# **Catalysts for Glycerol Reforming**

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The valuable products produced from glycerol transformation have become a research route that attracted considerable benefits owing to their huge volumes as well as a myriad of chemical and biological techniques for transforming glycerol into high-value compounds, such as fuel additives, biofuels, precursors, and other useful chemicals, etc. Steam, aqueous, and autothermal reforming processes have been primarily investigated in glycerol reforming. An update on glycerol reforming is given, with an exclusive focus on the various catalyst's performance in designing reaction operation conditions.

Keywords: glycerol ; biodiesel-biowaste ; reforming ; catalysts ; value-added products

#### 1. Introduction

Glycerol transformation carried out through combustion in the past was unsafe, uneconomic, and technically deficient due to the high temperature employed, unwanted gas emission, and complex product <sup>[1][2]</sup>. Reforming techniques have gained acceptance by industrialists and researchers in view of their efficiencies. Steam, aqueous, and autothermal reforming processes have been primarily investigated in glycerol reforming. The steam reforming reaction is one of the most common reactions used in hydrogen synthesis. Low pressure and very endothermic reactions promote hydrogen selectivity. The aqueous phase reforming (APR) method is regarded as an inexpensive method for producing H<sub>2</sub> due to its lower temperature and lack of vaporizing water and fuels <sup>[3][4]</sup>. Glycerol has a wide product distribution due to its complexity compared to low-chain hydrocarbons or alcohols and to the numerous reactions associated with the reforming process (**Figure 1**). However, this technique creates H<sub>2</sub> without vaporizing the feedstock, resulting in significant energy savings <sup>[5]</sup>. Supercritical water gasification (SCWG)) is a cost-effective method of turning biomass (such as food waste, paper industrial waste, sewage sludge, agricultural waste, and forestry residue) into hydrogen-rich syngas <sup>[6]</sup>. Chemical looping steam reforming (CLSR), which uses oxygen carriers (OCs) as a catalyst, has been widely recognized as a highly effective method for generating hydrogen from catalytic steam reforming <sup>[7]</sup>.



Bio-derived liquids steam reforming produces hydrogen and becomes interested due to the environment and raises hydrogen demand, specifically in proton-exchange membrane fuel cells (PEMFC) <sup>[B]</sup>. The low temperature and high-pressure process conditions, concentrated feed, and acidic catalysts are used for the supercritical water reforming process. High temperature and low pressure, diluted feed, and alkali catalyst are used for gasification <sup>[9]</sup>.

The glycerol reforming and endothermic reactions took place. Hence, the heat needed for the decomposition of glycerol (Equation (1)) is significantly larger than the water–gas shift (WGS) reaction (Equation (2)), where heat is produced as energy. As operated under atmospheric pressure, glycerol steam reforming (Equation (3)) becomes desirable with less fear of protection. Considerably, 1 mol of glycerol converts to produce 7 mol of hydrogen (Equation (2)). Vast amounts of steam and elevated temperature shift a reaction forward to equilibrium, and hence much more  $H_2$  is generated <sup>[10]</sup>.

 $C_3H_8O_3 \leftrightarrow 4H_2 + 3CO$  Decomposition Reaction (1)

 $CO + H_2O \leftrightarrow H_2 + CO_2$  Water Gas Shift Reaction (2)  $C_3H_8O_3 + 3H_2O \leftrightarrow 7H_2 + 3CO_2$  Steam Reforming Reaction (3)

The mentioned noble metal catalysts, Pt <sup>[11][12]</sup>, Ir <sup>[13]</sup>, Ru <sup>[14]</sup>, and Rh <sup>[15][16]</sup>, have shown good resistance to coke and catalytic activity. Vaidya and Rodrigues studied Ni, Pt, and Ru catalysts that promote hydrogen production but cause deactivation by dehydration <sup>[17]</sup>.

# 2. Platinum Catalysts for Glycerol Reforming

Doukkali et al. investigated Pt and/or Ni supported over  $\gamma$ -alumina catalyst for the generation of hydrogen by a method of APR through three preparation methods of catalyst: impregnation method, and sol-gel in acidic and basic medium. Total glycerol transformation occurred with maximum hydrogen production by sol-gel in basic method over PtNiAl (T = 250 °C, P = 30 bar, and WHSV = 2.6 hr<sup>-1</sup>). The acidity of the superficial hydroxyl groups on the -AlOOH surface could be to blame for the lower glycerol conversion into gaseous products, favoring dehydration processes and resulting in more OHCs in the liquid phase. In fact, by blocking surface hydroxyl sites on -Al<sub>2</sub>O<sub>3</sub>, structural alterations in hydrothermal settings were explored to create efficient alumina catalysts for APR processes. The drop in H<sub>2</sub> production could be explained by Ni particle aggregation and reoxidation of Ni particles. These behaviors combined with the adsorption of carbonaceous molecules/organic compounds identified on several of the catalysts could be the primary causes of their deactivation <sup>[11]</sup>.

