteristics render it a promising candidate for industrial application in glycerol hydrogenolysis to 1,3-PDO. However, the mechanism of electronic reconstruction at Pt-WO_x interface for regulating glycerol C–O bond activation and Brønsted acidity is still poorly understood and urgently needs clarification. Zhang et al.^[75] revealed the special effect of Pt loading on the electron reconstruction of WO_x. The C–O bond cleavage activity of glycerol is doubled by constructing a new hydrogen spillover path. Related characterizations show that increasing the Pt/W ratio generated additional O 2p orbital holes. This effect promotes charge transfer from the O to W sites, and then forms an electron reconstruction active center that could selectively activate the C–O bonds of glycerol. Based on the 2-butanol dehydration experiment, it was confirmed that the hydrogen spillover process would form Brønsted acid sites *in situ* through formation of H^{δ+}(WO₃)_n^{δ-}. In the 50% glycerol reaction system, the selectivity of Pt/W/Al catalyst to 1,3-PDO can reach 48.1%.

The interaction between Pt and oxygen vacancies can enhance the selective hydrogenolysis of glycerol to 1,3-PDO, and optimizing the concentration and distribution of oxygen vacancies further improves 1,3-PDO selectivity^[76]. Chen et al. reported a solid solution-supported Pt catalyst (Pt/Nb₂W₁₅O₅₀) for glycerol hydrogenolysis to 1,3-PDO, in which a strong interaction between active Pt and oxygen vacancies enables efficient tandem integration of deoxidation and hydrogenation steps^[77]. This strong Pt-oxygen vacancy interaction established by hydrogen spillover effect could induce the formation of 1,3-PDO. This effect enabled the Pt/Nb₂W₁₅O₅₀ catalyst to exhibit excellent catalytic performance under low H₂ pressure of 1.0 MPa. It achieves a glycerol conversion of 75.6% and 1,3-PDO selectivity of 66.5%. Structure-activity relationship study further confirmed that there is a linear correlation among the number of Pt active sites, oxygen vacancy concentration and 1,3-PDO yield. Pt-WO_x-based catalytic systems demonstrate potential for practical applications in glycerol hydrogenolysis to 1,3-PDO. However, these systems usually exhibit low W and Pt atomic efficiency in the production of 1,3-PDO. Zhao et al.^[78] prepared highly dispersed WO_x species on an inert α-Al₂O₃ support through simple high-temperature heat treatment. The number of Pt-WO_x interfacial active sites can be adjusted by Pt loading. The 2Pt/WO_x/α-Al₂O₃ catalyst shows excellent catalytic performance in the hydrogenolysis of glycerol, especially high W efficiency for 1,3-PDO (76 g_{1,3-PDO}/(g_W·h)). The high catalytic efficiency is due to the strong interaction between isolated WO₄ species and Pt, which can *in situ* generate Brønsted acid sites during the reaction, thereby promoting the conversion of glycerol to 1,3-PDO (Figure 10). Zhao et al.^[79] further study the effect of structure and chemical state of WO_x species on glycerol hydrogenolysis to 1,3-PDO.

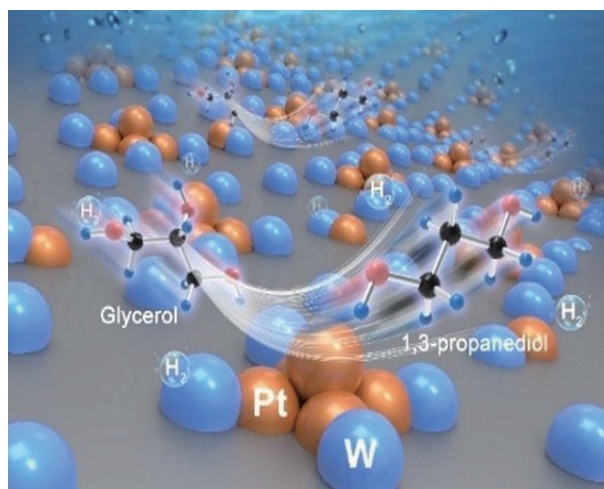


Fig. 10 The hydrogenolysis of glycerol to 1,3-PDO on Pt-WO_x/α-Al₂O₃^[78]

(with permission from Wiley-VCH Publications)

By regulating *in-situ* migration of WO₃ nanoparticles in H₂ atmosphere, they successfully construct single atom W-doped α-Al₂O₃ support with low chemical state. Characterization results show that compared with octahedral W⁶⁺ species, tetrahedral W⁵⁺ could disperse and stabilize Pt species more effectively, and exhibit stronger Pt-WO_x interaction. The improvement of catalytic performance of Pt-WO_x/γ-Al₂O₃ is attributed to the *in situ* generated tetrahedral WO_x with rich oxygen defects on catalyst surface. These defects not only promote the construction of the Pt-WO_x interface but also amplify the synergistic effect between them. Structure-activity relationship analysis reveals that monodispersed tetrahedral W⁵⁺ species [(–O–)₃W(=O)] play a key role in regulating catalyst acidity and improving catalytic performance, which can not only assist glycerol adsorption but also capture H atoms to *in situ* form Brønsted acid sites. These effects ultimately achieve dual regulation of catalytic activity and 1,3-PDO selectivity (1.36 g_{1,3-PDO}/(g_{Pt}·h)).

Strong metal-support interaction (SMSI) is a key concept in heterogeneous catalysis that plays a crucial role in enhancing catalytic performance. Interaction between Pt and WO_x is regarded as one of the key factors affecting catalytic activity and selectivity of glycerol hydrogenolysis. But interaction between WO_x and support has been rarely studied. In 2025, Li et al.^[80] systematically investigated the effect of SiO₂-WO_x interaction on glycerol hydrogenolysis over Pt/W-SiO₂ by regulating the number of silanol groups on the surface of SiO₂ support. Studies show that weak SiO₂-WO_x interaction could promote Pt-WO_x interaction (forming more Pt-WO_x coordination structures), which significantly improves the catalytic performance of glycerol hydrogenolysis to 1,3-PDO. Taking Pt/W-SiO₂-700 catalyst (most silanol groups are removed to enhance Pt-WO_x coordination) as an example, 70.9% glycerol conversion and 61.3% 1,3-PDO selectivity can be obtained at 140 °C (Table 2). Experimental characterization and theoretical calculations show that the enhanced Pt-WO_x coordination is

beneficial to hydrogen spillover, forming more isolated $\text{WO}_x\text{-H}$ active sites. $\text{WO}_x\text{-H}$ species play a key role in the selective hydrogenolysis of glycerol to 1,3-PDO. Eqi et al.^[81] further constructed a $\text{Pt}/\text{WO}_x/\text{Nb}_2\text{O}_5$ catalyst through oxygen vacancy engineering. It possessed abundant oxygen vacancies and strong $\text{Pt}^{\delta+}\text{-O-W}$ interaction. The optimized $\text{Pt}/\text{WO}_x/\text{Nb}_2\text{O}_5$ catalyst achieved remarkable catalytic performance in the hydrogenolysis of glycerol (50.0%), with a glycerol conversion of 94.9% and 1,3-PDO selectivity of 67.3%. The space time yield of glycerol is 0.490 g/(g_{cat}·h). This study found that $\text{Pt}^{\delta+}\text{-O-W}$ interaction could promote the selective adsorption of the secondary hydroxyl group of glycerol and the hydrogen spillover from Pt to WO_x for *in situ* generation of Brønsted acid sites. Both facilitate the selective hydrogenolysis of glycerol to 1,3-PDO (Figure 11)^[81]. In 2024, Chen et al.^[82] further studied the catalytic performance of $\text{Pt}/\text{Nb}_2\text{W}_3\text{O}_{14}$ catalyst in glycerol hydrogenolysis. Compared with Pt/WO_3 and Pt/NbO_x , the space-time yield of 1,3-PDO on Nb-doped $\text{Pt}/\text{Nb}_2\text{W}_3\text{O}_{14}$ catalyst could be increased by 13 times, reaching 596.4 mg/(g_{cat}·h). It is found that the cationic ordering of Nb and W at the atomic scale gave full play to their unique advantages. $\text{Nb}_2\text{W}_3\text{O}_{14}$ could effectively promote the dispersion and reduction of Pt nanoparticles. Strong interaction between $\text{Nb}_2\text{W}_3\text{O}_{14}$ and Pt could promote the adsorption and activation of the secondary hydroxyl group (C2-OH) of glycerol, as well as the subsequent hydrogenation, thereby selectively producing 1,3-PDO. In addition, the electronic structure of Pt-WO_x catalysts can be further optimized by introducing second promoters (such as Sn, Mo, etc.), thus improving their catalytic activity, stability and selectivity in the hydrogenolysis of glycerol. Shaikh et al.^[83] systematically investigated the effects of reaction temperature, pressure and second promoters (Cu,

