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Review Article

Harnessing Copper's Potential: A Review of Cu-Based Catalysts for Glycerol Conversion

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Abstract

The increasing depletion of fossil fuel reserves and environmental concerns have accelerated the search for sustainable alternatives, leading to the utilization of biodiesel as a renewable energy source. Glycerol, a key byproduct of biodiesel production, has been extensively investigated for conversion into value-added compounds such as lactic acid, acrylic acid, and 1,2-propanediol (1,2-PDO). Copper-based catalysts have gained popularity due to their low cost, high catalytic efficiency, and environmental friendliness. This review examines various copper-based catalytic systems for glycerol conversion through key processes such as hydrogenolysis, oxidation, steam reforming, and dehydration. The work focuses on how Cu-based bimetallic catalysts, such as Cu-Ni, Cu-Co, and Cu-Zn, improve reaction selectivity and conversion rates via synergistic interactions, better metal dispersion, and optimized redox properties. Furthermore, new catalyst manufacturing methods, such as ammonia evaporation, hydrothermal, and ion exchange approaches, have shown improved stability and reusability. The findings show that Cu-based catalysts successfully facilitate high glycerol conversion, with selective pathways favouring the generation of 1,2-PDO, lactic acid, and acrylic acid under optimal circumstances. However, catalyst deactivation caused by sintering and coke formation remains a concern. Future research should concentrate on creating stable, multifunctional catalysts, adding bio-derived support, and improving reaction conditions to increase long-term efficiency and industrial usability. This review emphasizes the potential of Cu-based catalytic systems in promoting glycerol valorisation and achieving a more sustainable chemical industry.

Keywords: copper-based catalysts; glycerol conversion; oxidation; oxidehydration; hydrogenolysis

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1. Introduction

Fossil fuels, the backbone of our global energy supply, are being depleted at an alarming rate. The overreliance on these non-renewable energy sources not only emptying our finest resources but also intensifying percentage of the greenhouse gases in our atmosphere [1]. To cope with this problem, scientists began working on the development of renewable and environmentally friendly fuels, leading to biodiesel synthesis through the esterification of vegetable oils and animal fats, among other sources [2,3].

Glycerol is generated as a major byproduct during biodiesel synthesis [4]. Glycerol is produced in substantial quantities, resulting in an annual surplus that far exceeds its demand, leading to its categorization as waste. Researchers are diligently exploring methods for catalytic glycerol conversion into valuable products. Various processes, like: oxidation [5], steam reforming [6], hydrogenolysis [7], and dehydration

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[8], are employed under specific conditions to transform glycerol into useful substances. These products include lactic acid, acrolein, glycolic acid, acrylic acid and 1,2-propanediol, which are all obtained through glycerol conversion. Among these, 1,2-propanediol, lactic acid, and acrylic acid hold particular importance.

Lactic acid serves as a vital fine chemical with diverse applications across a range of industries, including cosmetics, agriculture, and the food sector. In future lactic acid can be the precursor for a large variety of compounds. Commercially lactic acid is obtained from fermentation of carbohydrates but due to low efficiency and other limitations, it's necessary to synthesize other means for its production [9,10]. Because of that glycerol conversion to lactic acid holds important values. The catalytic conversion of glycerol to lactic acid has seen the application of various metal-based heterogeneous catalysts, including cobalt [11], nickel [12], platinum [13], palladium [14], and copper [15,16]. Among these, Cu-based catalysts have garnered particular attention due to their high catalytic activity, environmental friendliness, stability and cost-effectiveness.

Glycerol can be converted into lactic acid through different methods like hydrothermal conversion, hydrogenolysis, biomass conversion and selective oxidation reaction. For example, Conversion of glycerol through hydrothermal method using Cu/hydroxyapatite (HAP) [17], through hydrogenolysis using-Ni/MgO [18], and through oxidation using Cu-ZnO@C [19] as a catalyst gave nearly 90%, 50%, and 83.2% selectivity for lactic acid.

1,2-propandiol (1,2-PDO) is one of the most important products obtained by the glycerol conversion [20]. From an industrial perspective, 1,2-PDO holds significant value as a precursor to various useful products such as polyester resins, paints, adhesives and plays an important role in the pharmaceutical, cosmetics and food industries. Traditionally, 1,2-PDO is produced industrially by hydrating propylene oxide, which is derived from propylene through various process [21]. To reduce reliance on petrochemicals, a renewable approach to 1,2-PDO production, through glycerol conversion, is highly desirable.

On the other hand, acrylic acid has diverse applications in the chemical industry and serves as a raw material to produce resins, plastics, synthetic rubber, detergents, and more. Conventionally, acrylic acid is synthesized from propene through gas-phase oxidation, with acrolein as an intermediate [22]. Through this process in 2012 the production of acrylic acid was 4.5 million tons with increasing demand of 4% per year [23]. Since propene is obtained from fossil fuels, developing a renewable source for acrylic acid production, such as glycerol conversion, is essential to address sustainability concerns.

The conversion of glycerol to acrylic acid typically occurs through a dehydration reaction followed by an oxidation reaction, using a mild acidic catalyst [24]. This is a two-step reaction that can follow different pathways. In one common approach, glycerol is first dehydrated to acrolein, which acts as an intermediate. This dehydration step is usually catalyzed by acidic catalysts like zeolites and silicates and is considered the rate-determining step. However, catalyst deactivation through coke formation may occur at this stage. Following dehydration, acrolein is then oxidized to acrylic acid using various redox catalysts [25]. This step is crucial, as complete dehydration followed by selective oxidation of acrolein or allyl alcohol can produce high acrylic acid yields under controlled conditions. Nevertheless, this process presents certain limitations, such as a slow reaction rate and low selectivity for acrylic acid, which reduces its economic viability [26].

In the second type of reaction, dehydration and oxidation occur within a single reactor, a process known as oxidative dehydration or oxidehydration [27]. This reaction requires a bifunctional catalyst capable of both dehydrating and oxidizing the substrate. This method is particularly important for converting glycerol to acrylic acid, as it offers thermal stability by allowing both endothermic and exothermic reactions to occur simultaneously. Additionally, the presence of both acidic and oxidizing sites helps eliminate unwanted by-products [28]. The single-pot synthesis approach is attracting considerable research interest due to its environmental friendliness and the economic advantage provided by a multifunctional catalyst that facilitates both dehydration and oxidation in one step. However, challenges remain, such as optimizing selectivity for acrylic acid and designing conditions that support both reactions concurrently to achieve high yields.

Copper-based catalysts are commonly used for the single-step synthesis of acrylic acid from glycerol. Copper is often impregnated onto supports like zeolites or silicates, creating a bifunctional catalyst for this process. Chao Peng Fu [29] employed a Cu-based catalyst in his experiment, specifically using a Cu_2O/montmorillonite catalyst without additional oxygen or hydrogen. At 150 °C, a maximum glycerol conversion of 63% was achieved, with an acrylic acid selectivity of 49% and a 1,2-PDO selectivity of 17%. Under optimized conditions, complete glycerol conversion was achieved with 72% selectivity for acrylic acid and 10% selectivity for 1,2-PDO.

To conclude this, glycerol conversion represents a significant approach for producing valuable chemicals such as acrylic acid, lactic acid, glycolic acid, and 1,2-PDO through processes like hydrogenolysis, dehydration, oxidation, and steam reforming (Figure 1). This review will examine various methods for glycerol conversion using Cu-based catalysts, with a primary focus on the production of acrylic acid, 1,2-PDO and lactic acid. For this review, Scopus, ScienceDirect, ProQuest, Taylor and Francis and google scholar are used for data collection. Only original research articles with open access, were in English and uses copper-based catalyst for glycerol conversion were added in this review.

2. Glycerol Conversion

Glycerol can be converted into valuable chemicals through various chemical processes, including hydrogenolysis, oxidation, steam reforming, etherification, and dehydration. Each method, when applied under specific conditions, yields different products, such as 1,3-propanediol, lactic acid, acrolein, 1,2-propanediol, acrylic acid, glyceraldehyde, and glycerol acetate. Here, we focus on methods utilizing Cu-based catalysts.

2.1 Hydrogenolysis

Bond breakage in a molecule due to the addition of hydrogen is known as hydrogenolysis. The hydrogenolysis of glycerol yields an important product: propane-1,2-diol, acetol, ethanediol etc. Among them the most important is propane-1,2-diol. Although hydrogenolysis of glycerol can follow different routes, the most common involves dehydration followed by hydrogenation. This process has two steps: first, glycerol undergoes acid-catalyzed dehydration to form an intermediate; in the next step, the intermediate is hydrogenated in the presence of a metal-based catalyst. Therefore, a bifunctional catalyst is needed for this reaction [31]. However, coke deposition is still a major concern in this reaction and occurs through a multi-step mechanism influenced by temperature, catalyst composition, and reaction conditions. It involves the decomposition and polymerization of carbonaceous species, leading to different types of coke deposits. Type I coke is an amorphous deposit formed on metal active sites while type II coke accumulates at the metal-support interface whereas type III coke is a highly refractory form deposited on the support. Coke formation results in catalyst deactivation by blocking active sites, reducing efficiency, and altering catalytic selectivity [32].

2.1.1 Copper supported on alumina

Various metal-based catalysts exhibit catalytic activity, but Cu-based catalysts

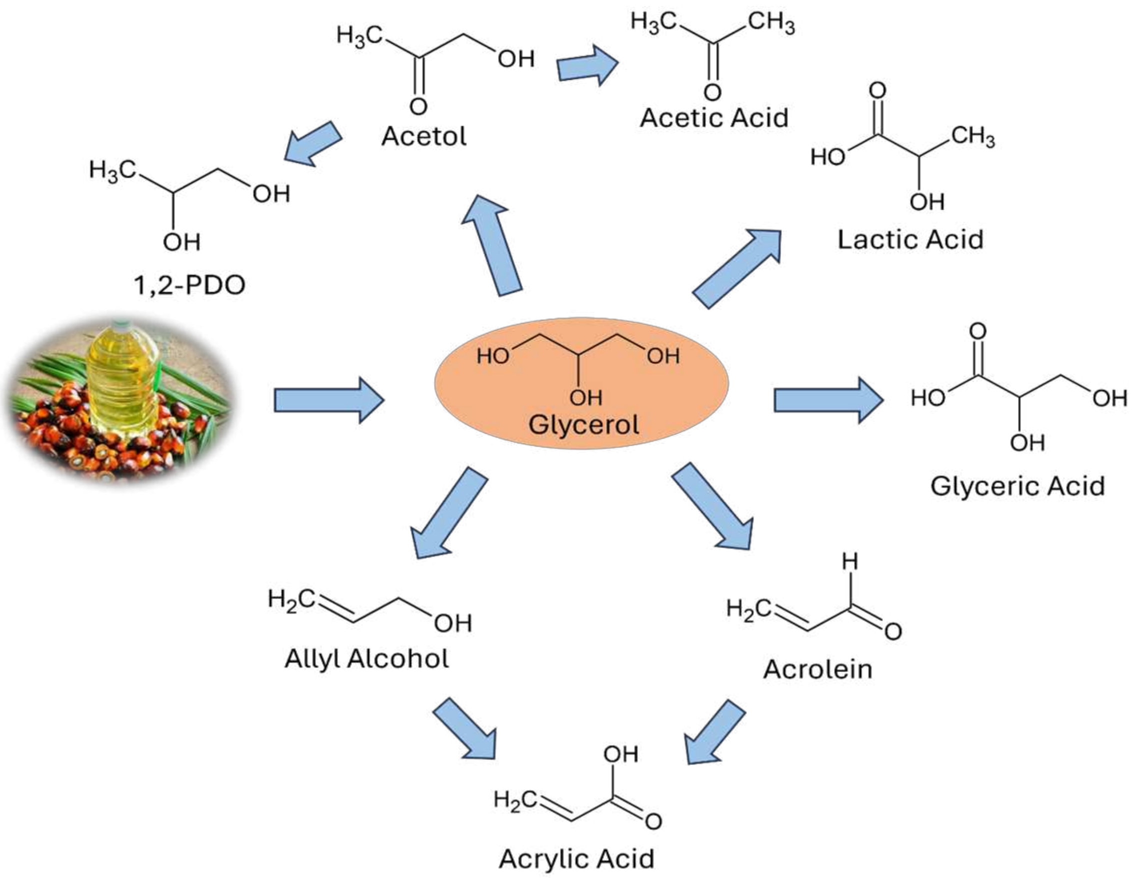


Figure 1. Various products derived from the conversion of glycerol, a byproduct of palm oil processing [30].

demonstrate both high stability and effectiveness for glycerol conversion via hydrogenation [33]. Jinxia Zhou and colleagues studied glycerol hydrogenolysis into propanediol using copper based bimetallic catalysts on different supports [34]. The incipient wetness impregnation method was used to synthesize bimetallic catalysts of Cu-Zn, Cu-Ag, Cu-Cr over Al_2O_3 and different supports. Among various combinations, Cu-Ag/Al_2O_3 catalysts, demonstrated superior activity, achieving 27% glycerol conversion with nearly 100% selectivity to propanediols at 200 °C and 1.5 MPa initial H_2 pressure. Characterization using XRD, TPR, and XPS confirmed that Ag played a crucial role in promoting the in-situ reduction of CuO to catalytically active Cu species, while also improving Cu dispersion. This synergistic interaction between Cu and Ag not only enhanced catalytic performance without requiring a reduction pretreatment but also maintained excellent selectivity to 1,2-propanediol (1,2-PDO), suppressing side reactions leading to undesired by-products. The catalytic performance of Cu-Ag/Al_2O_3 compared to other bimetallic and monometallic catalysts is further illustrated in Figure 2, which presents glycerol conversion and product selectivity for 1,2-PDO, 1,3-propanediol (1,3-PDO), and other by-products. As shown in the figure, Cu-Ag/Al_2O_3 not only delivered the highest glycerol conversion but also maintained nearly complete selectivity for 1,2-PDO, outperforming other catalysts such as Cu-Zn/Al_2O_3, Cu-Cr/Al_2O_3, and Ag/Al_2O_3. This highlights the superior ability of Cu-Ag/Al_2O_3 to guide the reaction pathway toward the desired 1,2-PDO product while minimizing unwanted side products. In contrast, catalysts supported on HY and Hb zeolites displayed lower glycerol conversion and higher by-product formation, emphasizing that the Al_2O_3 support offers optimal acidity and metal dispersion for selective hydrogenolysis.