Pompeo et al. investigated SiO<sub>2</sub> catalyst supported with Pt and Ni through the ion-exchange method for steam reforming to produce hydrogen. The experiment for the steam reforming reaction of glycerol has demonstrated that using 1 Pt and 2 Pt catalysts. The more active and stable catalyst was Pt compared to Ni catalyst. At 350 °C, a complete conversion to gas was achieved with a space-time of 1.66 and 0.88 min, respectively. Due to the fact that the Ni catalyzed the WGS reaction to remove the CO adsorbed on the surface and turn it into CO<sub>2</sub>, the selectivity of gas products was significantly different. Only 3% CO was obtained using the 5 Ni catalyst at 450 °C for 1.66 min. During 40 hr activity test on stream at 350 °C, the 2 Pt catalyst allowed entire conversion to gas without deactivation. It was also suggested that bimetallic catalyst research is required to obtain a system with high selectivity for H<sub>2</sub> and good stability <sup>[12]</sup>.

# 3. Ruthenium Catalysts for Glycerol Reforming

Ru catalyst supported over core-shell metal-ceramic micro composites, created at low temperature and 1 atm pressure through microwave-induced hydrothermal oxidation technique (MW-HTO) of aluminum (Al) metal particles. The highest glycerol turnover ratio was achieved over Al, and Ru-modified  $Al_2O_3$  at Al compared with Ru-modified  $MgAl_2O_4$  and Ru-modified  $Al_2O_3$  catalysts, suggesting that Al metal particles seem to be more effective in preparing  $MgAl_2O_4$  at Al and  $Al_2O_3$  at Al composite structure. The highest selectivity of hydrogen was 70% at Ru/MgAl\_2O<sub>4</sub> at Al catalyst at 550 °C reaction temperature, 1 atm pressure with 870 mm  $g_{cat}^{-1}$  h<sup>-1</sup> feed flow rate. The Ru/MgAl\_2O<sub>4</sub>@Al and Ru/Al\_2O\_3@Al catalysts have 2–3 times the glycerol conversion rates of their Ru/MgAl\_2O<sub>4</sub> and Ru/Al\_2O\_3counterparts, owing to enhanced heat transfer via the metal-ceramic composite catalytic architectures [14]. Glycerol steam reforming process over Ru doped Al\_2O\_3 catalyst. In total, 89.1% glycerol transformed to produce 0.49 (mol/mol) yield of hydrogen at T = 500 °C, P = 0.1 MPa and 1.98 W/FA0. This research has aided in developing reactor systems for producing hydrogen from glycerol steam reforming [15].

#### 4. Rhodium Catalysts for Glycerol Reforming

Martinez et al. studied hydrogen production from glycerol reforming using fluorite-type oxides CeZr-CoRh prepared by the sol-gel method. 100% glycerol was transformed to produce 86% hydrogen yield at 650 °C. The activity data showed that the catalysts' ability to activate H<sub>2</sub>O under reaction circumstances was connected to selective H<sub>2</sub> generation. This process guarantees that the by-products are steam reformed to H<sub>2</sub>. As this capacity deteriorates, H<sub>2</sub> generation decreases, steam reforming capability reduces, and glycerol decomposition takes over. In this scenario, the creation of condensable compounds, such as hydroxyacetone, acetaldehyde, and acrolein, was aided by the production of CO, CH<sub>4</sub>, and C<sub>2</sub>H<sub>4</sub> <sup>[18]</sup>.