Fe, Rh, Mn, Re, Ru, Ir, Sn, B and P) on the catalytic performance and deactivation behavior of $\text{Pt}/\text{WO}_x/\gamma\text{-Al}_2\text{O}_3$ catalysts. They found that when Rh, Mn, Re, Ru, Ir, B or P were introduced as second promoters, they could not only promote the dispersion of Pt, but also significantly improve the selectivity of 1,3-PDO by increasing the number of Brønsted acid sites. Analysis of fresh and spent catalysts by characterization methods like XRD, CO chemisorption and TEM shows that Pt particle sintering is the main cause of catalyst deactivation. Notably, the introduction of second promoters could affect the sintering behavior of the catalyst by changing the interactions between Pt, WO_x and $\gamma\text{-Al}_2\text{O}_3$. For example, Re and Mn promoters as electron acceptors could increase the content of Pt^{2+} on the catalyst surface. The formation of Pt^{2+} enhances the interaction between Pt and $\gamma\text{-Al}_2\text{O}_3$ as well as WO_x , and effectively inhibits Pt sintering. However, adding second promoters had no obvious improvement on metal leaching and coking. Their stability still faces challenges. Nevertheless, catalyst stability is crucial in practical applications. Lei et al.^[84] systematically investigated the stability of $\text{Pt}/\text{WO}_3/\text{Al}_2\text{O}_3$ catalyst and observed obvious deactivation in a 700 h continuous operation experiment. Glycerol conversion decreases by more than half during the whole process, from 57.5% to 25.1% at 700 h. In-depth analysis revealed that neither leaching of W species nor coking is the main cause of deactivation. Characterization results from XRD, HAADF-STEM and CO chemisorption clearly show that the significant aggregation of Pt particles led to a sharp decrease in Pt-WO_x interfacial sites. This structural change resulted in a decrease in the number of strong Brønsted acid sites originally formed *in situ* through H_2 dissociation at the Pt-WO_x interface. This issue ultimately led to catalyst deactivation.

Table 2 Comparison of catalytic properties over different catalysts for the hydrogenolysis of glycerol to 1,3-PDO

Entry	Catalyst	$t/^{\circ}\text{C}$	p/MPa	Conversion/%	Selectivity/%	Ref.
					1,3-PDO	
1	$\text{Pt}_6/\text{W}/\text{Al}$	180	4.0	80.1	48.1	[75]
2	$\text{Pt}/\text{Nb}_2\text{W}_{15}\text{O}_{50}$	130	1.0	75.6	66.5	[77]
3	$2\text{Pt}/\text{WO}_x/\alpha\text{-Al}_2\text{O}_3$	180	5.0	51.7	45.6	[78]
4	$\text{Pt-WO}_x/\gamma\text{-Al}_2\text{O}_3$	160	5.0	64.0	42.0	[79]
5	$\text{Pt}/\text{W-SiO}_2\text{-700}$	140	5.0	70.9	61.3	[80]
6	$\text{Pt}/\text{WO}_x/\text{Nb}_2\text{O}_5$	160	7.0	94.9	67.3	[81]
7	$\text{Pt}/\text{Nb}_2\text{W}_3\text{O}_{14}$	140	4.0	94.0	68.3	[82]
8	$\text{Pt}/\text{WO}_x/\gamma\text{-Al}_2\text{O}_3$	140	2.0	45.3	41.6	[83]
9	$\text{Fe}/\text{Pt}/\text{WO}_x/\gamma\text{-Al}_2\text{O}_3$	140	2.0	44.8	40.5	[83]
10	$\text{Mn}/\text{Pt}/\text{WO}_x/\gamma\text{-Al}_2\text{O}_3$	140	2.0	51.5	42.6	[83]
11	$\text{Ru}/\text{Pt}/\text{WO}_x/\gamma\text{-Al}_2\text{O}_3$	140	2.0	53.4	42.3	[83]
12	$\text{B}/\text{Pt}/\text{WO}_x/\gamma\text{-Al}_2\text{O}_3$	140	2.0	50.3	40.7	[83]
13	$\text{Pt}/\text{WO}_3/\text{Al}_2\text{O}_3$	180	5.0	57.5	40.4	[84]
14	$\text{Ir-ReO}_x/\text{SiO}_2$	120	8.0	58.6	44.8	[36]
15	$\text{Ir-ReO}_x/\text{rutile}$	120	8.0	52.0	57.0	[85]
16	$\text{Ir-ReO}_x/\text{H-ZSM-5}$	220	4.0	14.9	19.0	[86]

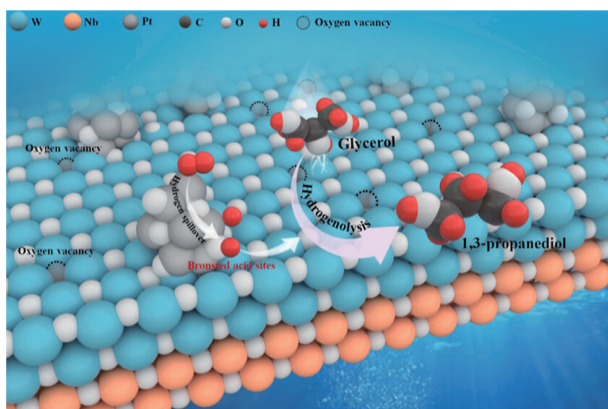


Fig. 11 Hydrogenolysis of glycerol to 1,3-PDO on Pt/WO_x/Nb₂O₅^[81]
(with permission from ACS Publications)

1.2.2 Ir-ReO_x catalytic systems

Due to the high cost, research on Ir-ReO_x based catalytic systems for the hydrogenolysis of glycerol to 1,3-PDO remains limited. In 2011, Amada et al.^[36] explored the reaction mechanism of the hydrogenolysis of glycerol to 1,3-PDO over Ir-ReO_x/SiO₂ catalysts. Systematic studies showed that glycerol conversion increases with the increase of Re content (reaching a maximum when Re/Ir = 2). In contrast, the high selectivity of 1,3-PDO (approximately 60%) is barely affected by Re content. XRD and TEM characterizations indicated that the average size of Ir particles gradually decreases with the increase of Re content. Characterization results of CO adsorption, TPR, XANES and EXAFS confirmed that the Ir metal surface is partially covered by ReO_x clusters regardless of the Re content. Kinetic studies showed that reaction order of Ir-ReO_x/SiO₂ (Re/Ir = 1) with respect to H₂ pressure is first-order. The low reaction order with respect to glycerol concentration indicated a strong interaction between glycerol and the catalyst surface. Combining reaction and characterization results, authors propose a reaction mechanism where glycerol is directly converted to 1,3-PDO via a 2,3-dihydroxypropoxy intermediate (“direct hydrogenolysis” route). Liu et al.^[85] further systematically investigated the effect of supports on the catalytic performance of Ir-ReO_x catalysts for the hydrogenolysis of glycerol to 1,3-PDO. It is found that rutile TiO₂ support exhibits extremely high catalytic activity, even superior to the aforementioned SiO₂ support. In contrast, Ir-ReO_x catalysts supported on anatase TiO₂, C, ZrO₂, CeO₂, Al₂O₃ and MgO all show low catalytic activity. Without adding H₂SO₄, even with a low Re/Ir ratio (0.24), Ir-ReO_x/rutile TiO₂ catalyst still exhibits higher Ir-based 1,3-PDO yield than Ir-ReO_x/SiO₂ at the initial stage of reaction. The important role of rutile TiO₂ support is that it can provide a unique environment to stabilize uniform small-sized Ir-ReO_x particles, which significantly increases the number of active sites per unit Re. Comprehensive characterization methods including TPR, TEM, XPS, XAS, CO adsorption

and CO FT-IR, combined with kinetic studies, show strong interaction between Ir and partially oxidized ReO_x clusters (the average valence state of Re is +3). The active sites are at the Ir-ReO_x interface. In 2021, Sarun Chanklang et al. explored the performance of Ir-ReO_x catalyst supported on H-ZSM-5 (Ir-ReO_x/H-ZSM-5) in the hydrogenolysis of glycerol to 1,3-PDO^[86]. It is found that glycerol conversion and 1,3-PDO yield largely depends on catalyst composition (Re/Ir ratio) and metal loading. Adding Re promotes the high dispersion of Ir. In addition, a strong electronic interaction between Ir and Re is observed in the Ir-ReO_x/H-ZSM-5 catalyst. In the study of the influence of reaction conditions, it is found that increasing reaction temperature and time can lead to higher glycerol conversion. But over-hydrogenolysis would occur, reducing the selectivity of 1,3-PDO. Increasing pressure has a positive effect on the selectivity of 1,3-PDO. Under optimal conditions, the conversion of glycerol is 14.9% with 19.0% 1,3-PDO selectivity on Ir-ReO_x/H-ZSM-5 (Table 2).