Coke formation was minimal on Cu-Ag/Al_2O_3, supported by the high selectivity to propanediols and the suppression of over-dehydration and polymerization pathways that typically lead to carbon deposition. Strong Cu-Ag interactions and well-dispersed active sites helped maintain catalyst stability, while only slight Cu agglomeration was observed after extended operation. Catalytic regeneration through oxidative treatment successfully removed surface carbon residues, restoring activity and ensuring good long-term reusability.

Daolai Sun and colleagues [35] investigated Ag-modified Cu/Al_2O_3 catalysts for vapor-phase hydrogenolysis of glycerol to 1,2-propanediol (1,2-PDO) under ambient hydrogen pressure. Ag incorporation inhibited ethylene glycol formation while enhancing 1,2-PDO yield, with 1 wt.% Ag providing the best balance between selectivity and hydrogenation activity. XRD and TPR analyses confirmed strong Cu–Ag interactions, which improved catalytic efficiency and reduced unwanted C–C cleavage. The highest performance was achieved using a dual-layer catalyst bed, where Ag–Cu/Al_2O_3 in the upper layer suppressed ethylene glycol formation, while Cu/Al_2O_3 in the lower layer promoted hydrogenation to 1,2-PDO, yielding 98.3% at 170–105 °C. Coke formation was identified as a potential cause of catalyst deactivation, occurring due to the polymerization and condensation of glycerol intermediates, particularly hydroxyacetone (HA), at high

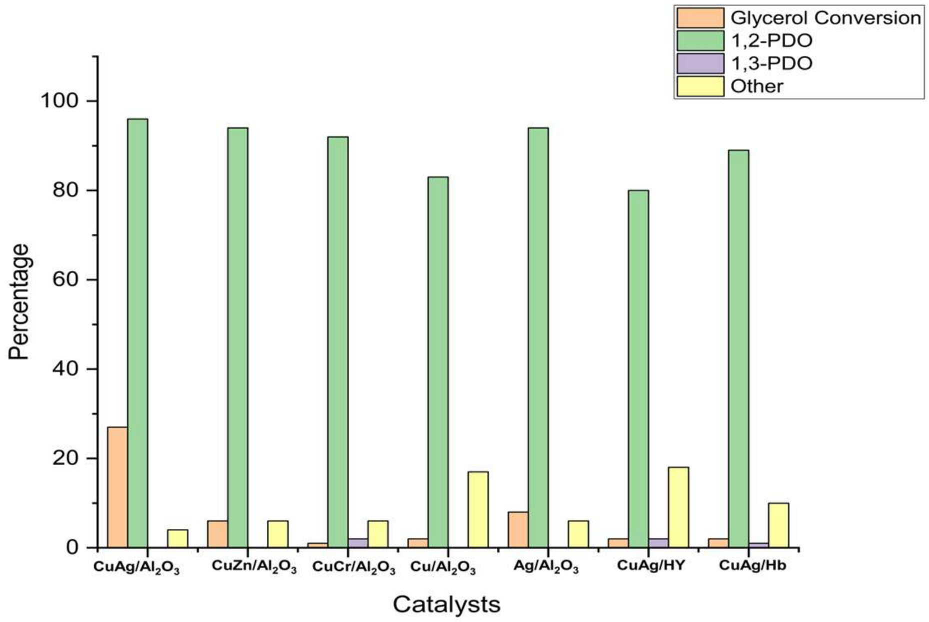


Figure 2. Glycerol hydrogenolysis using bimetallic copper-based catalysts supported on different supports [34].

temperatures. These carbonaceous deposits blocked active sites, reducing hydrogenation efficiency. However, Ag incorporation mitigated excessive coke formation by modifying Cu's electronic properties, which suppressed unwanted side reactions leading to carbon deposition. Additionally, the optimized reaction temperature gradient prevented glycerol over-dehydration, further minimizing coke accumulation. To counteract deactivation, catalytic regeneration was performed through thermal treatment and hydrogen reduction, effectively removing surface-adsorbed carbon species and restoring activity without significant structural degradation [35].

F. Vila and colleagues tried to increase the glycerol conversion and selectivity for 1,2-propanediol using Cu/γ-Al_2O_3 applying different activation techniques [36]. Reduction of catalyst in H_2/Ar increases the Cu°/Cu^{+} and this increases the glycerol conversion as well as selectivity for propanediol. On the other hand, calcination increases the surface Cu^{+2} decreasing the activity of catalyst. While reoxidation also increases the glycerol conversion but not much effect on selectivity. This shows the importance of surface species for effective selectivity and glycerol conversion.

Pussana Hirunsit and coworkers used DFT as well as experimental data to understand the effect of hydroxylation of alumina on glycerol conversion and selectivity towards 1,2-PDO [37]. The results demonstrated that Cu/Al_2O_3 exhibited high catalytic activity and selectivity for 1,2-PDO, with alumina hydroxylation playing a crucial role in modifying the electronic and acidic properties of the support. DFT calculations confirmed that hydroxylated alumina facilitated glycerol adsorption and reduced the activation energy for O–H bond cleavage, improving catalytic performance compared to non-hydroxylated alumina. However, excessive water content in the reaction medium was found to deactivate the catalyst by reducing the number of active acidic sites on alumina, which affected overall reactivity. Coke formation was relatively low, as the optimized Cu–Al interface prevented excessive polymerization of glycerol intermediates. Catalytic regeneration via oxidative treatment successfully restored activity by removing residual carbon deposits, further confirming the stability and reusability of Cu/Al_2O_3 for sustainable glycerol hydrogenolysis.

2.1.2 Copper supported on silica

Glycerol conversion was studied both in gas as well as in liquid phase by A. Bienholz [38] using Cu/SiO_2 catalyst. Their results indicated that 1,2-propanediol (1,2-PDO) was the predominant product in both stages. The maximum glycerol conversion in the liquid phase was 52%, with a remarkable 98% selectivity for 1,2-PDO using a CuO-ZnO (60:40) catalyst. In contrast, gas-phase hydrogenolysis achieved maximum glycerol conversion, although with exceptionally low selectivity for 1,2-PDO and high for acetol. To elucidate the influence of CuO concentration, a range of Cu-based catalysts with diverse metal oxide compositions were produced and evaluated in the liquid phase. The catalyst comprising 60% CuO and 40% ZnO surpassed others, yielding excellent conversion and selectivity due to highest Copper surface area. Conversely, other formulations, including CuO [40], ZnO [40] Al_2O_3 [20], and CuO [36], ZnO [48], Al_2O_3 [16], had markedly lower conversions of 10% and 17%, respectively as shown in Figure 3.

s-phase reaction

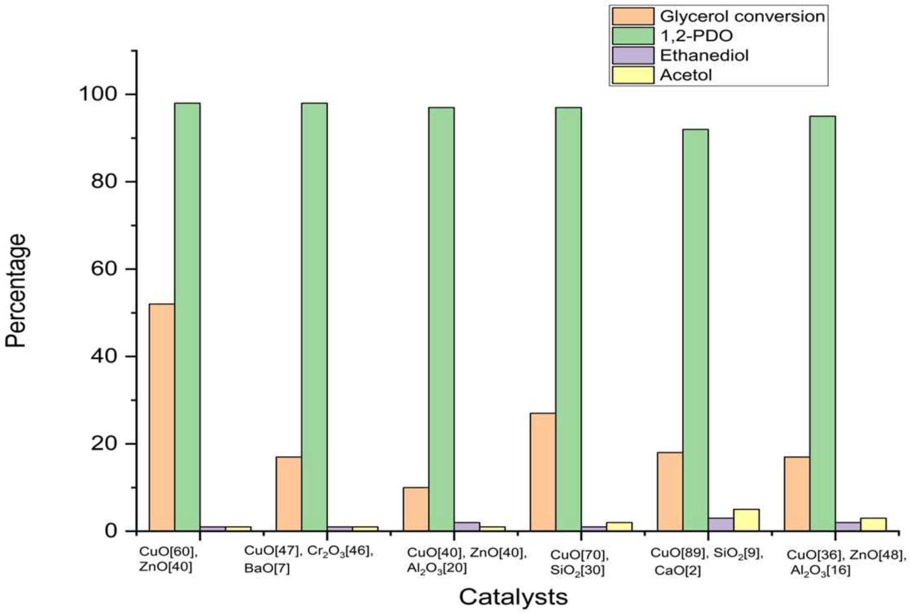


Figure 3. Hydrogenolysis of glycerol in liquid phase using catalysts with different concentrations of CuO [38].

were synthesized using both ion exchange (I.E.) and incipient wetness (I.W.) techniques, with differing Cu concentrations. The maximum conversion rate of 92% was achieved with Cu/SiO_2-I.E-0.05, where acetol was the predominant product, exhibiting a selectivity of 69% and only 20% for 1,2-PDO. The Cu/SiO_2-I.E-0.2 catalyst exhibited comparable acetol selectivity with a somewhat decreased conversion rate of 87%. This maximum conversion of glycerol is achieved in case of ion exchange synthesis is because of greater specific copper surface area compared to those catalysts produced by incipient wetness impregnation. Conversely, catalysts produced by the I.W. approach showed reduced glycerol conversion while exhibiting enhanced acetol selectivity. The 10Cu/SiO_2-IW catalyst shown superior performance in this category, but the 20Cu/SiO_2-IW-400 catalyst had an 82% selectivity for acetol, accompanied by a mere 27% conversion of glycerol as shown in Figure 4.

Leaching of Cu in Cu/SiO_2 was one of the major concerns in hydrogenation of glycerol. To decrease this Zhiwei Huang [39] prepared different catalysts with varying sodium content. Huang observed that having high Na content in the catalyst decreased BET surface area, Cu dispersion, and reducibility, negatively impacting activity. On the other hand, having a small amount of sodium in the catalyst acted as a base, enhancing conversion but also affecting selectivity by promoting ethylene glycol formation. Although the leaching and deactivation of catalysts is decreased but production of side products is still of a greater concern [39].

Shanhui Zhu [40] overcome these defects by synthesizing Cu/SiO_2 using ammonia evaporation hydrothermal (AEH) method. Compared to Cu/SiO_2 prepared by impregnation (IM), the AEH catalyst exhibited superior catalytic performance and long-term stability due to strong Cu–SiO_2 interactions derived from a copper phyllosilicate precursor. Structural characterization via XRD, TEM, and XPS confirmed well-dispersed Cu nanoparticles with cooperative Cu^0 and Cu^+ species, which played a crucial role in selective C–O bond hydrogenolysis while minimizing C–C cleavage. The optimized 25Cu/SiO_2-AEH catalyst achieved 100% glycerol conversion with 98.3% selectivity to 1,2-PDO, significantly outperforming the IM counterpart. Coke formation, a common deactivation factor in glycerol hydrogenolysis, was minimal due to the well-dispersed Cu species preventing excessive polymerization of intermediates. However, catalyst deactivation over extended operation was primarily caused by Cu nanoparticle sintering rather than coke deposition, as confirmed by TEM and TG analyses. The AEH-prepared Cu/SiO_2 catalyst maintained excellent stability over 300 hours of continuous reaction, whereas the IM-prepared catalyst deactivated within 30 hours due to severe Cu agglomeration. Catalytic regeneration through thermal treatment effectively restored activity by redistributing Cu species and eliminating surface carbon residues [40].