Lee and Doohwan synthesized Core-shell MgAl<sub>2</sub>O<sub>4</sub> metal-ceramic composites at Al catalyst by hydrothermal method, and Rh (1, 3, and 5 wt.% loadings) modified MeAl<sub>2</sub>O<sub>4</sub> catalysts were synthesized by incipient wetness impregnation method. Then, 100% glycerol transformed to produce Rh/MgAl<sub>2</sub>O<sub>4</sub> at Al catalyst [T = 450 °C, and WHSV = 34,000 mL  $g^{-1}$  h<sup>-1</sup>]. The high surface area and complex surface morphological properties of MeAl<sub>2</sub>O<sub>4</sub>@Al as a catalyst enhance increased Rh cluster dispersion while hindering their thermal sintering during glycerol steam reforming processes at high temperatures. Rh/MeAl<sub>2</sub>O<sub>4</sub>@Al had a 20-30% greater glycerol conversion turnover rate than Rh/MeAl<sub>2</sub>O<sub>4</sub> (both Rh cluster sizes are similar), indicating that the facilitated heat and mass transfer through the unique MeAl<sub>2</sub>O<sub>4</sub>@Al microstructures cooperated constructively for the reactions. These are being explored as future research topics <sup>[19]</sup>. Baca et al. studied Rh, Ni, and Co metal-doped over Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-TiO<sub>2</sub> (AZT) for syngas production through carbon dioxide reforming of glycerol. Then, 1 wt.% Rh doped AZT, 5 wt.% Ni-doped AZT, and 5 wt.% Co-doped AZT catalysts were synthesized through the incipient impregnation method. The glycerol transformation was 80% achieved with 24% maximum hydrogen yield on Rh doped AZT catalyst at 750 °C. Glycerol Conversion reduced in the given sequence: 1% Rh doped AZT > 5% Ni doped AZT > 5% Co-doped AZT. Rh doped AZT catalyst remained stable due to fewer coke formations and a shortage of sintering. During the 72-h testing, the decrease in CO<sub>2</sub> conversions was less than 13%, indicating the remarkable stability of Rh/AZT and Ni/AZT [16]. Delparish et al. produced syngas from glycerol by oxidative steam reforming. The impregnation technique was used to prepare 2 wt.% of Rh doped Al<sub>2</sub>O<sub>3</sub> catalysts. The glycerol was completely converted at 550 °C, and maximum hydrogen yield was achieved at 700 °C. Temperature influenced product distribution by increasing the amount of combustible species in the product mixture that were oxidized. The effect became more severe when C/O was lowered from 1.125 to 0.75. The promotion of WGS in the presence of steam was confirmed by reducing S/C from 5 to 4 and then from 4 to 3, which resulted in monotonically decreased H<sub>2</sub> and CO<sub>2</sub> yields and an increase in CO yield <sup>[20]</sup>. Danga et al. studied glycerol and ethanol for dry reforming with CaCO<sub>3</sub> to produce syngas. A series of metal components, such as nickel, iron, copper, platinum, palladium, ruthenium, and rhodium, were used to promote dry reforming. In these series of metals, nickel became a promising candidate due to its outstanding performance, as well as its low price. Here, 100% glycerol conversion along with approximate 92% syngas selectivity was achieved on 10 wt.% Ni contained in CaCO<sub>3</sub> catalyst [T = 550 °C, and P = 1 atm.]. The CO<sub>2</sub> released from the CaCO<sub>3</sub> catalyst eliminated cokes and attained stability. The direct use of CaCO<sub>3</sub> in this process was discovered viable, and the CO<sub>2</sub> generated from CaCO<sub>3</sub> decomposition may be used to modify the H<sub>2</sub>/CO ratio. Ni was the most promising contender among the active metals, including Ni, Co, Fe, Cu, Rh, Ru, Pt, and Pd, due to its great performance and low price. Over the 10 Ni–CaCO<sub>3</sub> catalyst, 100% conversion of glycerol and ethanol, 92% summed H<sub>2</sub> and CO selectivity, and an H<sub>2</sub>/CO ratio of 1.2 could be reached under ideal conditions. Meanwhile, the robustness of this integrated technique was proved over five dry reforming-regeneration cycles. The findings suggest a novel way to use CO<sub>2</sub> in the form of carbonates [21].

### 5. Nickel Catalysts for Glycerol Reforming

The catalyst based on Ni becomes a choice for the reason that the metallic sites of Ni work well enough in water gas shift reaction as well as C–H and C–O cleavage. Nevertheless, the tremendous challenge is how to control catalysts' deactivation triggered by sintering and deposition of carbon at catalyst active sites under optimum operating conditions <sup>[22]</sup>. Hence, various protocols <sup>[14][23]</sup> and supports like Al<sub>2</sub>O<sub>3</sub> <sup>[24][25][26]</sup>,  $ZrO_2$  <sup>[27][28][29]</sup>,  $CeO_2$  <sup>[30][31]</sup> were generated.

Yancheshmeh et al. suggested a new and simple method for preparing Ni-modified  $Al_2O_4$  spinel catalyst from the steam reforming technique of glycerol for the production of hydrogen. Solvothermal preparation method was used for catalyst represented as NiAl-G1, and the coprecipitation preparation method was used for catalyst described as NiAl-G2 as well as NiAl-C (NiAl\_2O\_4 catalyst synthesized via the coprecipitation method was designated as NiAl-C). The maximum hydrogen yield was 76.38% achieved with 95.42% maximum glycerol transformation on NiAl-G2 catalyst 630 °C, 1 atm, and 19,600 cm<sup>3</sup>/g<sub>cat</sub>/h space velocity reaction conditions. By creating an oxidative environment surrounding nickel active sites, the creation of a well-dispersed CeAlO<sub>3</sub> phase slowed the growth of filamentous carbon on the nickel surface and aided the gasification of carbon deposits. During the 16-h SRG process, the catalytic activity was maintained, and the rate of coke generation was as low as 0.0004  $g_{coke}g_{catal}h^{-1}$ . These findings support Ce/NiAl\_G2's potential as a catalyst for the