1.3 Hydrogenolysis of glycerol to 1-PO

As an important organic solvent and chemical raw material, 1-PO has broad industrial application prospects. Especially under strict environmental regulations and the development of green chemistry, the demand for 1-PO is gradually increasing. The selective hydrogenolysis of renewable glycerol to 1-PO can promote the healthy development of the biodiesel industry. It can also help alleviate the dependence of the 1-PO industry on fossil energy and contribute to the realization of the carbon neutrality goal^[87]. Currently, the catalysts for the hydrogenolysis of glycerol to 1-PO can be divided into two main categories: noble metal catalysts and non-noble metal catalysts.

1.3.1 Noble metal catalysts

Noble metal catalysts are widely used in the catalytic hydrogenolysis of glycerol to 1-PO due to their high hydrogenolysis activity. Li et al.^[88] prepared a series of Pt catalysts supported on Zr-Al composite oxides with varying Zr/Al molar ratios (denoted as 2.5%Pt/Zr_xAl_{1-x}O_y). Their performance in the selective hydrogenolysis of glycerol to 1-PO were evaluated. The results reveal that the Zr/Al molar ratio in the support markedly influenced both the Pt particle size and the nature of the acid sites on the catalyst surface. A clear correlation is observed between the catalytic behavior and acidity. Higher concentration of acidic sites promotes the conversion of glycerol. While strong acidic sites within a specific strength range favor deep hydrogenolysis of glycerol to 1-PO. Under the reaction conditions of 10% aqueous glycerol solution, 240 °C, and 6.0 MPa H₂ pressure, the 2.5%Pt/Zr_{0.7}Al_{0.3}O_y catalyst exhibited the best catalytic performance. It achieved 81.2% glycerol conversion with >86% selectivity to 1-PO (Table 3).

Table 3 Comparison of catalytic properties over different catalysts for the hydrogenolysis of glycerol to 1-PO and PA

Entry	Catalyst	$t/^{\circ}\text{C}$	p/MPa	Conversion/%	Selectivity/%		Ref.
					1-PO	PA	
1	2.5%Pt/Zr _{0.7} Al _{0.3} O _y	240	6.0	81.2	>86.0	—	[88]
2	ZrP+2%Ru/SiO ₂	315	2.0	100	76.5	—	[89]
3	Pt/7WO _x -ZrP	270	2.0	100	81.0	3.0	[90]
4	2Pt/TiP	220	0.1	100	~81.0	—	[91]
5	Pd/MoO ₃ -Al ₂ O ₃	210	0.1	80.0	~50.0	—	[92]
6	Pd/C	250	8.0	38.5	52.8	—	[93]
7	Ru/C	250	8.0	99.8	17.6	—	[93]
8	H-β ₂ Ni/Al ₂ O ₃	220	2.0	~100	69.0	—	[96]
9	HZSM-5 20Ni/Al ₂ O ₃	300 175	0.1	100	>73.0	—	[97]
10	Cu-HSiW	340	5.0	98.0	71.0	—	[98]
11	Cu20/HZSM-5	250	5.0	100	71.1	—	[99]
12	HZSM-5 Pd/α-Al ₂ O ₃	500 200	0.1	100	—	~40.8	[47]
13	Ru/CoO/ZrP	270	2.0	100	0.5	80.2	[104]

Additionally, Wang et al.^[89] developed a one-pot hydrogenolysis of glycerol to 1-PO using a double-layer catalyst system in a continuous flow fixed-bed reactor (Figure 12). The zirconium phosphate (ZrP) catalyst was placed in the upper layer and responsible for catalyzing the dehydration of glycerol to acrolein. Supported Ru catalyst in the lower layer was used for hydrogenating acrolein to 1-PO. This study found that the presence of strong acid sites on the lower hydrogenation catalyst promoted the formation of glycerol decomposition products, such as methanol, ethanol, methane, and CO₂. In contrast, 2%Ru/SiO₂ catalyst possessing only weak acid sites delivered the highest 1-PO selectivity (76.5%). This catalytic system also shows good long-term stability (80 h).

Metal phosphates usually possess abundant acidic sites and exhibit excellent hydrothermal stability, which are beneficial for the hydrogenolysis of glycerol to 1-PO. Luo et al.^[90] developed a WO_x-modified amorphous zirconium phosphate (ZrP)-supported Pt catalyst (Pt/7WO_x-ZrP) for the selective hydrogenolysis of glycerol to 1-PO in a fixed-bed reactor. Studies showed that introducing WO_x significantly increases the total acidity of the catalyst and dispersion of Pt nanoparticles. Among them, the Pt/7WO_x-ZrP catalyst achieved complete glycerol conversion with 1-PO yield of 81% in the long-term stability test (≥ 70 h). Catalytic performance tests and characterization results indicate that the acidic sites on the catalyst could promote the selective dehydration of glycerol to acrolein. Pt sites are responsible for H₂ molecule dissociation and subsequent hydrogenation of acrolein intermediate to 1-PO. Bhanuchander et al.^[91] synthesized a series of metal phosphate-supported Pt catalysts (Pt/AlP, Pt/TiP, Pt/ZrP and Pt/NbP) for the direct hydrogenolysis of glycerol to propanol. The reaction conditions for hydrogenolysis of glycerol to propanol has been optimized by systematically investigating parameters such as Pt loading, reaction temperature, hydrogen flow rate, glycerol concentration and reaction time.

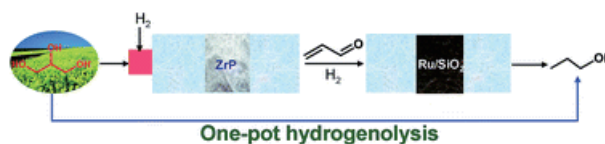


Fig. 12 ZrP+2%Ru/SiO₂ catalyzed the hydrogenolysis of glycerol to 1-PO^[89]
(with permission from RSC Publications)

Among them, 2Pt/TiP exhibits excellent catalytic performance in the gas-phase hydrogenolysis of glycerol. Under the conditions of 220 °C and atmospheric pressure, achieving complete glycerol conversion with 1-PO selectivity of approximately 81.0%. High catalytic efficiency of the 2Pt/TiP catalyst is attributed to its strong acidity and uniformly dispersed Pt nanoparticles on the TiP. These effects facilitate the conversion of glycerol to 1-PO via the “dehydration-hydrogenation” pathway. Samudrala et al.^[92] used Pd/MoO₃-Al₂O₃ as catalyst to realize the selective hydrogenolysis of glycerol to 1-PO and 2-PO in a fixed-bed reactor. Catalytic performance results showed that this system not only achieves a glycerol conversion of >80% but also exhibit a total selectivity of >90% for 1-PO (about 50.0%) and 2-PO. Characterization analysis indicated that the synergistic effect between Pd and MoO₃ on the Al₂O₃ support is the key factor for obtaining excellent catalytic activity. In addition, Ryneveld et al.^[93] compared Pd catalysts supported on different supports. They found that the Pd/C catalyst could achieve 38% glycerol conversion and 52% 1-PO selectivity under the reaction condition of 250 °C. Under the same operating conditions, although the Ru/C catalyst could reach approximately 99% glycerol conversion, its 1-PO selectivity decreases to about 18% due to the occurrence of C–C bond cleavage.