2.1.3 Copper supported on dolomite (Cu/dol)

In another study, Norsahida Azri and colleges [41] studied the impact of different supports on Cu- based catalyst for hydrogenolysis of glycerol to propane-1,2-diol. They synthesized different

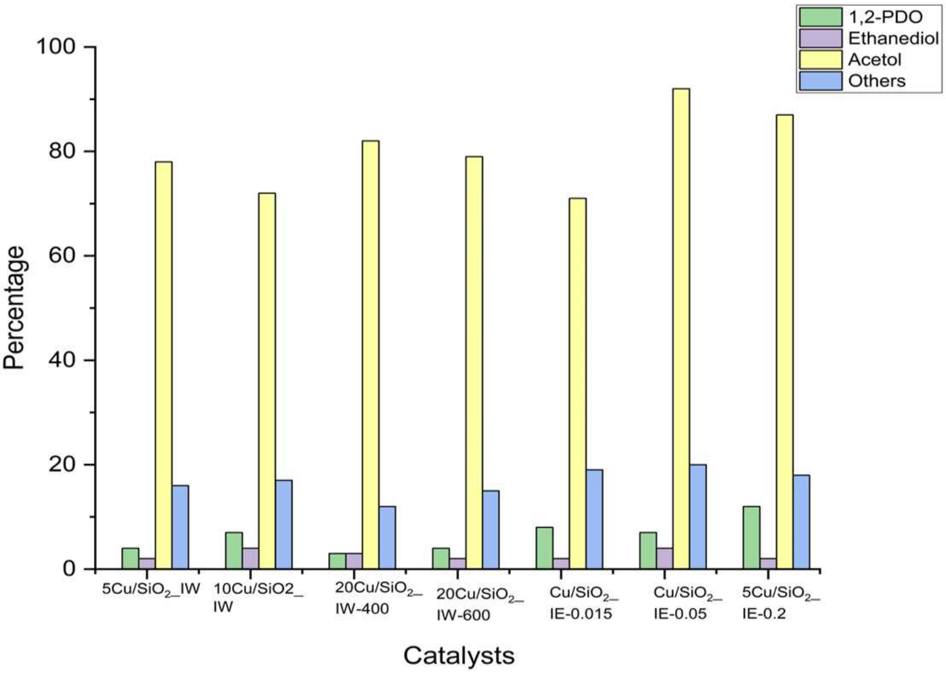


Figure 4. Hydrogenolysis of glycerol in vapor state using catalyst synthesized using different methods as well as different concentration of copper [38].

catalysts with 20% Cu loading on dolomite, alumina, bentonite, montmorillonite and talc using wet impregnation method. The results obtained are shown in Figure 5.

It can be observed that alone copper cannot hydrogenolyses the glycerol to 1,2-propandiol while introducing the support not only increases the glycerol conversion but also elevated the selectivity for desired products. Among supports, Cu/Dol catalyst demonstrated superior activity and 1,2-PDO selectivity owing to its higher surface acidity, which offered many acid sites for glycerol dehydration, and its efficient copper dispersion, enabling active metallic sites at reduced temperatures (291 °C). Cu/Al_2O_3 exhibited notable selectivity attributed to its comparable reducibility and reduced Cu particle size. In contrast, Cu/Bent, Cu/Mont, and Cu/Talc exhibited worse performance owing to their elevated metal reduction temperatures (≥313 °C), which suggest less stable metallic states and bigger Cu particles, resulting in less hydrogenation activity and 1,2-PDO selectivity [41].

To increase the conversion and selectivity, Azri and colleagues also used dolomite supported bimetallic catalysts Cu-Co/dol [42]. Individually Cu/dol showed 78.5% conversion with 79% selectivity, while the Co/dol catalyst had a lower 60.9% conversion and 58.1% selectivity. On the other hand, bimetallic catalysts exhibited the highest glycerol conversion (80.3%) and 1,2-PDO selectivity (85.9%). It was because bimetallic catalyst had a higher surface area (15.3 m^2/g) than monometallic catalysts and interaction between Co and Cu species on dolomite enhanced metal reducibility, acidity, and catalytic activity. Coke deposition was significantly reduced due to the robust metal-support interactions, which limited unwanted polymerization of reaction intermediates. Despite this, prolonged use led to a gradual decline in catalytic performance, primarily due to metal sintering and slight pore blockage. To counteract deactivation, catalytic regeneration via oxidative treatment successfully removed carbon deposits and redistributed active metal species, restoring the catalyst's efficiency across multiple cycles [42].

2.1.4 Copper supported on zeolites

Jianbin Huang and colleagues [7] demonstrated the use of copper supported on pure silica beta zeolites for the conversion of glycerol. The catalyst, produced by a hydrothermal technique using Si-beta zeolites, enabled the dispersion of copper nanoparticles. The reaction pathway starts with the dehydration of glycerol resulting in hydroxyacetone, which is further hydrogenated to generate 1,2-PDO. Copper nanoparticles and copper cations both facilitate the hydrogenation process. The process achieves a 96% conversion of glycerol with 99.9% selectivity for propane-1,2-diol. Although this method yields high selectivity, the dehydration reaction is relatively slow, limiting the overall reaction rate. Coke formation was observed over repeated cycles and attributed to the accumulation of carbonaceous species blocking active sites. However, strong metal-support interactions helped limit excessive coke buildup, maintaining catalytic efficiency. Stability tests showed that Cu/Si-Beta-HT maintained high activity across multiple cycles, with catalytic regeneration via oxidative treatment effectively restoring performance by removing coke deposits.

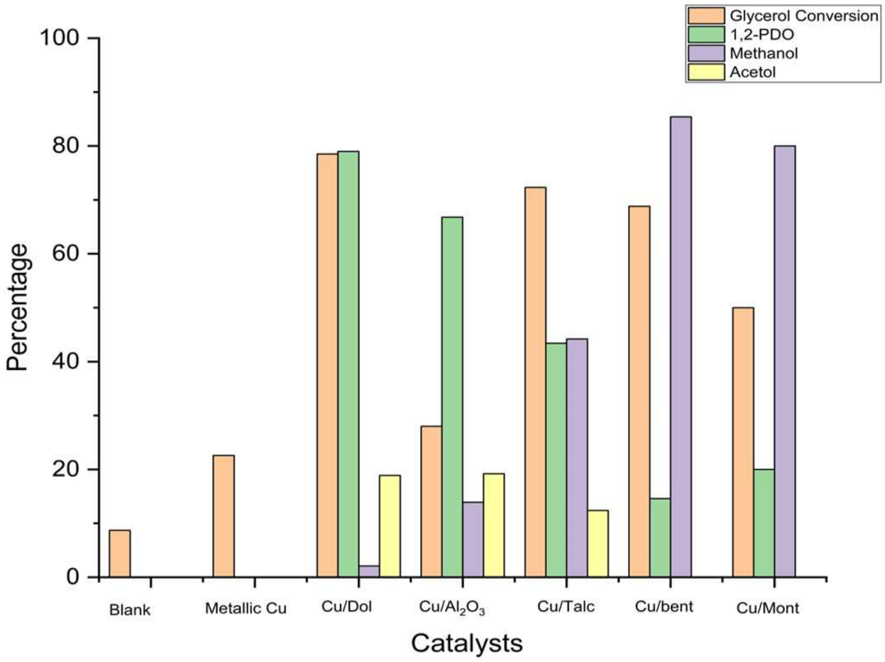


Figure 5. Glycerol hydrogenolysis using different support on copper catalysts [41].

Other than that, CuO on Y-zeolites was also used for glycerol conversion. A study by Harisekhar Mitta [43] showed that highly dispersed CuO on Y-zeolites exhibit glycerol conversion of 92% while 83% selectivity for 1,2-PDO. This was due to high Lewis's acidity and moderate Bronsted acidity which is essential for selective hydrogenolysis. Moderate loading is essential for obtaining high yield as higher Cu loading (>10 wt.%) led to lower dispersion, Cu agglomeration, and a decline in catalytic efficiency. To counteract this, catalytic regeneration via oxidative treatment followed by H_2 reduction effectively restored activity by eliminating carbon residues and redistributing Cu species [43].

Many researchers have investigated the glycerol conversion to 1,2-PDO using Cu on zeolites as shown in Table 1. Alone Cu on any zeolites gave very low glycerol conversion like Cu/SAPO-11 showed conversion of 45% while selectivity for 1,2-PDO of 65%. This increased to 93% and 97.7%, respectively, by the addition of Ni. This incorporation of Ni facilitates the formation of a highly dispersed Cu active phase, enhancing the performance of the bimetallic catalyst compared to its monometallic counterpart [44]. Likewise, Cu/Y-zeolites gave 12.6% selectivity for propanediol, but incorporation of Ni exhibit conversion of 96 % while selectivity increases to 44% [45]. But the results obtained using dealumination ultrastable Y-type zeolite (DUSY) showed high conversion of 78.7% as well as 98.6% selectivity for propanediol using only Cu. DUSY developed a substantial amount of secondary mesopores, which enhanced the diffusion of 1,2-propanediol (1,2-PDO) from the catalyst while also improving Cu dispersion. The Cu/DUSY catalyst featured isolated weak acid sites and a distinct reduced framework characteristic of Y-type zeolite, leading to a more selective product distribution, predominantly yielding 1,2-PDO [46].

The H-Beta zeolite exhibited greater Brønsted acidity and catalytic activity compared to metal-supported catalysts. The acidity of H-Beta and the presence of metal components were found to significantly influence the final product distribution. Bare H-Beta and Zr/H-Beta primarily yielded 1-propanol, whereas the addition of a Cu notably enhanced the production of 1,2-propanediol and 1,3-propanediol [47].

Si/Al ratio also influenced the selectivity as well as glycerol conversion in case of ZSM-5 support. Optimal Si/Al promotes the formation of 1,2-PDO but increasing the Si/Al ratio increases the acidity hence increases the glycerol hydrogenolysis, but the selectivity decreases for 1,2-PDO while increases for ethylene glycol and propanol [48].

2.1.5 Copper-Zinc based catalysts

Shan Liu [49] investigated the influence of Cu-based catalysts on glycerol hydrogenolysis, especially by synthesizing a copper-carbide composite catalyst in a microchannel reaction system adjusted for temperature and pressure, using ZnO as an acidic site. The conversion of glycerol was conducted in a fixed bed reactor, with ZnO promoting the dehydration process and CuXC (copper-carbide) catalyzing the hydrogenation process. Liu compared glycerol conversion rates and product selectivity using various Cu-based catalysts. The CuxC-Cu-ZnO catalyst achieved a 100% glycerol conversion with 92.3% selectivity for propane-1,2-diol, whereas using only Cu resulted in less than 10% glycerol conversion, primarily yielding acetol (Figure 6). The use of CuxC-Cu or Cu-ZnO alone was also less effective, yielding only 79.3% and 6.1% glycerol conversion, respectively, with significant amounts of acetol alongside propanediol. Liu concluded that the combination of copper carbide and ZnO is the most effective catalyst, as the carbon component enhances the stability of Cu, while ZnO accelerates the slower dehydration step.

Mzamo L. Shozi and colleagues [50] studied the effect of temperature change as well as Re metal incorporation in Cu/ZnO catalysts. It was

Table 1. Different copper based catalysts supported zeolites.

Catalysts	Methodology	Glycerol conversion %	1,2-PDO Selectivity%	References
Ni-Cu/NaY-Zeolites	Wet impregnation	96.4	44	[45]
Cu-Ni/SAPO 11 zeolite	Hydrothermal	93	97.7	[44]
6 wt% 15Cu/DUSY catalyst	coprecipitation	78.7	98.6	[46]
Cu-Zr/H-beta	sequential wetness impregnation	70	20	[47]
Cu/HZSM-5–23	incipient wetness impregnation	8	38	[48]

observed that Rhenium-containing catalysts showed higher activity due to their ability to increase surface acidity and enhance hydrogenolysis. At 150 °C, selectivity towards 1,2-propanediol (1,2-PDO) was highest while at higher temperatures (250 °C), C–C bond cleavage led to increased formation of methanol, ethanol, and 1-propanol. Coke formation was minimized due to the strong interaction between Cu, Re, and the ZnO support, which prevented excessive polymerization of reaction intermediates. However, prolonged operation led to minor catalyst deactivation, primarily due to metal sintering. Stability tests demonstrated that Cu–Re/ZnO maintained consistent activity and selectivity for at least 24 hours at 250 °C and 60 bar H_2 pressure. Catalytic regeneration via oxidative treatment successfully removed carbonaceous deposits, restoring catalyst performance [50]. The summery of all the catalysts showing best results for glycerol conversion to 1,2-PDO is shown in Table 2.

To maximize the yield of 1,2-propanediol (1,2-PDO) from glycerol hydrogenolysis, an optimal catalyst system should incorporate bimetallic Cu-based catalysts (e.g., Cu-Ag, Cu-Co, Cu-Ni) due to their enhanced H_2 activation, Cu dispersion, and catalytic stability. The choice of support significantly influences performance, with dolomite, SAPO-11, Al_2O_3, and Y-zeolites (Si/Al = 23-30) being the most effective in balancing acidity and metal-support interactions to facilitate selective hydrogenolysis. The preparation method also plays a crucial role, where ammonia evaporation hydrothermal (AEH) and ion exchange (I.E.) techniques have demonstrated superior Cu dispersion, prevented sintering, and enhanced stability. Reaction

Table 2. Summary of all supported Cu catalysts for maximum glycerol conversion to 1,2-propanediol.