SRG reaction <sup>[31]</sup>. Ni added to CaO-modified attapulgite (CaO–ATP) catalyst from reforming of glycerol for hydrogen manufacturing. Using the impregnation technique, Ni-Al<sub>2</sub>O<sub>3</sub>, Ni-ATP, and Ni-CaO-ATP catalysts can be synthesized. A maximum hydrogen yield of 85.3% was achieved on Ni-CeO-ATP catalyst with 93.71% glycerol conversion at T = 600 °C and GHSV = 1 h<sup>-1</sup> reaction condition. Stability of the catalyst showed that ATP had better resistance to carbon deposition compared to alumina and CaO addition further reduced the production of carbon. Due to its unusual intermediate structure, ATP outperformed Al<sub>2</sub>O<sub>3</sub> as a carrier. When CaO was utilized as an ATP modifier, it promoted the water gas shift reaction, resulting in increased hydrogen yield, hydrogen selectivity, and a reduction in CO production. The stability results revealed that ATP is more resistant to carbon deposition than Al<sub>2</sub>O<sub>3</sub>, and the addition of CaO lowered carbon formation even more. As a result, a Ni-based catalyst supported on a CaO-modified attapulgite could be a potential material for efficient glycerin steam reforming to create H<sub>2</sub> <sup>[32]</sup>.

Wu et al. explored the mesoporous Ni-Cu/CeO<sub>2</sub> for the production of renewable hydrogen via APR of glycerol. The C-C breakage of glycerol benefits from Ni, but Cu can amplify the WGS reaction. Cu metal's surface is amenable to adsorption of carbonyl radical following glycerol's decarbonylation and hydroxyl free radical in the solution, which facilitates the reaction. Consequently, the addition of Cu element enhanced the proportion of H<sub>2</sub> and CO<sub>2</sub> in the overall gas. It was discovered that increasing the catalyst's Cu concentration improved hydrogen production (125.08 to 195.57  $\mu$ mol min<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>). Additionally, the CO<sub>2</sub> in overall gas was absorbed by the addition of CaO and it lowers the activation energy. Hence, 1Ni2Cu/CeO<sub>2</sub> + 0.2gCaO catalyst shows H<sub>2</sub> production rate increased from 168.97 to 301.92  $\mu$ mol min<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>. Therefore, improved H<sub>2</sub> production as a result of the inclusion of Cu and CaO <sup>[3]</sup>.

Liu et al. studied MgO supported Ni-Co bimetallic catalyst prepared by sol-gel method followed by calcination. The resulted catalyst examined the APR of glycerol for hydrogen production. After the addition of MgO support,  $H_2$  production activity improves by 1.5 times compared to pure Ni-Co bimetallic catalyst. Due to the in-situ adsorption and removal of CO<sub>2</sub>, the WGS reaction was further stimulated with the addition of CaO, and the methanation reaction was inhibited, resulting in the catalyst having a high activity of hydrogen production. The stability test also showed that the gelatinous MgO supports had an impact on the catalyst's activity and stability <sup>[4]</sup>.

Veiga et al. studied crude glycerol steam reforming with oxalic acid to synthesize Ni-doped La-Zr catalysts. Ni-doped La-Zr catalysts are catalyst was prepared with the coprecipitation method at different calcination temperatures. Ni-doped La-Zr catalysts calcined at 850 °C achieved 90% hydrogen yield and 99.9% glycerol conversion. The catalyst prepared at 850 °C calcination and operated at 650 °C reaction showed higher catalytic stability, activity, and better resistance to carbon formation. The greatest performance seen for Ni-850 catalysts is mostly due to the development of oxygen vacancies caused by nickel substitution into the La-Zr lattice during calcination, favoring the oxidation of carbon deposits throughout the process <sup>[33]</sup>.

Charisiou et al. investigated Ni supported over  $Y_2O_3$ –Zr $O_2$  catalyst for the glycerol steam reforming. The catalyst synthesized through the impregnation technique was Ni modified Zr and Ni modified YZr. The maximum transformation was 90% achieved at 700 °C, and the maximum H<sub>2</sub> selectivity was 82% achieved at 450 °C over Ni modified YZr catalyst. The research on spent catalyst revealed the less carbon deposition on Ni/Zr (Ni modified Zr) catalyst as it was more graphitic in nature and higher carbon deposition on Ni/YZr spent catalyst. The addition of  $Y_2O_3$  stabilized the ZrO<sub>2</sub> tetragonal phase, resulted in more easily reducible NiO nanoparticles, increased the  $O_2$  storage capacity of the support and the medium strength acid sides of the catalyst, and, despite having a higher concentration of basic sites, the Ni/YZr presented more stable monodentate carbonates. Allyl alcohol, acetaldehyde, acetone, acrolein, acetic acid, and acetol were the primary liquid products detected for both catalysts. Although higher amounts of carbon were deposited on the Ni/YZr spent catalytic sample (0.70 g<sub>coke</sub>/g<sub>catal</sub> compared to 0.51 g<sub>coke</sub>/g<sub>catal</sub> for the Ni/Zr catalyst), the addition of  $Y_2O_3$  on to the ZrO<sub>2</sub> support resulted in structures with lower crystallinity (amorphous carbon) that are more easily oxidized during the reaction. The coke deposits found on spent Ni/Zr catalysts, on the other hand, were graphitic structures with little flaws, resulting in the deadly encapsulation of Ni particles <sup>[29]</sup>.