1.3.2 Non-noble metal catalysts

Although Ni-based catalysts have the disadvantages of

high reduction temperature, they often show high activity for the hydrogenolysis of glycerol to 1-PO. However, in hydrothermal reactions, Ni nanoparticles tend to be agglomerated or leached, leading to catalyst deactivation^[94]. To improve the stability of Ni-based catalysts, Gatt et al.^[95] investigated the catalytic performance of phosphorus-modified carbon supported Ni catalysts in the hydrogenolysis of glycerol to 1-PO. They prepared a series of nickel phosphide catalysts using mesoporous carbon as the support and $\text{Al}(\text{H}_2\text{PO}_4)_3$ and NiCl_2 as metal precursors. It was found that these Ni-based catalysts would form different phases (Ni_xP_y , NiPO_x , AlPO_x). Enhancement of acidity was directly related to the content of $\text{Al}(\text{H}_2\text{PO}_4)_3$. When the content of $\text{Al}(\text{H}_2\text{PO}_4)_3$ precursor was in the range of 4%–10%, the increase in catalyst surface acidity could improve glycerol conversion and enhance the selectivity of 1-PO. Studies showed that the presence of phosphate is necessary for achieving high catalytic activity. However, when the $\text{Al}(\text{H}_2\text{PO}_4)_3$ content exceeds 10%, the selectivity of 1-PO decreased due to the intensified dehydration reaction on the acidic sites of the support. Among them, the Ni/CPAl(10) catalyst achieved 97% conversion of glycerol and 74% 1-PO selectivity after reacting for 6 h in the 80% aqueous glycerol solution. Lin et al. adopted a double-layer catalyst system to realize the hydrogenolysis of glycerol to 1-PO through sequential catalysis^[96]. In a continuous flow fixed-bed reactor, the acidic H- β catalyst layer was placed upstream of the Ni/ Al_2O_3 catalyst layer. This double-layer catalyst system exhibited excellent 1-PO selectivity (up to 69%) with nearly 100% conversion of glycerol. Preliminary mechanism studies indicated that the conversion of glycerol to 1-PO proceeds *via* the two sequential dehydration-hydrogenation pathway. Solos et al.^[97] further studied the process of dehydration and hydrogenation of glycerol to 1-PO over a tandem catalytic system consisting of HZSM-5 and supported Ni catalysts. First, glycerol was completely converted to acrolein and PA (selectivity >82%) *via* dehydration over the first bed (HZSM-5) at 300 °C. Ni/MgO, Ni/SiO₂, Ni/Mg-Al-LDH, Ni/TiO₂ or Ni/ Al_2O_3 (20% Ni loading) were used as hydrogenation catalysts in

the second bed. Acrolein and PA produced in the first bed were hydrogenated to 1-PO in the second bed at 175 °C (Figure 13)^[97]. HZSM-5/20Ni/ Al_2O_3 system with high Ni dispersion provide high stability and 1-PO yield (>73%).

In addition to Ni-based catalysts, Cu-based catalysts also showed excellent performance in glycerol hydrogenolysis to 1-PO. In 2022, Folkard et al.^[98] explored the application of Cu-HSiW catalyst in glycerol hydrogenolysis to 1-PO. For the first time, the direct conversion of glycerol to 1-PO was achieved on the Cu-based catalysts. Systematic studies on fresh and spent catalysts were carried out using various characterization techniques. It was found that when silicotungstic acid with moderate acidity (maintaining intact Keggin structure units) is distributed near the Cu clusters, the catalytic performance and lifetime of the catalyst are significantly improved. 98% glycerol conversion was obtained with 71% selectivity to 1-PO (Table 3). In 2024, Zhou et al. prepared a simple Cu20/HZSM-5 (Si/Al = 120) catalyst. It achieved a 1-PO selectivity of approximately 71.1% under mild reaction conditions^[99]. This catalyst has a high Lewis acid site density and a favorable $\text{Cu}^{2+}/\text{Cu}^{0/1+}$ ratio, which significantly enhances the hydrogenolysis of glycerol to 1-PO. In addition, Cu20/HZSM-5 exhibited excellent selectivity for removing the secondary hydroxyl group from the intermediate 1,2-PDO. It is crucial for the high yield of 1-PO.

1.4 Hydrogenolysis of glycerol to PA

As another important C3 oxygenated chemical, PA can be widely used in food additives, pharmaceutical intermediates, pesticide synthesis and other fields. The traditional PA production process mainly relies on the hydroformylation of ethylene. This process not only consumes non-renewable petroleum-based ethylene resources but also faces environmental pressures^[100]. Therefore, developing a green synthesis route for PA production using renewable glycerol as raw material is of great significance (Figure 14).

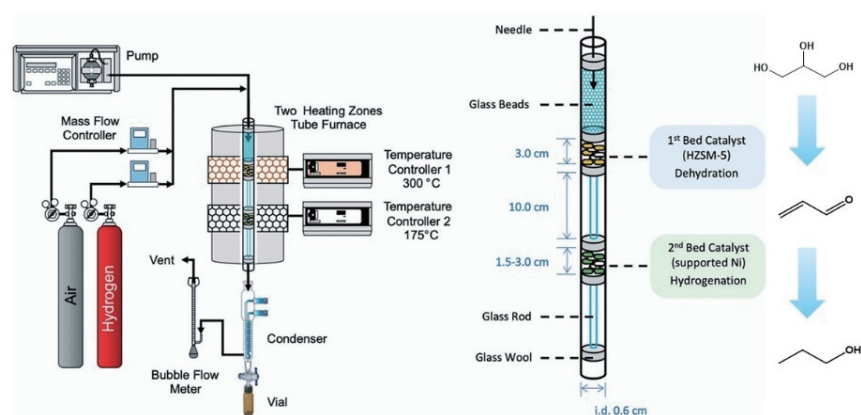


Fig. 13 Catalytic hydrogenolysis of glycerol to 1-PO on double layered HZSM-5/20Ni/ Al_2O_3 ^[97]
(with permission from RSC Publications)

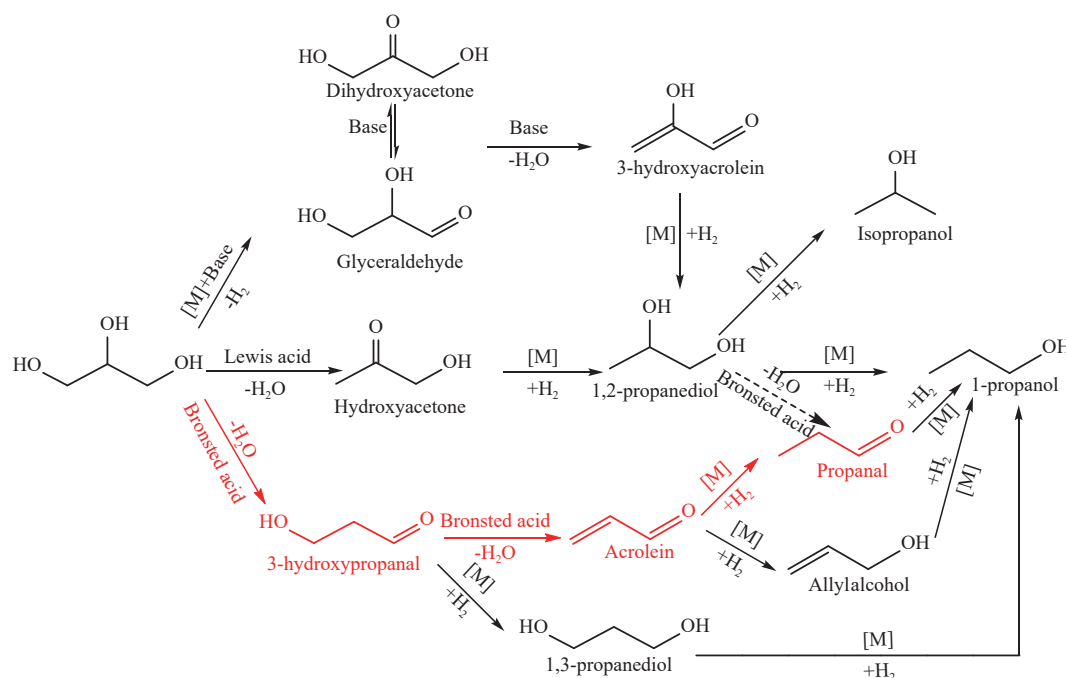


Fig. 14 Schematic diagram of possible reaction processes and products in the hydrogenolysis of glycerol to PA

The catalytic conversion of renewable biomass to PA can be mainly divided into 1,2-PDO dehydration method, acrolein hydrogenation method, and glycerol hydrogenolysis method (Figure 15). Among them, the 1,2-PDO dehydration method has been widely reported. This method uses 1,2-PDO, a hydrogenolysis product of glycerol, as the starting material. The selective dehydration of 1,2-PDO to PA can be achieved under the catalysis of Brønsted acid. For example, Chew et al.^[101] used triflic acid as the catalyst. Under the condition of 160 °C, the conversion of 1,2-PDO was 55% and the selectivity of PA

was 68%. Otomo et al.^[102] prepared a boron phosphate (BP) catalyst. Under 300 °C and atmospheric H₂ flow (60 mL/min), 1,2-PDO is completely converted on BP, and the initial yield of PA reached 95%. Although the 1,2-PDO dehydration method has high selectivity for PA, the issues of catalyst recovery and stability remain unsolved. Moreover, when glycerol is used as the starting material, this method involves multiple steps, long cycles and high energy consumption. These issues result in unpromising industrial application prospects.