Catalyst	Reaction conditions	Glycerol conversion (%)	1,2-PDO Selectivity (%)	References
Raney Cu	513 K	86	66	[51]
$CuAg/Al_2O_3$	473 K, Liquid phase	27	96	[34]
CuO-ZnO	Liquid phase	52	98	[38]
Cu/SiO_2-I. E	Vapor phase	92	20	[38]
Cu/dol	473 K, Liquid phase	78.5	79	[52]
Cn/Talc	473 K, Liquid phase	72.3	43.5	[41]
Cu_xC-Cu-ZnO	513 K, Liquid phase	100	90	[49]
Cu–STA/ Al_2O_3	513 K, Liquid phase	90	90	[53]
Cu–Al CAP(Na_2CO_3)	493 K	62	88	[54]

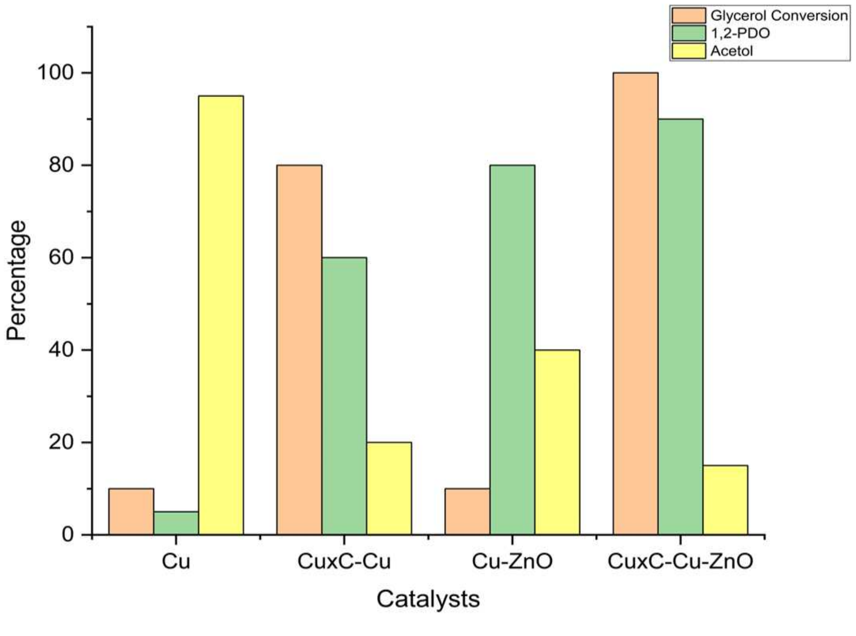


Figure 6. Glycerol conversion and selectivity for acetol and 1,2-PDO over copper carbide composite catalysts [49].

conditions must be optimized, with an ideal temperature range of 170 °C – 210 °C, a moderate H_2 pressure (H_2:glycerol = 700:1), and a dual-layered catalyst bed configuration (Cu-Ag/Al_2O_3 on top, Cu/Al_2O_3 on bottom), which has been shown to achieve 98.3% selectivity for 1,2-PDO by improving intermediate hydrogenation while minimizing side reactions. Despite these advancements, catalyst deactivation due to Cu sintering and coke deposition remains a major challenge, requiring further studies on hydrophobic-modified supports, operando catalyst monitoring, and regeneration techniques. Additionally, the transition from batch to continuous flow systems and the integration of AI-driven catalyst screening could further optimize reaction efficiency and scalability. Future research should focus on developing stable, water-tolerant catalysts, exploring solvent-free conditions, and leveraging bio-derived metal oxides to improve sustainability while maintaining high selectivity and conversion in large-scale 1,2-PDO production. The reactions for converting glycerol to produce 1,2-propanediol are illustrated in Scheme 1 and Scheme 2.

2.2 Oxidation

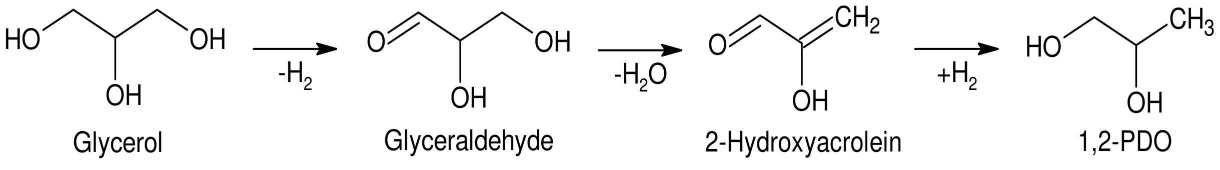
Oxidation of glycerol is an important method to synthesize industrial useful products such as glyceric acid, glycolic acid, lactic acid, dihydroxyacetone and tartronic acid. Traditionally, expensive metals, like Au [57], Pt [58], Pd [59], have been used for this process, though they are not economically viable. As a result, researchers are increasingly focusing on more cost-effective alternatives, particularly copper-based catalysts.

One of the major problems during oxidation of glycerol is catalytic deactivation due to coke formation. Coke formation is a multifaceted process influenced by thermal decomposition, polymerization, and condensation reactions. Initially, glycerol undergoes partial oxidation, forming oxygenated intermediates, such as aldehydes and organic acids, which can further polymerize and condense into carbonaceous coke deposits [50]. The mechanism involves the adsorption of these intermediates onto catalyst surfaces, where dehydrogenation and thermal cracking lead to the formation of unsaturated polyaromatic species, which progressively grow into graphitic carbon structures [19]. The extent and nature of coke deposition depend on reaction conditions, temperature, and catalyst composition. Several types of coke can form; catalytic coke, which accumulates on active sites, causing deactivation [60]; thermal coke, resulting from high-temperature pyrolysis; and filamentous coke, forming as carbon nanotube-like structures in the presence of metal catalysts [61]. Additionally, encapsulating coke covers catalyst particles, restricting accessibility to active sites, while amorphous coke deposits in a disordered manner, reducing catalyst efficiency [62].

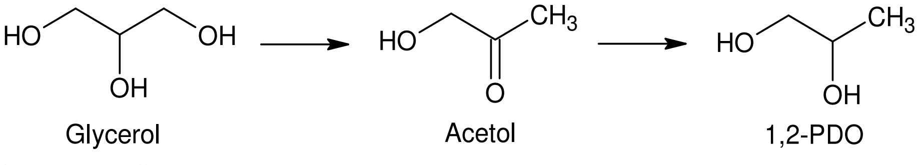
2.2.1 Copper and Cobalt based catalysts

Copper-cobalt (Cu-Co) catalysts have emerged as promising materials for glycerol oxidation due to their synergistic redox interactions, oxygen vacancies, and high catalytic stability. The cooperative effect between Cu and Co species enhances catalytic performance, enabling selective oxidation of glycerol into high-value chemicals such as dihydroxyacetone (DHA), glycolic acid, tartronic acid, and formic acid.

Paredes-Quevedo [63] investigated $CuCo_2O_4$ supported on porous dealuminized metakaolinite for the selective oxidation of glycerol to DHA. Their findings revealed that the synergistic interaction between Cu and Co ions within the $CuCo_2O_4$ spinel structure significantly enhanced catalytic activity and selectivity toward DHA and glycolaldehyde. Computational studies indicated that electron transfer, oxygen vacancies, and redox cycles play crucial roles in selectivity determination. The study reported a glycerol



Scheme 1. Glycerol hydrogenolysis to propanediol [55]



Scheme 2. Glycerol hydrogenolysis through acetol as an intermediate [56]

conversion of 70.6% with 88.2% DHA selectivity under optimal conditions. Furthermore, increasing the glycerol-to-H_2O_2 ratio from 1:2 to 1:4 enhanced DHA selectivity to 91%, but at the cost of reduced glycerol conversion (67%). Coke formation was minimal, however, minor metal leaching was observed in the first reaction cycle, causing a slight drop in conversion, though the catalyst remained stable in subsequent cycles. Stability tests confirmed that $CuCo_2O_4$ maintained consistent activity over five reaction cycles, with oxidative regeneration effectively restoring catalytic performance by re-oxidizing surface species and eliminating residual carbon deposits [63].

Zhiwei Xi and colleagues [64] explored the catalytic performance of $CuO–Co_3O_4$ nanoparticles supported on nickel foam (NF) for glycerol electro-oxidation. Their study demonstrated that the synergistic interaction between CuO and Co_3O_4, coupled with induced lattice strain, led to the formation of abundant oxygen vacancies, significantly improving catalytic activity. Electrochemical testing showed that a Cu:Co molar ratio of 1:1 exhibited the highest efficiency, requiring only 1.13 V vs. The catalyst displayed high stability over 12 hours, selectively converting glycerol into formic acid, glycolic acid, and glyceric acid, with formic acid achieving the highest selectivity (90.3%). These findings underscore the importance of oxygen vacancy formation and electronic structure modulation in Cu-Co catalysts for glycerol electro-oxidation [64].

Jihang Li and others [60] investigated CuCo/Ti-SBA-15 as a bifunctional catalyst for the selective oxidation of glycerol to tartronic acid, utilizing H_2O_2 as the oxidant. The study demonstrated that Cu and Co were uniformly dispersed on the Ti-modified SBA-15 support, maintaining its mesoporous structure and preventing metal agglomeration. The synergistic interaction between CuO and Co_3O_4 improved catalytic activity by facilitating valence changes and redox cycling, which enhanced glycerol conversion and tartronic acid selectivity. Under optimal reaction conditions (80 °C, 4 h, H_2O_2/glycerol molar ratio = 2:1, NaOH/glycerol molar ratio = 3:1), the CuCo/Ti-SBA-15 catalyst achieved a glycerol conversion of 53.8% with a tartronic acid selectivity of 54.5%. Notably, the catalyst exhibited high stability over five consecutive cycles, demonstrating the potential of non-noble metal-supported catalysts for sustainable glycerol valorization [60].

2.2.2 Copper and Nickel based catalysts

Ni-Cu-based catalysts have demonstrated significant potential in glycerol electrooxidation, particularly in alkaline media. Habibi and Delnavaz [65] investigated Ni-Cu nanoparticles supported on carbon-ceramic electrodes (CCE) and found that the alloying of Ni with Cu substantially enhanced catalytic activity compared to pure Ni. The Ni-Cu/CCE catalyst exhibited a lower onset oxidation potential (0.3 V vs. SCE) and higher anodic peak current, indicating superior electrocatalytic performance. The presence of Cu facilitated electron transfer and modified the oxidation states of Ni, enhancing the oxidation of glycerol into valuable intermediates such as glyceric acid, glycolic acid, and formic acid. The study highlighted that the hierarchical dendritic morphology of Ni-Cu nanoparticles contributed to increased surface area and improved electron conductivity, leading to efficient catalytic performance. However, the catalyst suffered from moderate long-term stability, with a gradual decline in activity due to surface oxidation and catalyst deactivation over extended cycling [65].

Joel Sankar and others [66] investigated the oxidation of glycerol using an inactivated electroless CuNiMoP catalyst, demonstrating its potential for both electrochemical and thermochemical conversion. Their study employed a full factorial design to assess the effects of temperature, reaction time, and pressure on product formation. The major oxidation products included glyceric, hydroxypyruvic, tartronic, oxalic, and formic acids, with a maximum glycerol conversion of 10.6% observed under optimized conditions. The study found that time and pressure significantly influenced glyceric acid selectivity, while temperature played a crucial role in tartronic acid formation. A comparative analysis revealed distinct differences between the electrochemical and thermochemical oxidation pathways, with electrochemical oxidation favoring the formation of aldehydes and ketones [66].

2.2.3 Copper and Magnesium based catalysts

On the other hand, Shuguang Xu [62] employed a Cu-Mg catalyst for glycerol conversion, achieving a glycolic acid yield of 78.1%, significantly higher than the typical yield of less than 50% with noble metals. Xu proposed that glycerol is first dehydrogenated to glyceraldehyde, which is subsequently oxidized to glycolic acid. The CuO catalyst initiates the dehydrogenation process, converting glycerol to glyceraldehyde (GLA). Meanwhile, MgO playoff a crucial role in promoting the cleavage of the C_2-C_3 bond in GLA, thereby inhibiting further oxidation to glyceric acid. This strategic intervention facilitates the formation of glycolaldehyde, which, under the catalytic influence of CuO, is oxidized to produce glyceric acid. The combined action of CuO and MgO effectively directs the reaction toward

C_2-C_3 bond cleavage. Notably, this collaborative catalytic process suppresses the production of lactic acid byproducts, which are typically formed when GLA is catalyzed solely by MgO. Coke formation was minimal due to the cooperative role of Cu and Mg in directing the reaction toward GcA rather than polymeric by-products. However, minor catalyst deactivation occurred due to Mg leaching over repeated cycles. Stability tests demonstrated that CuMg retained significant catalytic activity across multiple cycles, with oxidative regeneration effectively restoring performance by re-oxidizing active species and removing surface carbon deposits.