# 6. Cobalt Catalysts for Glycerol Reforming

Cobalt (Co) played an extensive role in the synthesis of hydrogen as many researchers represented this glycerol steam reforming. Ghungrud and Vaidya studied the synthesis of hydrogen by sorption–enhanced steam reforming technique (SESGR) on a Co-promoted hydrotalcites catalyst. 92.8% maximum glycerol conversion and 89.7% hydrogen yield were achieved over Co-Ca-HTlc catalyst represented as HM2 at T = 823 K, GHSV = 5600 mL g<sup>-1</sup> h<sup>-1</sup>. Ca, Co, and Zn promoted hydrotalcite catalysts were manufactured through the precipitation method. HM2 contained Cu showed the best performance for the dehydrogenation process, and it was known that basic sites promoted the dehydrogenation process. At 550 °C, Cu-bearing materials showed a long pre-breakthrough duration (40 min) and high H<sub>2</sub> purity (93.1 mol%). They

were also better adsorbents, removing 1.1 mol CO<sub>2</sub>/kg sorbent at 550 °C. Over 20 cycles of adsorption and regeneration, the cyclic stability of materials was examined. The potential of customized HTlc-materials for better H<sub>2</sub> production from the SESGR process is explored in this work <sup>[34]</sup>.

A feasible reaction pathway for the SESGR process was provided based on the product composition (**Figure 2**). Glycerol undergoes dehydration hydrogenation reactions upon adsorption, resulting in acetaldehyde. The adsorbed acetaldehyde was then further hydration-dehydrogenated into acetic acid. Over Co metal, acetic acid undergoes C-C bond breakage, yielding  $H_2$ , CO<sub>2</sub>, CO, and CH<sub>4</sub>. The basic catalyst promotes rapid dehydrogenation, which prevents the generation of olefins and carbon deposition. CO and CH<sub>4</sub> are converted to  $H_2$  and CO<sub>2</sub> by WGS reaction and steam reforming processes, with trace amounts of CO remaining <sup>[34]</sup>.



Figure 2. Plausible reaction mechanism for SESGR.

Zhou et al. investigated NiCo modified CNTs bimetallic catalysts with an appropriate distribution of Ni, as well as Co, metal for synthesizing hydrogen through the impregnation technique in which metal precursors were injected into the cave of CNTs by ultra-radiations. At 450 °C and 1 atm, 100% glycerol transformation was achieved with 91.4% H<sub>2</sub> selectivity over Ni(i)Co(i)/CNTs catalyst. Ni(i)Co(i)/CNTs exhibited the best stability and catalyst performance. Although the Ni and Co oxides were only partially reduced, the location of metal species had a significant impact on reducibility. The synergetic effect between Ni and Co species was found in Ni(i)Co(i)/CNTs and Ni(o)Co(o)/CNTs, where they had the same distribution on the internal or external wall. Sintering of active sites was markedly simpler on the external wall of CNTs, causing the catalyst to deactivate quickly and become less reactive for the water gas shift process. The result of this study revealed that there is a new and straightforward method for assembling bimetallic catalyst systems. The Ni-based bimetallic catalysts might be used to reform mono/multi-alcohols such as ethanol, ethylene glycol, sorbitol, and other organic wastes from second-generation biorefineries, as well as biogas and other organic wastes [11].

Al-Salihi et al. investigated Co-Ni-MgO-based SBA-15 nano-catalysts for the glycerol steam reforming for hydrogen manufacturing. The one pot hydrothermal method was used to create different mesoporous catalysts, such as Co-SBA-15, Ni-SBA-15, Co-MgO-SBA-15, Ni-MgO-SBA-15, and Co-Ni-SBA-15 and bimetallic 10 wt.% Co-5 wt.% Ni modified SBA-15 catalyst synthesized by the impregnation method. A glycerol conversion rate of 100% along with 82.8% hydrogen selectivity was achieved over 10 wt.% Co-5 wt.% Ni modified SBA-15 catalyst at 650 °C. At a low temperature (450 °C), the one-pot catalysts showed 50% glycerol conversion compared to 70% for the impregnated catalyst, while both yielded 62% H<sub>2</sub> selectivity. Cobalt-based SBA-15 catalysts have superior GSR activity and stability than nickel-based catalysts in monometallic catalysts. The addition of MgO to Co-SBA-15 improved glycerol conversion (up to 99%) and catalyst stability. The addition of MgO to Ni-SBA-15 reduced the quantity of carbon deposition on the catalysts by as much as 66%, according to TGA-TPO analyses of spent catalysts. It's worth noting that under the experimental conditions, all of the catalysts examined at the optimum temperature of 650 °C demonstrated a remarkable hydrogen selectivity of 70% <sup>[10]</sup>.