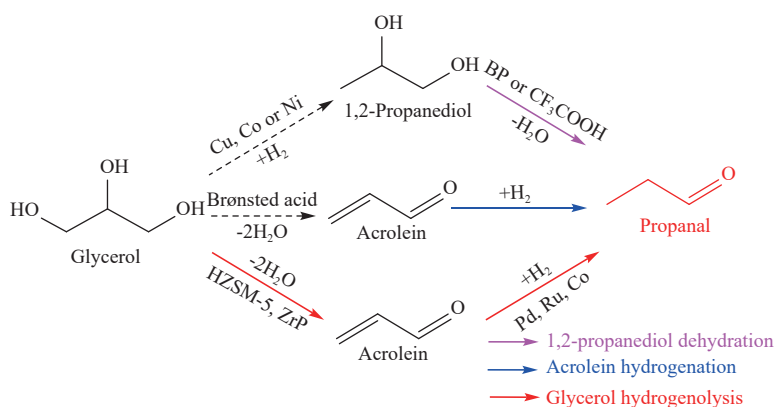


Fig. 15 Schematic diagram of the production of PA from glycerol via 1,2-PDO and acrolein

The acrolein hydrogenation method refers to the selective hydrogenation of the C=C bond of acrolein, a dehydrated product of glycerol, to obtain PA^[103]. This method has the advantages of mild reaction conditions, high catalytic activity, and high selectivity for PA. However, the substrate acrolein has disadvantages such as instability, difficult in transportation, and toxicity. These issues make it difficult to apply in industry. The direct hydrogenolysis of glycerol to

PA is considered the greenest, most energy-saving and efficient method. Thus, it has great industrial application prospects.

The catalysts used are typically solid acid-supported metal catalysts (Cu, Co, Pt, Ru and Pd) with appropriate hydrogenation activity, such as HZSM-5 + Pd/ α -Al₂O₃^[47], Ru/CoO/ZrP^[104] and Cu/Mo₂C^[105]. However, under reaction conditions, the C=C and C=O bonds of the intermediate

acrolein tend to be hydrogenated simultaneously. Therefore, the main product of the hydrogenolysis of glycerol is usually 1-PO. Blass et al.^[47] first used HZSM-5 as the catalyst to catalyze the dehydration of glycerol to acrolein (approximately 68% selectivity). Then, Pd/ α -Al₂O₃ was used to catalyze the selective hydrogenation of acrolein to PA (60% selectivity). Hou et al. use Ru/CoO/ZrP as the catalyst to catalyze the hydrogenolysis of glycerol to PA under 270 °C and 2 MPa H₂. The full conversion of glycerol was achieved and the selectivity of PA was 80.2% (Table 3), but the issues of catalyst recovery and long-term stability had not been solved^[104].

2 Conclusion and outlook

A comprehensive understanding of the mechanism of glycerol hydrogenolysis is crucial for developing high-efficiency catalysts. This review systematically summarizes the proposed reaction mechanisms for the catalytic hydrogenolysis of glycerol to C3 oxygenated chemicals, including “dehydration-hydrogenation”, “dehydrogenation-dehydration-hydrogenation”, and “direct hydrogenolysis” pathways. The selective cleavage mechanism of the C–O bond of glycerol in the hydrogenolysis reaction is described, and the inherent laws of different catalytic systems on the regulation of the reaction pathways are also revealed, which provide a theoretical basis for the directional regulation of product distribution. Recent advances in *in situ* characterization techniques and theoretical calculations have provided powerful tools for unraveling the reaction mechanisms of the hydrogenolysis of glycerol. For example, the formation and transformation of intermediates during the hydrogenolysis of glycerol can be observed by *in situ* FT-IR. Density functional theory (DFT) calculations can predict the influence of different active sites on the reaction pathways. As research in these areas deepens, the hydrogenolysis of glycerol to C3 oxygenated chemicals is expected to become a successful example of high-value utilization of biomass resources.

Although there are still challenges in selective control and catalyst stability during the hydrogenolysis of glycerol, with the development of new catalytic materials and the strengthening of process engineering, the hydrogenolysis of glycerol to C3 oxygenated chemicals will show good application prospects. As a promising strategy for biomass valorization, the hydrogenolysis of glycerol to 1,2-PDO faces challenges including catalyst stability and insufficient mechanism understanding. Future research should focus on the rational design of high-performance catalysts and in-depth mechanism investigations. For the study of the hydrogenolysis of glycerol to 1,3-PDO, the future research focus should be on improving the yield of 1,3-PDO and the stability of the catalyst. In order to achieve this goal, it is necessary to develop new metal-Brønsted acid bifunctional catalysts with excellent catalytic stability and high 1,3-PDO selectivity, and to clarify the synergistic effect of metal and

acid sites. Furthermore, exploring the feasibility of replacing traditional noble metal catalysts (e.g., Pt- or Ir-based) with cost-effective transition metal catalysts like Cu, Co or Ni is essential for reducing the production costs of 1,3-PDO. As another important route for the high-value utilization of glycerol, the production of 1-PO *via* hydrogenolysis of glycerol has made remarkable progress in recent years. However, several challenges remain for its industrial application. First, the activity and stability of existing catalysts require further improvement, particularly regarding their adaptability to complex raw materials. Second, mechanism studies need to be deepened, especially concerning the dynamic characterization of intermediate species and active sites. Regarding hydrogenolysis of glycerol to PA, both the selectivity of PA and catalyst stability need further enhancement. Moreover, noble metals are often used, which is not conducive to industrial applications. Additionally, a crucial reason for the low selectivity of PA is that the highly selective activation of the C=C bond in the acrolein intermediate cannot be achieved during the hydrogenolysis of glycerol. Therefore, the rational design of cost-effective non-noble metal catalysts capable of precisely activating the C=C bond of acrolein remains a critical research priority.

Declaration of Competing Interest

The authors declare no conflict of interest.

References

- [1] LI G-Y, WANG R, PANG J-F, et al. Production of renewable hydrocarbon biofuels with lignocellulose and its derivatives over heterogeneous catalysts[J]. Chem Rev, 2024, 124(6): 2889–2954.
- [2] ZHANG B, BISWAL B K, ZHANG J-J, et al. Hydrothermal treatment of biomass feedstocks for sustainable production of chemicals, fuels, and materials: Progress and perspectives [J]. Chem Rev, 2023, 123(11): 7193–7294.
- [3] KUMAR A, DAW P, MILSTEIN D, Homogeneous catalysis for sustainable energy: Hydrogen and methanol economies, fuels from biomass, and related topics[J]. Chem Rev, 2022, 122(1): 385–441.
- [4] CHONG C-T, LOE T-Y, WONG K-Y, et al. Biodiesel sustainability: The global impact of potential biodiesel production on the energy-water-food (EWF) nexus[J]. Environ Technol Innov, 2021, 22: 101408.
- [5] ZHANG Q, LI W, ZHAO Y, et al. Application progress of MOFs-based composite materials for biodiesel production[J]. Petrochem Technol, 2024, 53(2): 240–250.
- [6] VANDER M P J M, BITTERMARC H C H, PESCARMONA T M K P. Electrochemical and non-electrochemical pathways in the electrocatalytic oxidation of monosaccharides and related sugar alcohols into valuable products[J]. Chem Rev, 2024, 124(12): 11915–11961.
- [7] GERARDY D R, DEBECKER P, ESTAGER J, et al.