Chun-Hui Zhou [61] investigated Cu-containing layered double hydroxide (LDH) catalysts for the selective oxidation of glycerol with molecular oxygen. The study examined the effect of various metal dopants (Ni, Zn, Cu, Co) incorporated into MgAl LDH materials on catalytic activity and selectivity. The results demonstrated that CuAlMg LDH catalysts exhibited the highest activity, achieving 97.3% glycerol conversion with 70% selectivity toward glyceric acid under optimal conditions. The incorporation of Cu significantly enhanced oxidation performance compared to other metal elements, with Cu species acting as key active sites. Additionally, calcined CuAlMg catalysts showed improved catalytic activity due to phase transformation into mixed oxides, which promoted selective oxidation pathways. Furthermore, coke formation was minimal due to the well-dispersed Cu active sites, which reduced the over-oxidation of intermediates and prevented excessive carbon deposition. However, prolonged use led to gradual catalyst deactivation, primarily due to Cu aggregation and minor structural changes. Stability tests demonstrated that oxidative regeneration effectively restored catalytic performance by eliminating carbon residues and reactivating Cu species.

2.2.4 Copper and Gold based catalysts

Copper and gold-based catalysts have gained significant attention for glycerol oxidation due to their excellent redox properties, ability to activate oxygen species, and high selectivity toward value-added products. Liu [67] synthesized the gold nanoparticles supported on CuO using precipitation method. They conducted the oxidation reaction in a Parr autoclave reactor, finding that the copper-based support significantly enhances the yield of dihydroxyacetone, which can further isomerize into lactic acid.

Yanxia Wang and colleagues [68] further explored the role of mineral-derived CuO-ZnO supports in enhancing Au-based catalysts for selective glycerol oxidation to DHA. Their study demonstrated that CuO-ZnO interactions significantly influenced catalytic performance, with the rosasite-derived Au/CuO-ZnO catalyst achieving the highest DHA yield (70%) and glycerol conversion (76%). Characterization techniques, such as XRD, H_2-TPR, TEM, and XPS, revealed that the strong metal-support interactions, high Au dispersion, and an optimal balance of Au^0 and basic surface sites were key factors driving superior catalytic activity. Stability tests showed that the rosasite-derived catalyst-maintained activity and selectivity even after five reaction cycles, indicating excellent structural robustness. In contrast, the aurichalcite-derived catalyst exhibited lower DHA yield (20%) due to weaker metal-support interactions.

Kaminski and colleagues [69] further investigated the catalytic performance of Cu-Au bimetallic systems for glycerol oxidation under varying reaction conditions. Their study highlighted that the incorporation of Cu significantly altered the electronic structure of Au, enhancing oxygen activation and redox cycling, which in turn improved selectivity toward glyceric acid. Advanced characterization techniques, including XRD, UV-Vis, XPS, TEM, and SEM, confirmed the formation of strong metal-support interactions that contributed to high catalyst stability and recyclability. Under optimal conditions, the Cu-Au catalyst achieved a glycerol conversion of 92% with 78% selectivity for glyceric acid, significantly outperforming monometallic gold catalysts. Additionally, the catalyst maintained its stability over five reaction cycles, exhibiting only a slight decline in activity [69].

Lingqin Shen and others [70] also synthesized bimetallic $CuAu_x$ ($x = 0.01$–0.04) catalysts using the wet chemical reduction method, where Cu and Au precursors were reduced using hydrazine hydrate in ethanol with CTAB as a modifier. Characterization confirmed a well-alloyed Cu-Au structure, enhancing electron transfer and catalytic efficiency. These catalysts achieved >83% lactic acid yield under hydrothermal conditions (200 °C, 2 h, NaOH/glycerol ratio 1.1:1), with Au reducing the activation energy (from 64.0 to 36.9 kJ/mol) and Cu facilitating oxidation. The $CuAu_x$ catalysts demonstrated high stability, with minimal coke formation (carbon deposition <3.3%), attributed to the synergistic Cu-Au effect, which prevents polymeric by-product accumulation. Unlike monometallic catalysts, they maintained a carbon balance above 90%, ensuring efficient glycerol utilization. After six cycles, $CuAu_2$ retained 95% activity, confirming excellent reusability and reduced deactivation. These findings highlight $CuAu_x$ nanoparticles as a stable and efficient catalyst for glycerol oxidation to lactic acid, minimizing coke formation while ensuring long-term catalytic performance [70].

Izabela Sobczak [71] synthesized bimetallic Au-Cu catalysts supported on Nb_2O_5 and Nb/MCF via aqua regia-based deposition and $NaBH_4$ reduction, with Cu introduced through Cu $(NO_3)_2$ impregnation, forming metallic Au and CuO-like species with Cu^+ and Cu^{2+} clusters, as confirmed by XRD, TEM, UV-Vis, XPS, and H_2-TPR. The Au-Cu interaction enhanced redox properties, facilitating oxygen activation and promoting oxidative dehydrogenation of glycerol to glycolic and formic acids rather than solely glyceric acid. At 363 K, AuCu-Nb_2O_5 achieved 90% glycerol conversion, with 27% selectivity to glycolic acid, compared to 11% for Au-Nb_2O_5, confirming Cu's role in deep oxidation pathways. Coke formation was minimal, with carbon balance >90%, ensuring efficient substrate utilization and low by-product formation. Stability tests showed AuCu-Nb_2O_5 retained 95% catalytic activity after six cycles, highlighting strong structural stability and high reusability [71].

Building on the high glycerol oxidation efficiency of Au-Cu/Nb_2O_5 catalysts, further studies on Au-Cu and Au-Ni bimetallic systems supported on SiO_2, Cu, and Ni revealed enhanced selective oxidation pathways. Synthesized via nano-Au transfer and sol–gel methods, these catalysts exhibited highly porous structures with strong metal-support interactions, as confirmed by XRD, TEM, XPS, and EDXRF. In H_2O_2-mediated oxidation, Au-SiO_2 achieved 100% conversion with 90% selectivity toward acetic acid (AA), while Au-Cu and Au-Ni promoted glycolic acid formation. Acetonitrile and surfactants improved AA yields and reaction rates, but Cu and Ni leaching led to progressive deactivation. In contrast, SiO_2-supported Au catalysts retained 60% activity after four cycles, ensuring greater durability. Reusability and stability were key factors, with Au-Cu/Nb_2O_5 retaining 95% activity after six cycles, showing minimal coke formation and >90% carbon balance. Strong Au-Cu interactions prevented deactivation, while Au-SiO_2 catalysts significantly reduced coke formation. However, Cu and Ni catalysts suffered increased carbon deposition, leading to stability concerns. These findings highlight that bimetallic Au-Cu catalysts offer strong reusability and high catalytic efficiency, but further optimization is needed to enhance metal leaching resistance and long-term stability in glycerol oxidation [72].

A series of Au catalysts supported on Cu–Al composite oxides were synthesized by Yi-Hu Ke [73] via deposition–precipitation with urea, with Cu–Al oxides prepared through a constant-pH co-precipitation method. XRD, TEM, XPS, and H_2-TPR confirmed highly dispersed Au nanoparticles and CuO species, enhancing redox properties and oxygen activation. The optimal Au/CuAlO-3 catalyst (Cu/Al = 5:1) achieved 76.7% glycerol conversion with 97.3% DHA selectivity at 353 K and 10 bar O_2. Cu improved catalytic efficiency by increasing surface-active oxygen, while Al_2O_3 provided structural stability. However, catalyst deactivation occurred due to coke formation, Cu leaching, and Au nanoparticle agglomeration, as shown by XPS and TEM. Coke deposition from overoxidation blocked active sites, reducing oxygen activation, though overall carbon balance remained high (>90%) [73].

2.2.5 Copper and Zinc based catalysts

Junjie Zhang [19] proposed converting glycerol to lactic acid using a Cu-ZnO catalyst supported on carbon. According to Zhang, the catalytic activity of Cu-ZnO on carbon support is influenced by various parameters. At 750 °C, the Cu-ZnO@C-1.4 catalyst exhibited 76.3% lactic acid selectivity and 93.1% glycerol conversion, yielding optimal results. The Cu/Zn molar ratio also impacted the results, with the Cu-ZnO@C-3.5-750 catalyst showing the best selectivity (72.9%) and glycerol conversion (95.1%). Increasing the reaction temperature positively correlated with glycerol conversion and lactic acid selectivity. Zhang also outlined the conversion mechanism, indicating that glycerol is first converted into hydroxyacetone, which is then dehydrogenated to form pyruvaldehyde, ultimately leading to lactic acid production through oxidation. Coke formation was negligible due to the stabilizing effect of the carbon coating, which prevented excessive Cu nanoparticle aggregation and preserved the active sites. However, slight catalyst deactivation was observed after multiple runs, primarily due to the leaching of Cu and Zn species. Despite this, post-reaction characterization confirmed that the catalyst maintained structural integrity, with oxidative regeneration effectively restoring catalytic performance [19].

Iveta Kaskow [74] investigated the effect of copper on the properties of an Au-ZnO catalyst and its activity in glycerol oxidation. The study found that introducing Cu significantly altered the electronic state of gold due to electron transfer between metals, forming $(Au^0)^{\eta-}$ centers that enhanced catalytic performance. Cu-ZnO systems exhibited increased glycerol conversion (95%) compared to Au-ZnO (50%), highlighting the synergistic interaction between Cu and Au in promoting oxygen activation and substrate oxidation. Furthermore, Cu species facilitated oxidative dehydrogenation, leading to higher selectivity toward tartronic and glycolic acid. Structural characterization via XPS and UV-Vis confirmed the presence of Cu^+/Cu^{2+} species, with reduced copper species playing a crucial role in catalyst activity. The study emphasized that Cu-modified Au-ZnO catalysts demonstrated superior activity and selectivity in glycerol oxidation due to optimized electronic properties and improved oxygen chemisorption [74].

2.2.6 Copper and platinum-based catalysts

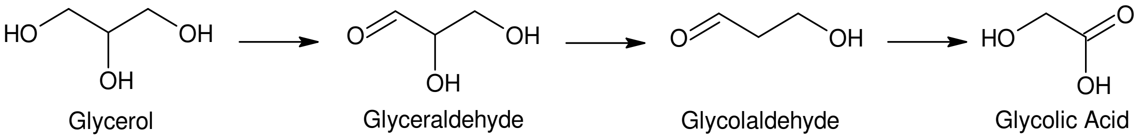
Cu-promoted Pt catalysts supported on activated carbon (Cu-Pt/AC) were synthesized by Chen Zhang and colleagues [15] via impregnation and deposition–precipitation methods to enhance glycerol oxidation to lactic acid (LA). The 0.5%Cu-1.0%Pt/AC catalyst exhibited the highest activity, achieving a lactic acid yield 2.4 times greater than that of the 1.0%Pt/AC catalyst under identical reaction conditions. Characterization via TEM, XPS, and H_2-TPR revealed that Cu addition improved Pt dispersion, forming Pt-Cu interfaces that facilitated glycerol transformation. The presence of Cu^0 and Cu^+ species played a key role in promoting glycerol oxidation, while large CuO particles favored the formation of glyceric acid rather than lactic acid. Coke formation, which could lead to catalyst deactivation, was minimal due to the strong interaction between Pt and Cu, as well as the high dispersion of active metal sites. The catalyst demonstrated excellent stability, retaining 95% of its activity after three cycles, confirming the role of Cu in enhancing both catalytic performance and durability [15].

Following this, Dan Liang [75] synthesized carbon-supported bimetallic Pt–Cu catalysts via impregnation and deposition–precipitation methods for glycerol oxidation in a base-free aqueous solution. Structural characterization using XRD and TEM confirmed the formation of highly dispersed Pt–Cu nanoparticles, predominantly in a $PtCu_3$ alloy phase, which significantly enhanced catalytic activity compared to monometallic Pt/C catalysts. The 5Pt–Cu/C catalyst exhibited superior performance, achieving 86.2% glycerol conversion with 70.8% selectivity to glyceric acid, highlighting the beneficial role of Cu in improving catalytic efficiency by reducing C–C cleavage activity and minimizing peroxide formation. Strong metal-support interactions contributed to minimal coke formation, ensuring efficient substrate utilization and preventing active site blockage. Stability tests demonstrated that the 3Pt–Cu/C catalyst maintained high activity over multiple cycles, indicating excellent durability and reusability, further supporting the role of $PtCu_3$ alloy in sustaining long-term catalytic performance [75].

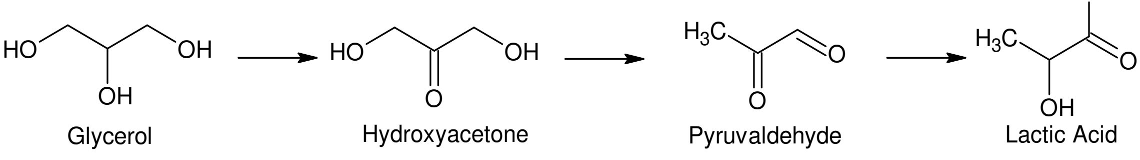
Copper-based catalysts have emerged as cost-effective alternatives to noble metals for glycerol oxidation, offering high selectivity for value-added products, such as glyceric acid, glycolic acid, lactic acid, and dihydroxyacetone (DHA). The incorporation of transition metals such as Co, Ni, Zn, and Mg has further improved catalytic efficiency by enhancing oxygen activation, redox cycling, and metal-support interactions. While Cu-Co catalysts demonstrate excellent oxygen vacancy formation, Cu-Ni catalysts enhance electron transfer and surface conductivity, and Cu-Mg systems provide strong basicity for C–C bond cleavage, long-term stability remains a key challenge due to metal leaching, sintering, and surface oxidation. Additionally, Cu-Au and Cu-Zn catalysts have shown superior selectivity and conversion rates, but their scalability and cost-effectiveness require further optimization. Future research should focus on improving catalyst stability, tuning metal oxidation states, integrating electrochemical/photo-assisted oxidation techniques, and developing bio-based supports to enhance sustainability and industrial applicability. By addressing these challenges, Cu-based catalysts can play a crucial role in advancing glycerol valorization and green chemical processes. The oxidation reactions of glycerol are presented in Scheme 3 and Scheme 4.