Duo et al. developed chemical looping steam reforming process for glycerol conversion to hydrogen over Al-MCM-41 and SBA-15 well-order mesoporous OCs containing NiO and CeO<sub>2</sub> nanoparticles <sup>[Z]</sup>. It was discovered that the NiO and CeO<sub>2</sub> in the OCs were reduced by glycerol, and the reduced OCs were in charge of producing hydrogen. It was shown remarkable stability in 60 redox cycles (180 h), and the carbon conversion and hydrogen selectivity were both over 60% and 85%, respectively. Oxygen transport was enhanced by heavily loading mesoporous MCM-41 and SBA-15 with NiO and CeO<sub>2</sub>, which also produced outstanding redox CLSR cycles and long-term stability <sup>[Z]</sup>.

The summary of some more reported literature related to glycerol reforming over various catalysts to produce hydrogen is represented in **Table 1**. Noble metal catalysts, such as Pd, Ru, Ir, Rh, and Pt, are known for their high catalytic activity, which results in good performance and coke resistance. Other catalysts, such as Ni, Co, and Cu, on the other hand, are less expensive and more readily available and have a desirable catalytic activity for boosting hydrogen production. Their stability, on the other hand, is undesirable since the coking process frequently deactivates them. As a result, developing a highly active and stable catalyst requires the employment of metals as catalysts in combination with the proper selection of support (based on porosity, redox characteristics, and thermal stability, among other factors). Alumina and silica are the most common catalytic supports in research, but some catalysts can also be supported on active carbon, nanotubes, mesoporous carbon, nanoparticles, and other materials. Due to its high specific surface and thermal stability, alumina is the preferred and most used support for this purpose. However, carbon deposition tends to render it inactive. The optimal bimetallic catalyst must possess excellent thermal strength, mechanical resistance, and redox characteristics to produce H<sub>2</sub> with high selectivity.

S. No.	Catalyst	Reaction Condition/Reactor	X (%)	S (%)	Y (%)	References
	Co-Ni-MgO-based SBA-15	T = 650 °C				
1	(one-pot hydrothermal and impregnation method)	P = 1 atm	100	82.8	82.8	[10]
		(Fixed bed reactor)				
	Pt and/or Ni supported over y-alumina	T = 250 °C				
2	(Sol–gel method)	P = 30 bar	100	-	-	[ <u>11</u> ]
		WHSV = 2.6 $h^{-1}$				
	Pt and Ni supported $SiO_2$	T = 350 °C				
_	(Ion exchange method)	P = 1 atm	100 70			[12]
3		Feed flowrate = 0.5 cm <sup>3</sup> h <sup>-1</sup>		70	70	
		(Fixed bed reactor)				
		T = 500 °C,				
		P = 0.1 MPa	89.1			<u>[15]</u>
4	Ru doped Al <sub>2</sub> O <sub>3</sub>	Cat. Wt. = 0.1 g		-	-	
		W/FA0 = 1.98				
		T = 650 °C,				
_	CeZr-CoRh	P = 0.1 MPa	100	86	86	[18]
5		Cat. Wt. = 55 mg				
		WHSV = 8.4 $g_{gly}g_{cat}^{-1}$				
		T = 723 K			[19]	
6	Rh modified MeAl <sub>2</sub> O <sub>4</sub> at Al	WHSV = 34,000 mL g <sup>-1</sup> h <sup>-1</sup>	100	-	-	(10)
7	Rh/Al <sub>2</sub> O <sub>3</sub>	T = 823 K				[20]
	(Impregnation technique)	WHSV = $4.8 \times 10^3$ N mL/g <sub>cat</sub> min	100	-	-	
8		T = 550 °C				[21]
	Ni/CaCO <sub>3</sub>	P = 1 atm	100	92	92	

Table 1. Hydrogen production from glycerol reforming using various catalytic systems under optimal reaction conditions.