- Continuous flow upgrading of selected C2-C6 platform chemicals derived from biomass[J]. *Chem Rev*, 2020, 120(15): 7219–7347.
- [8] ZHAO J-G, HAO S, ZHAO P-P, et al. On-demand catalytic platform for glycerol upgrade and utilization[J]. *J Am Chem Soc*, 2025, 147(11): 9210–9219.
- [9] XIA Z-C, MA C-Y, FAN Y, et al. Vacancy optimized coordination on nickel oxide for selective electrocatalytic oxidation of glycerol[J]. *ACS Catal*, 2024, 14(3): 1930–1938.
- [10] BAJPAI H, NIVEDHITHA T R, DAIS E, et al. Oxidative and selective C–C cleavage of glycerol to glycolaldehyde with atom-like Cu on Cu-TiO₂: Photocatalytic water reduction with concurrent glycerol oxidation in sunlight[J]. *J Catal*, 2024, 437: 115644.
- [11] DODEKATOS G, SCHUNEMANN S, TUYSUZ H. Recent advances in thermo-, photo-, and electrocatalytic glycerol oxidation[J]. *ACS Catal*, 2018, 8(7): 6301–6333.
- [12] JIE Y, DAPPOZZE F, MARTIN-GOMEZ J, et al. Glyceraldehyde production by photocatalytic oxidation of glycerol on WO₃-based materials[J]. *Appl Catal B: Environ*, 2021, 299: 120616.
- [13] JIANG D, WANG S, LI H-P, et al. Insight into the mechanism of glycerol dehydration and subsequent pyridine synthesis[J]. *ACS Sustainable Chem Eng*, 2021, 9(8): 3095–3103.
- [14] MA T-L, YUN Z, XU W, et al. Pd-H₃PW₁₂O₄₀/Zr-MCM-41: An efficient catalyst for the sustainable dehydration of glycerol to acrolein[J]. *Chem Eng J*, 2016, 294: 343–352.
- [15] KOVACEVIC B, BARIC D, BARIC D, et al. A computational tale of two enzymes: Glycerol dehydration with or without B12[J]. *J Am Chem Soc*, 2018, 140(27): 8487–8496.
- [16] PANDIT K, JEFFREY C, KEOGH J, et al. Techno-economic assessment and sensitivity analysis of glycerol valorization to biofuel additives via esterification[J]. *Ind Eng Chem Res*, 2023, 62(23): 9201–9210.
- [17] HU H-Q, ZHANG Y, FAN M, et al. Complete kinetic model for esterification reaction of lauric acid with glycerol to synthesize glycerol monolaurate[J]. *Chin J Chem Eng*, 2024, 70: 211–221.
- [18] JIANG Y-Y, LI X-W, ZHAO H-Y, et al. Esterification of glycerol with acetic acid over SO₃H-functionalized phenolic resin[J]. *Fuel*, 2019, 255: 115842.
- [19] CANNILLA C, BONURA G, MAISANO S, et al. Zeolite-assisted etherification of glycerol with butanol for biodiesel oxygenated additives production[J]. *J Energy Chem*, 2020, 48: 136–144.
- [20] SILVA M J, CHAVES D M, FERREIRA S O, et al. Impacts of Sn(II) doping on the Keggin heteropolyacid-catalyzed etherification of glycerol with tert-butyl alcohol[J]. *Chem Eng Sci*, 2022, 247: 116913.
- [21] MOREIRA R, BIMBELA F, GANDIA L M, et al. Oxidative steam reforming of glycerol. A review[J]. *Renew Sust Energ Rev*, 2021, 148: 111299.
- [22] ROCHA D H D, SOUZA T A Z, CORONADO C J R, et al. Exergoenvironmental analysis of hydrogen production through glycerol steam reforming[J]. *Int J Hydrogen Energ*, 2021, 46: 1385–1402.
- [23] CHUNAKIAT P, PANARMASAR N, KUCHONTHARA P, Hydrogen production from glycerol and plastics by sorption-enhanced steam reforming[J]. *Ind Eng Chem Res*, 2023, 62(49): 21057–21066.
- [24] CALLISON J, SUBRAMANIAN N D, ROGERS S M, et al. Directed aqueous-phase reforming of glycerol through tailored platinum nanoparticles[J]. *Appl Catal B: Environ*, 2018, 238: 618–628.
- [25] ZHOU Z, REN X, CAO Y-Q, et al. Acid-mediated construction of oxygen-free Ir-Re coordination for matching configuration of glycerol to selective hydrogenolysis[J]. *Chem Eng J*, 2025, 508: 160976.
- [26] SI Y-X, HUANG Y-C, QIN C, et al. Selective production of C3 polyols from cellulose over hydrogen spillover promoted Pd-Mo/TiO₂ catalyst with adjacent lewis acid pairs[J]. *ACS Catal*, 2024, 14(22): 17180–17190.
- [27] VANAPALLI K R, NONGDREN L, MAITY S K, et al. Comparative life cycle assessment of glycerol valorization routes to 1, 2- and 1, 3-propanediol based on process modeling[J]. *ACS Sustainable Chem Eng*, 2024, 12(40): 14716–14731.
- [28] VERA-HINCAPIE N, IRIARTE-VELASCO U, AYASTUY J L, et al. Aqueous-phase hydrogenolysis of glycerol over NiCeZr catalysts using in-situ produced H₂: Effect of Ce/Zr ratio[J]. *J Environ Chem Eng*, 2024, 12: 112357.
- [29] WANG H, WANG H, LUO G, et al. Research progress of catalyst in catalytic hydrogenolysis of glycerol to 1, 2-propanediol[J]. *Chem Ind Eng Prog*, 2018, 37(6): 2214–2221.
- [30] SUN D-L, YAMADA Y, SATO S, et al. Glycerol hydrogenolysis into useful C3 chemicals[J]. *Appl Catal B: Environ*, 2016, 193: 75–92.
- [31] HUANG J-B, ZHANG J, LU S-Y, et al. Pure silica beta zeolite supported copper species for efficient hydrogenolysis of glycerol to 1, 2-propanediol[J]. *Biomass Bioenergy*, 2023, 174: 106818.
- [32] CAI F-F, ZHU W, XIAO G-M, Promoting effect of zirconium oxide on Cu-Al₂O₃ catalyst for the hydrogenolysis of glycerol to 1, 2-propanediol[J]. *Catal Sci Technol*, 2016, 6: 4889–4900.
- [33] ZHAO H-Y, ZHENG L-P, LI X-W, et al. Hydrogenolysis of glycerol to 1, 2-propanediol over Cu-based catalysts: A short review[J]. *Catal Today*, Volume, 2020, 355: 84–95.
- [34] ANDRADE T S, SOUZA M M V M, MANFRO R L. Hydrogenolysis of glycerol to 1, 2-propanediol without external H₂ addition in alkaline medium using Ni-Cu catalysts supported on Y zeolite[J]. *Renew Energy*, 2020, 160: 919–930.
- [35] MANE R, JEON Y, RODE C. A review on non-noble metal catalysts for glycerol hydrodeoxygenation to 1, 2-propanediol with and without external hydrogen[J]. *Green Chem*, 2022, 24: 6751–6781.
- [36] AMADA Y, SHINMI Y, KOSO S, et al. Reaction mechanism of the glycerol hydrogenolysis to 1, 3-propanediol over Ir-ReO_x/SiO₂ catalyst[J]. *Appl Catal B: Environ*, 2011, 105: 117–127.
- [37] FANG W, YAO X, YANG J, et al. Research progress of