2.3 Steam Reforming

Steam reforming is a chemical method to obtain hydrogen and carbon monoxide from hydrocarbons. Glycerol conversion using steam reforming is among the best ways to synthesize



Scheme 3. Oxidation of glycerol into glycolic acid [62].



Scheme 4. Oxidation of glycerol to lactic acid [76].

unlimited amounts of hydrogen. Various catalysts have been employed for glycerol steam reforming, including rhodium [77], ruthenium [78], cobalt [79], nickel [80], and copper, with Ni demonstrating the highest catalytic activity. However, coke formation and catalyst deactivation are significant challenges associated with Ni catalysts. Coke formation is a multi-step process that begins with the decomposition, dehydration, and polymerization of glycerol and its oxygenated intermediates on the catalyst surface, resulting in carbonaceous deposits [81]. The Boudouard reaction and methane cracking further contribute to coke formation, especially at lower steam-to-carbon (S/C) ratios and higher temperatures [82]. These deposits can gradually graphitize over time, becoming harder to remove [81]. Different types of coke are commonly observed, including catalytic coke, which forms directly on active sites and leads to rapid deactivation; filamentous coke, which forms carbon nanotube-like structures often associated with metal particles; encapsulating coke, which forms a dense layer around catalyst particles, blocking reactant access; and amorphous coke, which is more disordered and accumulates randomly [83]. Ni-based catalysts are particularly prone to coke formation, but incorporating promoters like Cu or Cr can disrupt large Ni ensembles and modify metal-support interactions to reduce carbon deposition [84].

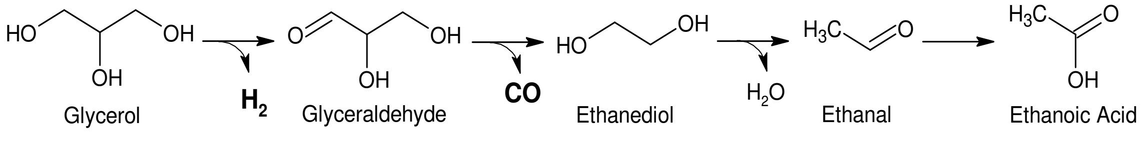
2.3.1 Nickel-Copper based catalysts

Chao Wang [85] reported that using a Ni-Cu catalyst for glycerol reforming within a temperature range of 450-650 °C achieves a glycerol conversion of 90.9% with hydrogen selectivity of 92.9%. The catalyst was synthesized using the co-precipitation method, and the reaction was conducted in a continuous flow fixed-bed reactor to achieve these results. The complete process of glycerol steam reforming is illustrated in Scheme 5.

Vivian V. Thyssen [82] also studied the addition of Cu to Ni supported on SiO_2 and γ-Al_2O_3. Alone Ni on support like Ni/SiO_2 has achieved 98% glycerol conversion but suffered from severe carbon deposition. In contrast, Ni/γ-Al_2O_3 showed 93% conversion with better stability due to the formation of $NiAl_2O_4$, which improved Ni dispersion and reduced coke formation. The incorporation of Cu into Ni catalysts lowered the reduction temperature and modified metal-support interactions, but Cu alone showed negligible catalytic activity for glycerol steam reforming. While Cu-Ni catalysts exhibited moderate activity, their conversion was lower than pure Ni-based catalysts due to the weaker hydrogenation ability of Cu. Coke formation, primarily due to the Boudouard reaction and methane decomposition, was significant in Ni-based catalysts but was mitigated in $NiAl_2O_4$ due to stronger metal-support interactions, which limited carbon diffusion. The study also found that increasing reaction temperature reduced coke formation by shifting equilibrium away from carbon deposition pathways [82].

Binlin Dou and colleagues [86] also studied the effect of Ni-Cu-Al catalyst on glycerol conversion and hydrogen production at temperatures ranging from 500–600 °C. The results showed that the catalyst effectively facilitated hydrogen production, with glycerol conversions of 45.0%, 52.0%, and 71.9% at 500 °C, 550 °C, and 600 °C, respectively. Hydrogen selectivity increased with temperature, reaching a maximum of 78.6% at 600 °C. However, catalyst deactivation was observed due to carbon deposition, leading to a reduction in conversion over time. The high conversion rates were attributed to the efficient redox properties of Ni, which facilitated glycerol dehydrogenation and C–C bond cleavage, while Cu improved oxygen activation and prevented excessive carbon deposition. The Al support stabilized the active Ni species, preventing agglomeration and maintaining catalyst integrity over prolonged operation. Additionally, the co-precipitation synthesis method with rising pH led to well-dispersed active sites, further enhancing catalytic efficiency [86].

Incorporation of Cu, Co, or Cr in Ni/ SBA-15 silica was also observed for glycerol steam reforming. The addition of Cu, Co, and Cr significantly influenced catalytic performance by modifying Ni dispersion, metal-support interaction, and reducibility. Among the tested catalysts, Ni-Cr/SBA-15 exhibited the highest glycerol conversion (~100% initially, maintaining over 93% after 60 hours) and superior hydrogen yield (61.4%), while also demonstrating the lowest coke formation (13 mg/gcat·h). This improved performance was attributed to the strong metal-



Scheme 5. Mechanism of steam reforming of glycerol [85]

support interaction facilitated by Cr, which reduced Ni crystallite size and enhanced stability. In contrast, Ni-Cu/SBA-15 showed significant deactivation due to higher coke accumulation because of the formation of carbon nanofibers due to Cu's affinity for graphitic carbon, while Ni-Co/SBA-15 maintained moderate activity and hydrogen selectivity. Despite these differences, all catalysts were able to undergo catalytic regeneration via oxidative treatment, effectively removing carbon deposits and restoring activity [83].

In another study Ni/Ce-Sm-Cu catalysts were investigated for glycerol steam reforming (GSR) to enhance hydrogen production. The Ni/Ce-Sm-10Cu catalyst achieved the highest H_2 yield (5.4 mol H_2/mol glycerol) and selectivity (~85%), with 94% glycerol conversion at 750 °C. Cu incorporation improved WGS (water gas shift) activity, metal dispersion, and reducibility, but excessive coke formation was a key challenge, with all catalysts accumulating significant carbon deposits during extended runs at 650 °C. Raman spectroscopy revealed that higher Cu content increased the degree of carbon graphitization, indicating that Cu influences both the nature and extent of carbon formed. While the bimetallic Ni-Cu composition suppressed methanation and improved hydrogen yield, it also introduced more carbon formation pathways, likely due to altered Ni-Cu alloy surface properties. Regeneration through oxidative treatment effectively removed carbon deposits and partially restored activity, although long-term stability remained limited by sintering and structural changes induced by carbon build-up [84].

2.3.2 Copper Cobalt based catalysts

Surendar Moogi and colleagues investigated the catalytic performance of copper-promoted cobalt-magnesium oxide (Cu-Co/MgO) catalysts for glycerol steam reforming (GSR) to produce hydrogen. The study revealed that the 5 wt% Cu-20 wt% Co/MgO catalyst (5Cu20CM) exhibited the highest hydrogen yield (74.6%) with complete glycerol conversion to gaseous products at 650°C. The enhanced catalytic activity was attributed to smaller Co nanoparticle size (7 nm), higher cobalt dispersion (35%), and increased surface area (56 m^2/g). The addition of Cu lowered the reduction temperature of cobalt oxide due to the hydrogen spillover effect, facilitating better catalyst activation. Furthermore, Cu incorporation suppressed the accumulation of amorphous and filamentous carbon, leading to stable performance over 30 hours [87].

Wang *et al.* [88] investigated the electrocatalytic performance of CuCo-ZIF nano dodecahedrons for hydrogen production via glycerol oxidation reaction (GOR) as a substitute for oxygen evolution reaction (OER). The study demonstrated that Cu-Co bimetallic interactions enhanced electron transfer and optimized the electronic structure of Co, leading to superior catalytic activity compared to ZIF-67. The Cu_1Co_1-ZIF catalyst exhibited a higher Faradaic efficiency (94.4%) and reduced the cell voltage by 18.81% compared to traditional KOH electrolyzes. The glycerol oxidation process significantly lowered the required anodic voltage and increased current density, highlighting the potential of Cu-Co catalysts in energy-efficient hydrogen production. Stability tests confirmed the structural robustness of Cu-Co-ZIF catalysts, making them promising alternatives for sustainable hydrogen generation from glycerol reforming [88].

To conclude this, steam reforming of glycerol primarily utilizes nickel catalysts due to their high catalytic activity. However, the addition of copper to nickel not only enhances catalytic efficiency and reusability but also reduces coke formation.

2.4 Oxidehydration Reaction

Oxidehydration of glycerol is the most important step for the transformation of glycerol into useful products such as acrolein, acrylic acid, acetol and I,2-PDO [89]. If dehydration occurs at the primary carbon of glycerol, acetol is formed, while removal of the hydroxyl group from the secondary carbon first results in the formation of 3-hydroxypropanal. Subsequent removal of hydrogen from 3-hydroxypropanal leads to the production of acrolein.

Among different products, acrylic acid holds significant industrial and chemical value due to its applications in the production of adhesives, resins, plastics, rubber, and more [90]. The conversion of glycerol to acrylic acid is a multi-step reaction [91]. Initially, acid-catalyzed dehydration of glycerol results in the formation of various intermediates, including acrolein, acetol, acetaldehyde, and acetone. Among these, acrolein is the primary and most critical intermediate; it is conventionally produced from the oxidation of propylene through a multi-step process. Producing acrolein from glycerol offers a renewable alternative, reducing dependence on petrochemicals.

The second step in acrylic acid production involves the oxidation of acrolein in the presence of oxygen or H_2O_2, facilitated by various metal-based catalysts such as copper [27], vanadium [92], and molybdenum [93]. Copper-based catalysts are gaining considerable attention for this step, as they not only enhance catalytic oxidation toward acrylic acid but also offer high selectivity for acrylic acid while reducing coke formation during the dehydration step.

Coke formation during oxidative dehydration of glycerol is a complex process influenced by the interaction between oxygenates, hydrocarbons, and catalytic properties. The mechanism begins with the dehydration of glycerol into intermediates like acetol, acrolein, and hydroxyacetone, which then undergo deoxygenation, aldol condensation, and aromatization, producing coke precursors such as olefins and polyaromatic hydrocarbons (PAHs) [94]. In zeolite-based catalysts, coke formation is driven by the adsorption and polymerization of these heavy carbon species within the micropores, where strong Brønsted acid sites accelerate polymerization and condensation reactions, eventually leading to pore blockage and catalyst deactivation [95].

The types of coke formed include soluble coke, which consists of lighter paraffinic and aromatic hydrocarbons extractable by solvents during early stages, and insoluble coke, which consists of condensed polyaromatics firmly attached to the catalyst surface, particularly in acidic catalysts or catalysts with strong Brønsted acid sites [94]. Highly condensed carbon is typically combustible at temperatures between 600-800 °C, indicating that the coke becomes increasingly structured over time [96]. In bifunctional catalysts with transition metal oxides (like W, Mo, Cu), coke is also observed as oxygenated coke, comprising polyacrylic and polyaromatic species, which form through the oxidation of intermediates. In contrast, amorphous coke is randomly deposited disordered carbon, formed through incomplete oxidation and polymerization processes, especially in systems with excessive acidity. Filamentous coke, though more common in steam reforming processes, is rare in oxidative dehydration but could form on metallic sites in bimetallic catalysts if excessive hydrocarbons accumulate without sufficient oxidation [97].

This dehydration, followed by oxidation of glycerol, can yield acrylic acid through two approaches: a two-step reaction in which dehydration and oxidation occur in separate reactors, or a single-step process where both reactions take place simultaneously in one reactor using a bifunctional catalyst. The reaction pathway for acrylic acid production from glycerol via dehydration-oxidation is shown in Scheme 6.

2.4.1 Dual step process

The dual-step process for converting glycerol to acrylic acid involves using separate reactors for dehydration and oxidation. First, complete water removal from glycerol, resulting in acrolein formation, is performed in one reactor using acid-based catalysts like zeolites, silicates, or inorganic acids.