S. No.	Catalyst	Reaction Condition/Reactor	X (%)	S (%)	Y (%)	References
	Rh/y—Al <sub>2</sub> O <sub>3</sub> @CeO <sub>2</sub> , MgO, La <sub>2</sub> O <sub>3</sub>	T = 600 °C				
	(Co-precipitation method)	P = 1 atm				
9		GHSV = 5000	90	78	78	[24]
		N mL g <sup>-1</sup> hr <sup>-1</sup>				
		(Fixed bed reactor)				
10	Ni supported over Y <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub>	T - 700 °C		01	82	[ <u>29]</u>
10	(Impregnation technique)	1 = 700 °C	90	91		
	Ni	T = 630 °C				
11	modified Al <sub>2</sub> O <sub>4</sub>	P = 1 atm press., WHSV = 19,600 cm <sup>3</sup> /g <sub>cat</sub> /h	95.42	80	76.4	[31]
	(Coprecipitation method)					
	Ni added to CaO—modified attapulgite	T = 600 °C				
12	(Impregnation method)	Cat. Wt. = 0.5 g	93.7	91	85.3	[32]
		$GHSV = 1 h^{-1}$				
10	Co-promoted hydrotalcite	T = 550 °C	02.0	06.7	89.7	[ <u>34]</u>
13	(Precipitation method)	GHSV = 5600 mL g <sup>-1</sup> h <sup>-1</sup>	92.8	96.7		
	NiCo modified CNTs bimetallic catalysts	T = 450 °C				
14	(Impregnation method)	P = 1 atm	100	91.4	91.4	[35]
		(Fixed bed reactor)				
		T = 200–240 °C				
15	Pt/Al <sub>2</sub> O <sub>3</sub>	P = 16–33.5 bar	84	16.8	14.1	[36]
		(Batch reactor)				
		T = 240 °C				
16	Pt/Al <sub>2</sub> O <sub>3</sub>	P = 42 bar	34	36.8	12.5	[37]
		(Batch reactor)				
	Pt/SiO <sub>2</sub>	T = 300–400 °C				
17	(Sol-gel method)	P = 1 atm	96.8	90	89.7	[38]
		(Microchannel reactor)				
	Pt/y—Al <sub>2</sub> O <sub>3</sub> , SiO <sub>2</sub> & silica—alumina	T = 225 °C				
10	(Impregnation method)	P = 29 bar	11.0	70		[39]
18		WHSV = 4.2 h <sup>-1</sup>	11.9 73	73	8.9	
		(Fixed bed reactor)				
	Pt/ZrO <sub>2</sub>	T = 350 °C				
19	(Impregnation method)	P = 29 bar	100	69	6.9	[40]
		(Fixed bed reactor)				
	Pt/Al <sub>2</sub> O <sub>3</sub> , Puralox, Catapal B	T = 250 °C				
	(Impregnation method)	Cat. Wt. = 300 mg			OF	[41]
20		Feed flowrate = 0.5 mL/min	5/	-	85	
		(Fixed bed reactor)				

S. No.	Catalyst	Reaction Condition/Reactor	X (%)	S (%)	Y (%)	References
	Pt—Re/C	T = 225 °C				
01	(Impregnation method)	P = 420 psi	90.4	26.1	22	[ <u>42]</u>
21		WHSV = 5 $hr^{-1}$	05.4	20.1	23	
		(Fixed bed reactor)				
	10 Ni/Al <sub>2</sub> O <sub>3</sub> /5 CeO <sub>2</sub>	T = 550–800 °C				
22	(Impregnation method)	<b>P</b> = 1 atm	100	99 C	96	[43]
22		WHSV = 10 hr <sup>-1</sup>	100	00.0	00	<u> </u>
		(Fixed bed reactor)				
	Ru-Mg-Al hydrotalcite- mixed oxides	T = 400–700 °C				
	(Impregnation method)	P = 1 atm	45		40 5	[44]
23		GHSV = 69,000 h <sup>-1</sup>	45	90	40.5	
		(Fixed bed reactor)				
	Ru/Al <sub>2</sub> O <sub>3</sub>	T = 400–600 °C				
	(Wet co-impregnation method)	P = 1 atm				
24		Cat. Wt. = 200 mg	100	80	80	[45]
		W/F = 1.05 mg min mL <sup>-1</sup>				
		(Fixed bed reactor)				
	Ru/C	T = 500 °C				
25	(Impregnation method)	P = 1 atm	94.6	99.8	94.5	[46]
		(Fixed bed reactor)				
	Mg(Al)O/Ru	T = 450–650 °C				
26	(Impregnation method)	P = 1 atm	97	96	90	[47]
		(Fixed bed reactor)				
	C/Pt and Pt/Ru	T = 225 °C				
27	(Impregnation method)	P = 1 bar	24	-	-	[ <u>48]</u>
		(Fixed bed reactor)				
	Rh/ZrO <sub>2</sub> , Rh/CeO <sub>2</sub>	T = 650–750 °C				
28	(Impregnation method)	Cat. Wt. = 20 mg	79	30.6	24.2	[49]
		(Fixed bed reactor)				
	Rh/Al <sub>2</sub> O <sub>3</sub>	T = 250 °C				
	(Impregnation method)	P = 50 bar				
29		Cat. Wt. = 250 mg	82	85.2	69.9	[50]
		WHSV = 2.45 h <sup>-1</sup>				
		(Fixed bed reactor)				
	Pt and Pt-Rh/ $\alpha$ -Al <sub>2</sub> O <sub>3</sub>	T = 230 °C				
30	(Impregnation method)	Cat. Wt. = 300 mg	67	1.67	1.12	[51]
		(Batch reactor)				