- catalysts in hydrogenolysis of bioglycerol to 1, 3-propanediol[J]. *J Mol Catal (China)*, 2018, 32(6): 581–593.
- [38] ALISSON D S R, ANA C, ANDREIA S, et al. A novel chemical route for 1, 3-propanediol production from crude glycerol: Process simulation and environmental assessment [J]. *J Environ Chem Eng*, 2025, 13(3): 116864.
- [39] BHOWMIK S, DARBHA S. Advances in solid catalysts for selective hydrogenolysis of glycerol to 1, 3-propanediol[J]. *Catal Rev*, 2020, 63(4): 639–703.
- [40] CHEN Y, ZENG Y, HUNG C-T, et al. Interfacial synergism of hollow mesoporous Pt/WO_x/SiO₂-TiO₂ catalysts enable highly selective hydrogenolysis of glycerol to 1, 3-propanediol[J]. *Nano Res*, 2023, 16: 9081–9090.
- [41] YANG M, WU K, SUN S-D, et al. Regulating oxygen defects via atomically dispersed alumina on Pt/WO_x catalyst for enhanced hydrogenolysis of glycerol to 1, 3-propanediol[J]. *Appl Catal B: Environ*, 2022, 307: 121207.
- [42] LAO D B, OWENS A C E, HEINEKEY D M, et al. Partial deoxygenation of glycerol catalyzed by iridium pincer complexes[J]. *ACS Catal*, 2013, 3(10): 2391–2396.
- [43] PRIYA S S, KUMAR V P, KANTAM M L, et al. Metal-acid bifunctional catalysts for selective hydrogenolysis of glycerol under atmospheric pressure: A highly selective route to produce propanols[J]. *Appl Catal A: Gen*, 2015, 498: 88–98.
- [44] XI Z, HONG Z, HUANG F, et al. Hydrogenolysis of glycerol on the ZrO₂-TiO₂ supported Pt-WO_x catalyst[J]. *Catalysts*, 2020, 10(3): 312.
- [45] YUAN Y, MOU T-Y, HWANG S, et al. Controlling reaction pathways of ethylene hydroformylation using isolated bimetallic rhodium-cobalt sites[J]. *J Am Chem Soc*, 2025, 147(14): 12185–12196.
- [46] ANJALI G, PRANAB S. Prospects of ethylene hydroformylation beyond Rh-based catalysts[J]. *Catal Sci Technol*, 2025, 15: 6196–6201.
- [47] BLASS S D, HERMANN R J, PERSSON N E, et al. Conversion of glycerol to light olefins and gasoline precursors[J]. *Appl Catal A: Gen*, 2014, 475: 10–15.
- [48] PANDEY D K, BISIS P. Review of the development of heterogeneous catalysts for liquid and vapor phase hydrogenolysis of glycerol to propylene glycol (1, 2-propanediol): State-of-the-art and outlook[J]. *Energy Fuels*, 2023, 37(10): 6879–6906.
- [49] WANG M-T, LIU Y-Q, MAO J-B, et al. An Ag-promoted Co/Al₂O₃ catalyst without reduction pretreatment for the selective hydrogenolysis of high-concentration glycerol to 1, 2-propanediol[J]. *New J Chem*, 2024, 48: 20234–20245.
- [50] FU C-P, SHE Q-M, TESSER R, et al. Cleaner one-pot transformation of glycerol to acrylic acid and 1, 2-propanediol over bifunctional Cu₂O/montmorillonite catalysts without external oxygen and hydrogen[J]. *Catal Sci Technol*, 2022, 12: 6495–6506.
- [51] SHAO S-C, LI F, ZHANG Q-X, et al. Ru₂Pt₂/AC catalysts with tunable electronic configurations for in-situ hydrogenolysis of glycerol[J]. *Chem Eng J*, 2025, 504: 158674.
- [52] VALLE W F, SOARES A V-H, XING Y-T, et al. Probing supported bimetallic Pt-In sites in glycerol hydrogenolysis[J]. *New J Chem*, 2021, 45: 6512–6520.
- [53] ZHANG M-W, HONG C-B, DING Z-Y, et al. Selective hydrogenolysis of glycerol toward 1-propanol and 1, 2-propanediol via tuning the reduction temperature of (Mn)/Pt/WO_x catalysts[J]. *Chem Eng J*, 2024, 502: 158100.
- [54] SHU G-Q, LIN Y-Q, WANG S-H, et al. Dynamic metal-support interaction-activated sub-nanometer Pt clusters on FeO_x supports for aqueous phase reforming and hydrogenolysis of glycerol[J]. *ACS Catal*, 2023, 13(13): 8423–8436.
- [55] ZHANG J-Z, LI Z, HE X-F, et al. Sulfate-functionalized metal-organic frameworks supporting Pd nanoparticles for the hydrogenolysis of glycerol to 1, 2-propanediol[J]. *New J Chem*, 2021, 45: 21263–21269.
- [56] BARBELLI M L, SANTORI G F, NICHIO N N. Aqueous phase hydrogenolysis of glycerol to bio-propylene glycol over Pt-Sn catalysts[J]. *Bioresour Technol*, 2012, 111: 500–503.
- [57] PAMPHILE A J, FLOREZ P P, XING Y, et al. Ir-Fe bimetallic catalysts for selective glycerol hydrogenolysis[J]. *Catal Today*, 2025, 443: 114952.
- [58] ARDIAL A N, ARRIOLA E, BARRERA R, et al. Fuentes, kinetic study of liquid-phase glycerol hydrodeoxygenation into 1, 2-propanediol over CuPd/TiO₂-Na[J]. *ACS Omega*, 2023, 8(17): 14907–14914.
- [59] WEI L-F, BIBI R, TIAN W, et al. Comparative study of WC_x-based catalysts for aqueous phase hydrogenolysis of glycerol into bioadditives[J]. *New J Chem*, 2018, 42: 3633–3641.
- [60] PIRES M H M, PASSOS F B, XING Y-T. Hydrogenolysis of glycerol over ZSM-5 supported ruthenium and copper catalysts: Structural study and effects in reaction[J]. *Catal Today*, 2023, 419: 114161.
- [61] MANE R, POTDAR A, JEON Y, et al. Calcination temperature impacting the structure and activity of CuAl catalyst in aqueous glycerol hydrogenolysis to 1, 2-propanediol[J]. *Top Catal*, 2025, 68: 318–331.
- [62] KUMAR, P, ABDUL K S, LEE J, et al. Selective hydrogenolysis of glycerol over bifunctional copper-magnesium-supported catalysts for propanediol synthesis[J]. *Ind Eng Chem Res*, 2020, 59(14): 6506–6516.
- [63] COLMENARES-ZERPA J, GAJARDO J, PEIXOTO A F, et al. Turning glycerol to value-added chemicals in the absence of external hydrogen over copper catalysts supported on SBA-15-type materials containing zirconium[J]. *Top Catal*, 2024, 67: 422–453.
- [64] OMAR L, ONFROY T, DANIELE S, et al. Copper zinc aluminate synthesized by sol-gel method with polyacrylic acid as catalysts for glycerol hydrogenolysis[J]. *ChemCatChem*, 2023, 15(4): e202201297.
- [65] LIU S, YU Z-Q, LU C-Y, et al. Copper carbide composite catalyst for hydrogenolysis of glycerol to 1, 2-propanediol[J]. *Fuel*, 2023, 334: 126763.
- [66] KUMAR P, KAUR R, VERMA S, et al. Catalytic hydrogenolysis over Cu-based oxide derived from hydrotalcite-like structured materials: Reaction condition