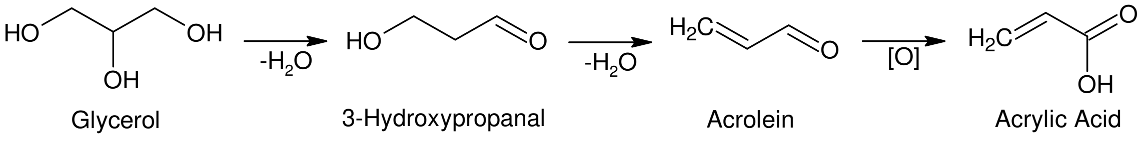
2.4.1.1 Acid-catalyze dehydration

Heng Zhao [99] employed sulfuric acid-activated montmorillonite clay for glycerol dehydration at 592 K, achieving 54.2% glycerol conversion with 44.9% acrolein yield. In another study, Lauriol-Garbay [100] prepared ZrNbO catalysts via the wet impregnation method by impregnating hydrated zirconium oxide with per oxo-niobate solution. This catalyst was used for dehydration at 300 °C under atmospheric pressure in a glass plug flow microreactor, achieving 82% glycerol conversion and 72% acrolein selectivity after 24 hours. Shan Liu [8] used a molybdenum phosphide (MoP) catalyst to synthesize acrolein via glycerol dehydration. The MoP catalyst was prepared through the in-situ H_2-TPR method, and the reaction was carried out in a fixed-bed reactor. Liu [8] concluded that using MoP catalysts at 565 K for 43 hours yields an acrolein selectivity of 89%. However, it should be noted that higher temperatures increase the likelihood of coke formation, which reduces catalytic activity. In another study, Abdullah Alhanash [101] synthesized a cesium 12-tungstophosphate catalyst via the impregnation method. They used a vertically fixed-bed Pyrex tubular reactor for gas-phase glycerol dehydration, finding that at 547 K and 1 atm pressure, a 100% glycerol conversion with 98% selectivity for acrolein was achieved.

To conclude, these acidic catalysts are the best for the dehydration of glycerol to acrolein, but the major problem is coke formation. Strong acid favor coke formation, hence, causes catalytic deactivation. However mild acidic conditions favor acrolein and hence show high acrolein selectivity.

2.4.1.2 Using copper-based catalysts for glycerol dehydration

The study by Wladimir Suprun [97] investigated the catalytic activity of copper-based transition metal oxides supported on phosphated alumina for the gas-phase dehydration of glycerol. The CuOx–Al_2O_3-PO_4 catalyst demonstrated high glycerol conversion and acetol selectivity (50%), while its selectivity for acrolein was lower than that of Mo and W-based catalysts. The strong



Scheme 6. Dehydration of glycerol to acrylic acid via acrolein as an intermediate [98].

acidity and redox properties of Cu contributed to its catalytic performance, promoting selective dehydration pathways. Characterization techniques, such as NH_3-TPD, XPS, and TPR, revealed that Cu facilitated coke removal and improved catalyst stability. However, a gradual deactivation was observed over prolonged use, attributed to the formation of strong Brønsted acid sites during the reaction [97].

S. Basu and colleagues [102 used cerium as promoters in copper chromite catalysts to cheak the effect on glycerol dehydration. The cerium-promoted CuCr catalyst supported on silica was synthesized using a sol-gel method and characterized by XRD, BET, Raman spectroscopy, and Py-FTIR. Among different cerium loadings, the 5 wt% Ce-doped CuCr catalyst (SiCuCr40-Ce5) exhibited the highest BET surface area, better oxygen vacancies, and strong Lewis's acid sites, resulting in the highest acetol selectivity (60.35%) at 200 °C for 3 hours with 98.6% glycerol conversion. The cerium promotion improved catalyst stability by preventing metal sintering and leaching. However, the presence of impurities, such as iron in lower-grade glycerol, led to reduced acetol selectivity. Spent catalyst analysis revealed carbon deposits and a decrease in surface area, indicating the need for regeneration strategies to maintain long-term catalytic efficiency [102].

The study by Basu and Sen [103] investigated the dehydration of glycerol using a silica–phosphate-supported copper catalyst to produce acetol, a valuable intermediate in the chemical industry. The catalyst was synthesized via neutralization of sodium silicate with orthophosphoric acid, followed by the addition of copper nitrate and subsequent calcination at 550 °C. Characterization techniques such as XRD, H_2-TPR, and pyridine–FTIR confirmed the presence of CuO nanoparticles and Lewis's acid sites, which played a crucial role in the reaction. The catalyst with the highest Cu loading (40 wt%) exhibited 100% glycerol conversion at 220 °C, with a maximum acetol selectivity of 58.3% and an 80% yield of distilled liquid products. The high Lewis acid site density facilitated selective dehydration while minimizing C–C bond cleavage, reducing byproduct formation. However, catalyst deactivation due to carbon deposition limited its long-term use, highlighting the need for improved regeneration strategies [103].

Sasaki and colleagues also explored the vapor-phase dehydration of glycerol to acetol using Cu/SiO_2 catalysts prepared with organic additives. The results indicated that 12-crown-4-ether (12C4) significantly improved copper dispersion on the SiO_2 support, leading to enhanced catalytic activity. The optimized 12C4-Cu/SiO_2 catalyst exhibited a maximum acetol yield of 94.3% at 270°C, with 100% glycerol conversion. Characterization techniques confirmed that the glycerol dehydration was catalyzed by Cu^0 nanoparticles rather than Lewis's acid sites. The study also demonstrated that a higher Cu surface area correlated with increased catalytic efficiency. The catalyst-maintained stability over an extended reaction period, showcasing its potential for industrial applications in glycerol valorization [104].

2.4.1.3 Oxidation of intermediate using metal catalysts

For the next step, oxidation of acrolein to acrylic acid catalysts depends upon the first step. If the acrolein's yield is high, then the overall yield of acrylic acid will also be high. Deleplanque *et al.* [26] used multi metal oxides (V, Cu, Mo) catalysts for oxidation of acrolein to acrylic acid. Using separate reactors for dehydration and oxidation, they achieved a 73% yield of acrylic acid with a dehydration temperature of 564 K and an oxidation temperature of 542 K.

The dual-step process for converting glycerol to acrylic acid offers several benefits, such as high selectivity for the desired product, controlled conditions for each step, flexibility in product choice, and high efficiency. However, it presents challenges that have led researchers to explore alternative methods, such as one-pot synthesis. Issues with the dual-step process include catalytic deactivation due to coke formation, making it less practical for industrial applications. Additionally, using two separate reactors increases energy consumption and costs, while requiring distinct catalysts for dehydration and oxidation further complicates the process. These challenges have driven researchers to focus on simpler, more environmentally friendly, and cost-effective approaches for acrylic acid production from glycerol, ultimately leading to interest in the one-pot process.

Satoshi Ishikawa [105] also studied the role of Mo-V-Cu oxides (MoVCuO) in the selective oxidation of acrolein to acrylic acid, focusing on the structural influence of trigonal Mo-V-M3rd oxides (M3rd = -, Fe, Cu, W). The research demonstrates that MoVCuO, along with MoVFeO, incorporates Cu and Fe into heptagonal channels, significantly altering catalytic behavior. While MoVO and MoVWO exhibited high catalytic activity in the oxidation of acrolein, MoVCuO and MoVFeO displayed low conversion rates due to structural constraints blocking active sites. However, for allyl alcohol oxidation, MoVCuO and MoVFeO selectively promoted acrolein formation, while MoVO and MoVWO favored both acrolein and propanal. Notably, MoVFeO achieved an acrylic acid yield of 83.1% at 350 °C due to its ability to prevent isomerization, enhancing the direct oxidation pathway [105].

2.4.2 One pot synthesis

One-pot synthesis involves both dehydration and oxidation reactions occurring within a single reactor, making it increasingly important and gaining interest due to its simplicity, economic efficiency, and improved yield of acrylic acid. However, the main challenge in this process is the synthesis of bifunctional catalysts that possess both acidic and oxidative properties. Copper-based catalysts supported by zeolites and other siliceous materials, in the presence of oxygen and hydrogen peroxide, provide an optimal environment for the one-step conversion of glycerol to acrylic acid.

2.4.2.1 Cu based catalysts on zeolites

Tambunan *et al.* [27] synthesized Cu-modified HY zeolite catalysts using both pro-analytical and natural resource precursors, such as Indonesian natural zeolite and kaolin, for the one-pot conversion of glycerol to acrylic acid. Structural characterization confirmed the preservation of the Y-zeolite framework and the uniform dispersion of Cu nanoclusters within the zeolite structure. The Cu sites enhanced oxidation capacity, while the weak acid sites of the modified HY zeolite facilitated the dehydration of glycerol to acrolein, followed by acrolein oxidation to acrylic acid. Under optimal conditions (363K, 6 hours, and H_2O_2 as the oxidant), the CuHY catalyst derived from synthetic precursors achieved a maximum acrylic acid yield of 27.5%, while the natural-resource-based CuHY reached 25.8%, demonstrating comparable performance. Coke formation was minimized by the well-balanced acidity and strong Cu-zeolite interactions, which prevented excessive polymerization of intermediates and carbon deposition. However, minor carbonaceous deposits were detected after multiple reaction cycles, leading to a slight decline in performance. Stability and reusability tests showed that the CuHY catalysts retained good activity across successive cycles, with oxidative regeneration successfully restoring performance by removing carbon residues and maintaining the zeolite structure.

Billy Joy Vargas [96] investigated Cu-modified HZSM-5 catalysts for gas-phase glycerol valorisation, focusing on the impact of Cu impregnation on catalyst structure, product distribution, and coke formation. The CuZSM-5 catalysts were synthesized by wet impregnation with Si/Al ratios of 25 and 100. Characterization by SEM, XRD, NH_3-TPD, and TPR revealed that Cu species were weakly bound to the ZSM-5 framework, resulting in low interaction between Cu and the support. This weak interaction facilitated Cu agglomeration and the progressive reduction of Cu^{2+} to Cu^0 during the reaction, which significantly influenced product selectivity. The catalytic performance of these catalysts is summarized in Figure 7.

ZSM-5(25) and HZSM-5(100) exhibited the highest selectivity for acrolein, with values around 65-70%, while Cu modification led to a substantial shift towards allyl alcohol formation. Notably, CuZSM-5(25) achieved around 93.5% glycerol conversion, with ~55% selectivity to allyl alcohol, indicating that Cu^0 species promoted hydrogen transfer and acrolein reduction to allyl alcohol. This performance shift highlights the critical influence of Cu in modifying product selectivity compared to parent HZSM-5 catalysts, which favoured acrolein formation. Coke

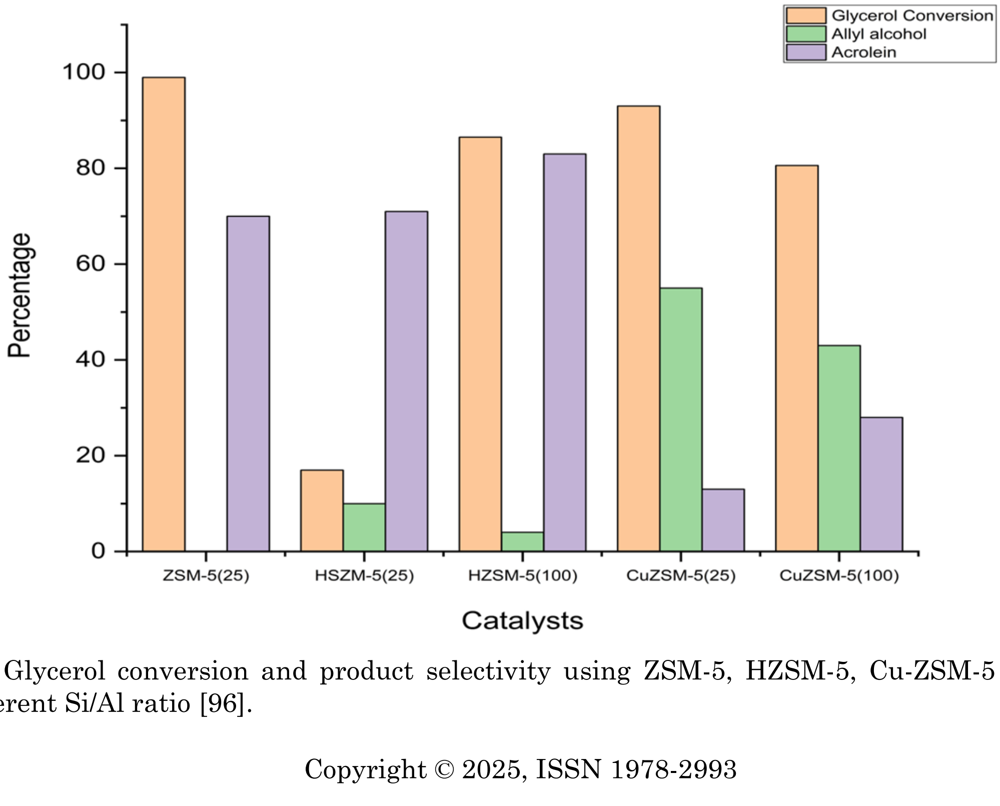


Figure 7. Glycerol conversion and product selectivity using ZSM-5, HZSM-5, Cu-ZSM-5 synthesized using different Si/Al ratio [96].