S. No.	Catalyst	Reaction Condition/Reactor	X (%)	S (%)	Y (%)	References
	Rh and Ni/y—Al <sub>2</sub> O <sub>3</sub>	T = 450-800 °C				
31	(Impregnation method)	P = 1 atm	69	50	34.5	[52]
		GHSV = 5000 to 30,000 mL <sub>gly</sub> h <sup>-1</sup> mL <sub>cat</sub> <sup>-1</sup>				
	Ni-La-Ti oxide	T = 500–650 °C				
	(Coprecipitation method)	P = 1 bar				
32		Cat. Wt. = 0.1 g	99.7	90.3	90	[53]
		WHSV = $3 h^{-1}$				
		(Fixed bed reactor)				
	NiAl <sub>2</sub> O <sub>4</sub>	T = 600 °C				
33	(Impregnation method)	Feed flowrate = 2.5 mL/h	99	98.9	98	[ <u>54]</u>
		(Fixed bed reactor)				
		T = 650–850 °C				
34	La-promoted Ni/Al <sub>2</sub> O <sub>2</sub>	P = 1 atm	96	98.9	95	[55]
•	La-promoted NI/AI <sub>2</sub> O <sub>3</sub>	WHSV = $3.6 \times 10^4 \text{ mL}^{-1} \text{ h}^{-1}$		00.0		
		(Fixed bed reactor)				
	$La_{1-x}Ca_xNiO_3$ perovskite-oxides	T = 550 °C				
	(Impregnation method)	P = 1 atm				
35		Cat. Wt. = 200 mg	100	80	80	<u>[56]</u>
		WHSV = $2.5 \text{ hr}^{-1}$				
		(Fixed bed reactor)				
	Ni and Ni—Co/alumina	T = 300–700 °C	-	-	83	[ <u>57]</u>
36	(Impregnation method)	P = 1 atm				
		WHSV = 10 hr <sup>-1</sup>				
		(Fixed bed reactor)				
	Ni/ $\alpha$ —Al <sub>2</sub> O <sub>3</sub> and $\alpha$ —Al <sub>2</sub> O <sub>3</sub> modified by ZrO <sub>2</sub> and CeO <sub>2</sub>	T = 600 °C				
37	(Impregnation method)	P = 1 atm	90	95.6	86	<u>[58]</u>
		Feed flow rate = 0.022 cm <sup>3</sup> min <sup>-1</sup>				
		(Fixed bed reactor)				
		T = 700 °C				
38	LaNiO <sub>3</sub> and LaCoO <sub>3</sub>	<b>P</b> = 1 atm	100	98	98	<u>[59]</u>
		(Fixed bed reactor)				
	0.25 CoAl, 0.625 CoAl	T = 260 °C				
39	C0 <sub>3</sub> O <sub>4</sub>	P = 5 MPa	98 29	29	10	[60]
		WHSV = 24.5 $h^{-1}$				
		(Fixed bed reactor)				
	Co-Ce/Hap	T = 750 °C				
40	(Impregnation method)	P = 1 atm	99	79	7.2	[61]
		(Fixed bed reactor)				

S. No.	Catalyst	Reaction Condition/Reactor	X (%)	S (%)	Y (%)	References
	Co/SBA-15 with Zr, Ce and La	T = 500–600 °C				
41	(Impregnation method)	P = 1 atm	100	72	72	[62]
		WHSV = 7.7 h <sup>-1</sup>				
	La <sub>x</sub> -Ce <sub>y</sub> -CoO <sub>3</sub>	T = 700 °C				
42	(Co—precipitation method)	P = 1 atm	100	68	68	[63]
		(Fixed bed reactor)				
	Co/Al <sub>2</sub> O <sub>3</sub>	T = 450–650 °C				
42	(Impregnation method)	<b>P</b> = 1 atm	65	80	50	[64]
43		GHSV = $5 \times 10^4 \text{ mL g}_{cat}^{-1} \text{ h}^{-1}$	05		52	
		(Fixed bed reactor)				
	Ceria/Ir, Co and Ni	T = 250–600 °C				
44	(deposition—precipitation method)	P = 1 atm	100	05	05	[65]
44		GHSV = 11,000 mL $g_{cat}^{-1} h^{-1}$	100	00 00	_	
		(Fixed bed reactor)				

X = Conversion, S = Selectivity, Y = Yield.

The knowledge of various catalysts, such as platinum, ruthenium, rhodium, nickel and cobalt-based catalysts for glycerol reforming was reviewed and cataloged. Today, researchers and engineers are exploring new technologies, highly novel and tolerant catalysts, improving reactor systems and activation methods, and coordinating the chemical and biological catalysts to improve the weaknesses involved with each catalyst. The modern improvement in technology and economical use of crude glycerol in hydrogen fuel production clearly demonstrate that crude glycerol may play a critical part in the biorefining industry's fulfillment.

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