- optimization and artificial neural network modelling[J]. *Appl Clay Sci*, 2023, 232: 106762.
- [67] CAI F-F, GUO Y-J, XIAO G-M. Selective hydrogenolysis of glycerol to 1, 2-propanediol over Co-Al₂O₃ catalysts in batch and continuous reactors[J]. *Chem Eng Technol*, 2023, 46: 256–263.
- [68] GONG H-H, ZHAO X-G, LI X-Y, et al. Boosting the long-term stability of hydrotalcite-derived catalysts in hydrogenolysis of glycerol by incorporation of Ca(II)[J]. *ACS Sustainable Chem Eng*, 2021, 9(5): 2246–2259.
- [69] HU T-Y, YU Z-Q, LIU S, et al. Citric acid modified Ni₃P as a catalyst for aqueous phase reforming and hydrogenolysis of glycerol to 1, 2-PDO[J]. *New J Chem*, 2021, 45: 21725–21731.
- [70] NIMBAIKAR A S, OH K-R, HAN S J, et al. Nickel-tin nanoalloy supported ZnO catalysts from mixed-metal zeolitic imidazolate frameworks for selective conversion of glycerol to 1, 2-propanediol[J]. *ChemSusChem*, 2024, 17(3): e202301315.
- [71] LIU L-J, KAWAKAMI S, NAKAGAWA Y, et al. Highly active iridium-rhenium catalyst condensed on silica support for hydrogenolysis of glycerol to 1, 3-propanediol[J]. *Appl Catal B: Environ*, 2019, 256: 117775.
- [72] RUY A D S, ALVES R M B, HEWER T L R, et al. Catalysts for glycerol hydrogenolysis to 1, 3-propanediol: A review of chemical routes and market[J]. *Catal Today*, 2021, 381: 243–253.
- [73] MIAO G, SHI L, ZHOU Z-M, et al. Catalyst design for selective hydrodeoxygenation of glycerol to 1, 3-propanediol[J]. *ACS Catal*, 2020, 10(24): 15217–15226.
- [74] WANG J, YANG M, WANG A-Q, Selective hydrogenolysis of glycerol to 1, 3-propanediol over Pt-W based catalysts[J]. *Chin J Catal*, 2020, 41: 1311–1319.
- [75] ZHANG D-P, LIU T, ZHOU Z-Q, et al. Revealing alternative mechanism for H-spillover and C–O bond cleavage reactions over interfacial Pt-WO_x catalysts during glycerol hydrogenolysis[J]. *Chem Eng Sci*, 2025, 310: 121521.
- [76] YU F, NIU B-B, ZHAO Y, et al. Promoting role of oxygen deficiency on a WO₃-supported Pt catalyst for glycerol hydrogenolysis to 1, 3-propanediol[J]. *Ind Eng Chem Res*, 2020, 59(16): 7389–7397.
- [77] CHEN J-H, HUANG H, PAN H, et al. Synchronizing deoxygenation and hydrogenation to effect glycerol hydrogenolysis over Pt/Nb₂W₁₅O₅₀ at low H₂ pressure[J]. *ACS Sustainable Chem Eng*, 2024, 12(16): 6242–6251.
- [78] ZHAO B-B, LIANG Y, LIU L, et al. Facilitating Pt-WO_x species interaction for efficient glycerol hydrogenolysis to 1, 3-propanediol[J]. *ChemCatChem*, 2021, 13: 3695–3705.
- [79] ZHAO B-B, ZOU J-Q, CHEN C, et al. Single tungsten atom-modified Pt/Al₂O₃ to boost glycerol hydrogenolysis to 1, 3-propanediol[J]. *Chem Eng J*, 2023, 478: 147396.
- [80] LI Y, ZHANG J, MENG H, et al. A significant enhancement for hydrogenolysis of glycerol to 1, 3-propanediol over Pt/W-SiO₂ catalyst by tungsten oxide and silica interaction[J]. *Appl Catal B: Environ*, 2025, 360: 124524.
- [81] EQI M, YANG Y-Q, WU G-J, et al. Oxygen vacancy engineering on Pt/WO_x/Nb₂O₅ catalysts toward efficient 1, 3-propanediol production from glycerol hydrogenolysis[J]. *ACS Catal*, 2025, 15(6): 5142–5154.
- [82] CHEN J-H, WANG M-M, ZHANG S-D, et al. High performance Pt/Nb₂W₃O₁₄ catalyst for glycerol valorization to 1, 3-propanediol[J]. *Chem Eng J*, 2024, 486: 150327.
- [83] SHAIKH R R, DAMRUANG S, KHAN R A, et al. Understanding the catalytic performance and deactivation behaviour of second-promoter doped Pt/WO_x/γ-Al₂O₃ catalysts in the glycerol hydrogenolysis for selective and cleaner production of 1, 3-propanediol[J]. *J Energy Chem*, 2024, 94: 486–507.
- [84] LEI N, MIAO Z-L, LIU F, et al. Understanding the deactivation behavior of Pt/WO₃/Al₂O₃ catalyst in the glycerol hydrogenolysis reaction[J]. *Chin J Catal*, 2020, 41(8): 1261–1267.
- [85] LIU L-J, ASANO T, NAKAGAWA Y, et al. Selective hydrogenolysis of glycerol to 1, 3-propanediol over rhenium-oxide-modified iridium nanoparticles coating rutile titania support[J]. *ACS Catal*, 2019, 9(12): 10913–10930.
- [86] CHANKLANG S, MONDACH W, SOMCHUEA P, et al. Hydrogenolysis of glycerol to 1, 3-propanediol over H-ZSM-5-supported iridium and rhenium oxide catalysts[J]. *Catal Today*, 2022, 397–399: 356–364.
- [87] ZHU S-H, ZHU Y-L, HAO S-L, et al. One-step hydrogenolysis of glycerol to biopropanols over Pt-H₄SiW₁₂O₄₀/ZrO₂ catalysts[J]. *Green Chem*, 2012, 14: 2607–2616.
- [88] LI C, HE B, LING Y, et al. Glycerol hydrogenolysis to *n*-propanol over Zr-Al composite oxide-supported Pt catalysts[J]. *Chin J Catal*, 2018, 39: 1121–1128.
- [89] WANG M-P, YANG H-M, XIE Y-Z, et al. Catalytic transformation of glycerol to 1-propanol by combining zirconium phosphate and supported Ru catalysts[J]. *RSC Adv*, 2016, 6: 29769–29778.
- [90] LUO R-H, ZHAO X-G, GONG H-H, et al. Effect of tungsten modification on zirconium phosphate-supported Pt catalyst for selective hydrogenolysis of glycerol to 1-propanol[J]. *Energy Fuels*, 2020, 34: 8707–8717.
- [91] BHANUCHANDER P, PRIYA S S, KUMAR V P, et al. Direct hydrogenolysis of glycerol to biopropanols over metal phosphate supported platinum catalysts[J]. *Catal Lett*, 2017, 147: 845–855.
- [92] SAMUDRALA S P, BHATYACHARYA S. Toward the sustainable synthesis of propanols from renewable glycerol over MoO₃-Al₂O₃ supported palladium catalysts[J]. *Catalysts*, 2018, 8: 385.
- [93] RYNEVELD E, MAHOMED A S, HEERDEN P S & FRIEDRICH H B. Direct hydrogenolysis of highly concentrated glycerol solutions over supported Ru, Pd and Pt catalyst systems[J]. *Catal Lett*, 2011, 141: 958–967.
- [94] GANDARIAS I, ARIAS P L, REQUIES J, et al. Liquid-phase glycerol hydrogenolysis to 1, 2-propanediol under nitrogen pressure using 2-propanol as hydrogen source[J]. *J Catal*, 2011, 282(1): 237–247.
- [95] GATTI M N, MIZRAHI M D, RAMALLO-LOPEZ J M, et al. Ni-supported catalysts on mesoporous carbon modified

- by $\text{Al}(\text{H}_2\text{PO}_4)_3$ to obtain 1-propanol[J]. Catal Today, 2021, 372: 136–145.
- [96] LIN X-F, LV Y-H, XI A-Y, et al. Hydrogenolysis of glycerol by the combined use of zeolite and $\text{Ni}/\text{Al}_2\text{O}_3$ as catalysts: A route for achieving high selectivity to 1-propanol[J]. Energy Fuels, 2014, 28(5): 3345–3351.
- [97] SOLOS T, METHIRITTHIKUL N, HOMLA-OR C, et al. Direct conversion of glycerol to n-propanol over a tandem catalytic dehydration-hydrogenation system[J]. Catal Sci Technol, 2022, 12: 5053–5066.
- [98] FOIKARD A L, FARAHANI D M D, MAHOMED D A S, et al. Sustainable selective propanol production via continuous flow conversion of glycerol over synergistic bifunctional catalysts: An exploration into factors affecting activity[J]. ChemCatChem, 2022, 14: e202200602.
- [99] ZHOU W-G, WNAG Z, LONG J-R, et al. Enhancing glycerol hydrogenolysis to n-propanol: Key role of Lewis acid in HZSM-5 supported Cu catalyst[J]. Bioresour Technol, 2025, 417: 131879.
- [100] ZAKEM G, CHRISTOPHER P. Active site entropy of atomically dispersed $\text{Rh}/\text{Al}_2\text{O}_3$ catalysts dictates activity for ethylene hydroformylation[J]. ACS Catal, 2023, 13(8): 5502–5515.
- [101] CHEW A, WAILKER T, SHEN Z, et al. Effect of mixed-solvent environments on the selectivity of acid-catalyzed dehydration reactions[J]. ACS Catal, 2020, 10: 1679–1691.
- [102] OTOMO R, YAMAGUCHI C, IWASAKO D, et al. Selective dehydration of 1, 2-propanediol to propanal over boron phosphate catalyst in the presence of steam[J]. ACS Sustainable Chem Eng, 2019, 7: 3027–3033.
- [103] DOSTERT K-H, O'BRIEN C P, MIRABELLA F, et al. Selective partial hydrogenation of acrolein on Pd: A mechanistic study[J]. ACS Catal, 2017, 7(8): 5523–5533.
- [104] GONG H, ZHOU C, CUI Y, et al. Direct transformation of glycerol to propanal using zirconium phosphate-supported bimetallic catalysts[J]. ChemSusChem, 2020, 13: 4954–4966.
- [105] WAN W, AMMAL S, LIN Z, et al. Controlling reaction pathways of selective C–O bond cleavage of glycerol[J]. Nat Commun, 2018, 9: 4612.

甘油氢解制备 C3 含氧化化学品的研究进展

毛红宇, 王 飞, 贡红辉*

(河南理工大学化学化工学院 河南省煤炭绿色转化重点实验室, 河南 焦作 454003)

摘 要: 生物柴油产业的快速发展对实现“双碳”目标、推进能源结构转型具有重要的科学意义, 但副产物甘油过剩限制了生物柴油产业的进一步发展。因此, 将副产物甘油进行绿色转化有利于生物柴油产业的良性发展。由甘油氢解制备 C3 含氧化化学品是甘油绿色转化研究中最具应用前景的途径之一。本工作介绍了甘油化学及氢解反应机理, 重点综述了近年来甘油氢解制备 1,2-丙二醇、1,3-丙二醇、正丙醇和丙醛等高值 C3 含氧化化学品催化剂的研究进展, 并展望了甘油氢解反应未来发展的方向与趋势。

关键词: 甘油; 氢解; C3 含氧化化学品; 生物质

中图分类号: TQ032.4

文献标识码: A

作者简介:



毛红宇(2002), 硕士, 研究方向为杂原子掺杂炭载过渡金属催化材料可控制备及可再生生物质催化转化, m15511823133@163.com。



贡红辉(1992), 博士, 研究生导师, 研究方向为杂原子掺杂炭载过渡金属催化材料可控制备、二氧化碳与生物质碳资源催化转化及有机含氮化合物的催化合成, gonghonghui@hpu.edu.cn。