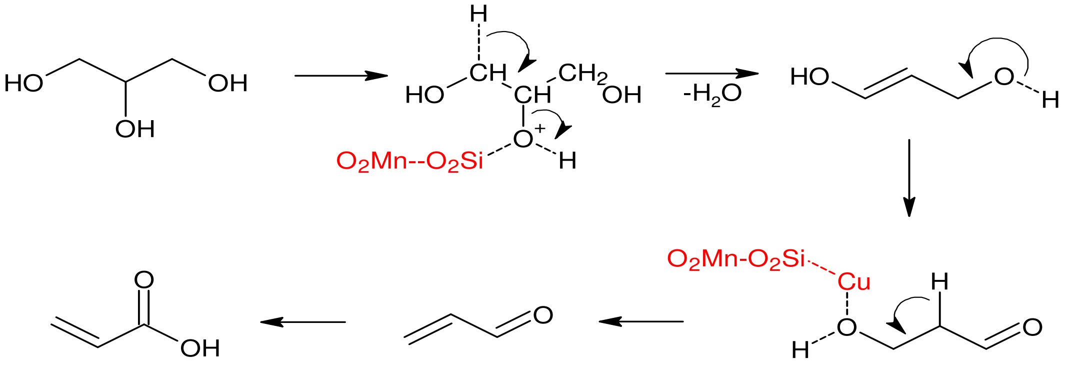
formation was minimal in the CuZSM-5 catalysts compared to HZSM-5. The presence of Cu reduced strong acid site density, lowering the catalyst's susceptibility to coke formation. Moreover, the lower reaction temperature (523 K) further suppressed carbon deposition. After 6 hours, CuZSM-5(25) showed only minor coke accumulation, and oxidative regeneration effectively removed surface carbon residues, restoring catalytic performance.

2.4.2.2 Cu and SiO_2 based catalysts

Bipul Sarkar [106] synthesized Cu nanocluster on nanocrystalline SiO_2-MnO_2 using hydrothermal method. Characterization techniques revealed that the catalyst contained 0.9 wt% of copper, and the catalytic reaction was conducted in a single step in the liquid phase. The results showed that the catalyst achieved a glycerol conversion of 72.8% with an acrylic acid selectivity of 72.1%, both of which are notably high. Importantly, the catalyst demonstrated the ability to be reused four times without deactivation at a maximum temperature of 362 K in the presence of H_2O_2. However, a longer reaction time was necessary to achieve maximum efficiency and yield. The clarified mechanistic pathway for producing acrylic acid involves a catalytic process characterized by two primary functions as shown in Scheme 7. The acidic sites of SiO_2 and hexagonal MnO_2 facilitate the dehydration of glycerol to acrolein, while Cu^+ sites aid in the oxidation of acrolein to acrylic acid. This proposed reaction proceeds through at least two intermediate compounds: 3-hydroxypropionaldehyde and acrolein. Initially, glycerol undergoes a gradual process of water removal, yielding 3-hydroxypropionaldehyde, which is subsequently dehydrated to form acrolein. The final stage involves the rapid oxidation of acrolein to acrylic acid in the presence of H_2O_2 on the Cu sites. Experimental validation using acrolein as a substrate confirmed total transformation and exclusive production of acrylic acid within a timeframe of 3 hours. The rate-limiting step of the reaction is the dehydration phase, where acrylic acid acts as a Brønsted acid, enhancing the overall reaction rate once formed.

2.4.2.3 Copper on MMT-H

Chao Peng Fu [29] synthesized bifunctional Cu_2O-supported montmorillonite (Cu_2O/MMT-H) catalysts via a hydrothermal method for the one-pot transformation of glycerol into acrylic acid (AA) and 1,2-propanediol (1,2-PDO) without requiring external oxygen or hydrogen. Among the catalysts tested, the optimized Cu_2O/MMT-H-150 catalyst exhibited the highest performance, achieving a complete 100% glycerol conversion with 72% selectivity for AA and 10% for 1,2-PDO at 80 °C. Structural characterization using XRD, TEM, and XPS confirmed the well-dispersed Cu_2O particles, while acidity measurements highlighted the synergistic role of Brønsted and Lewis acid sites in promoting glycerol dehydration. The reaction mechanism involved the conversion of glycerol to acrolein through dehydration, followed by oxidation to AA, while acetol was selectively hydrogenated to 1,2-PDO. The catalytic efficiency of Cu_2O/MMT-H was further evaluated against other catalysts, as illustrated in Figure 8. The results showed that Cu_2O/MMT-H significantly outperformed other catalyst systems, exhibiting the highest glycerol conversion (~100%) and AA selectivity (~72%). Cu_2O/MMT also demonstrated high catalytic efficiency with comparable conversion but slightly lower AA selectivity (~65%). In contrast, Cu_2O alone facilitated moderate glycerol conversion (~55%) with a more balanced distribution between AA and 1,2-PDO. Meanwhile, MMT and MMT-H exhibited lower catalytic performance (~55% and 60% conversion, respectively) with minimal selectivity for AA and 1,2-PDO. These findings confirm that the incorporation of Cu_2O onto the montmorillonite support plays a crucial role in enhancing catalytic activity and product selectivity. Additionally, coke formation, a common issue in glycerol conversion, was effectively minimized due to the strong metal-support interactions and the controlled oxidation



Scheme 7. Reaction mechanism for one step conversion using Cu/SiO_2-MnO_2 [106].

environment. Stability tests further demonstrated that the Cu_2O/MMT-H-150 catalyst retained high activity over three catalytic cycles without significant structural degradation.

In conclusion, Cu-based catalysts perform exceptionally well in the one-pot conversion of glycerol to acrylic acid, resulting in high glycerol conversion and significant acrylic acid selectivity. CuHY, Cu/SiO_2-MnO_2, Cu-ZSM-5, and Cu_2O/MMT-H catalysts optimize dehydration and oxidation processes. Reaction conditions, catalyst morphology, and oxidizing agents are crucial factors to consider. Cu-based catalysts' industrial applicability is further enhanced by innovations such as reduced coke formation and extended catalyst lifespan, which position them as a promising solution for sustainable acrylic acid production. Overall, the bifunctional Cu-based catalyst and acrylic acid selectivity is shown in Table 3.

3. Critical Analysis and Future Recommendations

The extensive research on Cu-based catalysts for glycerol transformation highlights their efficiency in hydrogenolysis, oxidation, dehydration, and steam reforming. However, several key limitations persist. One major challenge is catalyst deactivation due to sintering, coke deposition, and leaching, particularly in oxidation and dehydration reactions. While bimetallic catalysts such as Cu-Co, Cu-Ni, and Cu-Zn improve selectivity and stability, their long-term catalytic efficiency requires further optimization. Metal-support interactions play a crucial role in stabilizing active species, yet conventional supports like alumina and silica still suffer from metal aggregation. Recent studies show that doping with Mg, Ce, and Zr oxides enhances catalyst dispersion and reusability, but their scalability remains an issue. Moreover, reaction conditions significantly impact product selectivity—higher temperatures favor C–C cleavage, while mild conditions improve selectivity for desired products such as lactic acid or acrylic acid.

Copper based catalysts showed higher conversion as well as selectivity towards propanediol through hydrogenolysis. Effective synthesis of bi or trimetallic catalysts that can

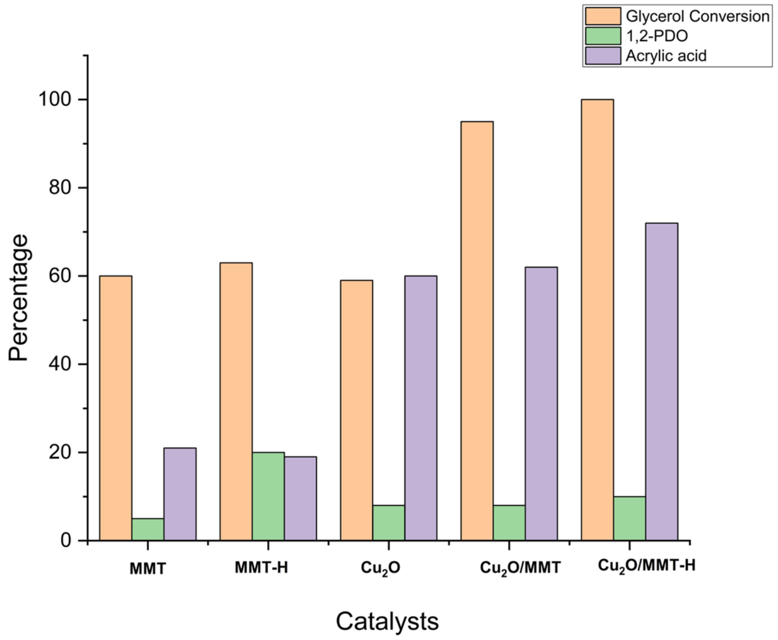


Figure 8. Comparison of different catalysts on glycerol conversion and selectivity for useful products [29].

Table 3. Comparison of different copper-based catalysts used in dehydration of glycerol.

Catalyst	Reaction conditions	Glycerol conversion (%)	Product selectivity	References
Cu/HY Zeolites	362 K, Liquid phase	80	Acrylic acid (27.51%)	[27]
Cu/SiO_2-MnO_2	342 K, Liquid phase	77.1	Acrylic acid (74.7%)	[106]
Cu_2O/MMT-H	352 K, Liquid phase	100	Acrylic acid (72%) 1,2-PDO (10%)	[29]
CuZSM-5(25)	522K, Liquid phase	93	Acrolein (13%) Allyl alcohol (51%)	[96]
CuZSM-5(100)	522K, Liquid phase	80.6	Acrolein (28%) Allyl alcohol (34%)	[96]

enhance copper dispersion as well as decrease coke deposition should be the main focus for future research. In case of oxidation of glycerol, different reaction conditions lead to different intermediates and then different products. To obtain the desired product it's recommended to first check the suitable condition and then use the base and supporting metal that can enhance the oxidative nature of catalysts as alone Cu on any support favors hydrogenolysis or dehydration reaction. In case of steam reforming, Ni-based catalysts showed superior activity, while presence of copper decreases the reduction temperature. Trimetallic catalysts with Ni, Cu and any other suitable metal should be the best catalyst for glycerol steam reforming. Future work should be focused on trimetallic catalysts deposited on any support for effective steam reforming and hydrogen production. For oxidehydration of glycerol, alone copper on acidic support converts the glycerol to acrolein or allyl alcohol but also decreases the coke formation. Since both copper and acidic support like zeolites are effective for dehydration step, the focus should be on bifunctional catalysts capable for both dehydration as well as oxidation. Incorporation of V and Mo can give results because of their selective oxidation.

However, challenges such as catalyst deactivation due to sintering, coke deposition, and leaching remain significant barriers to large-scale applications. Future research should focus on developing highly stable and recyclable Cu-based catalysts, optimizing bifunctional catalyst design for single-pot reactions, and integrating computational and machine learning techniques to accelerate catalyst screening. Additionally, exploring bio-derived supports and green reaction conditions further enhance the sustainability and industrial viability of glycerol valorization. The advancements in Cu-based catalytic systems underscore their potential in driving a circular economy while reducing reliance on fossil-based chemical synthesis.

The choice of catalyst synthesis method, reaction conditions, and support material plays a crucial role in optimizing selectivity and stability. However, difficulties such as catalyst deactivation from sintering, coke deposition, and leaching continue to be serious obstacles to large-scale use. Future research should focus on creating extremely stable and recyclable Cu-based catalysts, enhancing bifunctional catalyst design for single-pot reactions, and using computational and machine learning techniques to speed up catalyst screening. Furthermore, research into bio-derived supports and green reaction conditions would improve the sustainability and industrial viability of glycerol valorisation. The improvements in Cu-based catalytic systems demonstrate its potential to drive a circular economy while lowering dependency on fossil-based chemical synthesis.

4. Concluding Remarks

Copper-based catalysts are highly effective in converting glycerol into various industrially important products, including acetol, acrylic acid, acrolein, propane-1,2-diol, propionaldehyde, lactic acid, and glyceric acid. These products are synthesized through oxidation, dehydration, hydrogenolysis, and steam reforming, with the choice of catalyst and reaction medium playing a crucial role in product selectivity. Acidic catalysts favor dehydration reactions, enhancing acrylic acid yields, while basic environments primarily promote lactic acid formation. A key challenge in glycerol conversion is coke formation and catalytic deactivation. However, copper-based catalysts help mitigate coke buildup, extending catalyst lifespan and enabling repeated reuse. Additionally, bifunctional catalysts—combining acidic and oxidizing properties—are gaining attention for their efficiency in single-step glycerol conversion. Their application in hydrogenolysis and dehydration offers economic advantages by minimizing unwanted by-products, reducing coke formation, improving process efficiency, and increasing the yield of desired products.

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CRedit Author Statement

Author Contributions: S. Ahmed: Methodology, Investigation, Formal Analysis, Data Curation, Writing Draft Preparation, Visualization, Review and Editing; I. Abdullah: Conceptualization, Methodology, Writing, Review and Editing, Supervision; Y.K. Krisnandi: Review and Editing, Supervision. All authors have read and agreed to the published version of the manuscript.

Data Availability Statement

All the data utilized in this study came from publicly available, open-access sources. References are provided for all quoted information to ensure transparency and accessibility.

Conflicts of Interest

There is no conflict of interest.

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