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Recent advancements in catalytic conversion of glycerol into propylene glycol: A review

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ABSTRACT

The renewability of bio-glycerol has made it an attractive platform for the production of diverse compounds. Selective hydrogenolysis of glycerol to propylene glycol (PG) is one of the most promising routes for glycerol valorization, since this compound is an important chemical intermediate in a number of applications. In this article, advancements in the catalytic conversion of glycerol into propylene glycol are reviewed, which include advances in process development, effects of preparation and activation methods on catalytic activity and stability, and the performance of various types of catalysts. The feasibility of using bio-hydrogen and the challenges of utilizing crude glycerol for glycerol hydrogenolysis are also discussed.

1. Introduction

Depletion in fossil fuel reserves and its increasing impact on the environment have intensified interest in the development of renewable fuels mainly bio-ethanol and bio-diesel (1, 2). Currently, biodiesel is produced by the transesterification of triglycerides with simple alcohols such as methanol or ethanol catalyzed by alkaline or acidic catalysts. Glycerol is produced as a byproduct of this process, comprising ~10 wt% of the product stream. The increased production of biodiesel globally has resulted a large surplus of glycerol that has caused the saturation of the glycerol market (3). Therefore, new economical ways of using glycerol for value-added products must be developed to strengthen the sustainable development of the biodiesel industry.

The presence of three hydroxyl groups in glycerol makes it a versatile compound with a wide range of properties and it is used in a wide variety of applications, particularly in cosmetics, pharmaceuticals and food industries (4). Moreover, glycerol can be converted into different high-value chemicals via chemical and biochemical processes (5). In recent years only a few applications have been identified where glycerol could be utilized on a large scale. Hydrogenolysis of glycerol to propylene glycol (PG) is one of these

applications which have attracted major attention both in research and industrial communities. It is quite evident from the increase in the number of academic and industrial papers, patents and meeting abstracts relating to glycerol hydrogenolysis published in recent years (Fig. 1).

Propylene glycol (PG) is a non-toxic chemical, produced by selective hydrogenolysis of glycerol. It is extensively used as a monomer for polyester resins, as an antifreeze agent, in liquid detergents, paints, cosmetics, food, etc. (Fig. 2) (6). Worldwide production of propylene glycol is given in Fig. 3. The current global production of propylene glycol is 2.18 million tons per year which is mainly produced from propylene oxide and sold at $1.0–2.2 per kg (3, 7). The world's PG market is growing at a rate of 4.5% per annum and is expected to reach 2.56 million tons by 2017 (7) Dow Chemicals, Eastman Chemical, Lyondell Chemical, Global Bio-Chem Technology Group, Ineos Oxide, Archer Daniels Midland Co., SKC Chemicals Group, Arrow Chemical Group Corp., BASF AG, and Huntsman Corp are the major producers for PG.
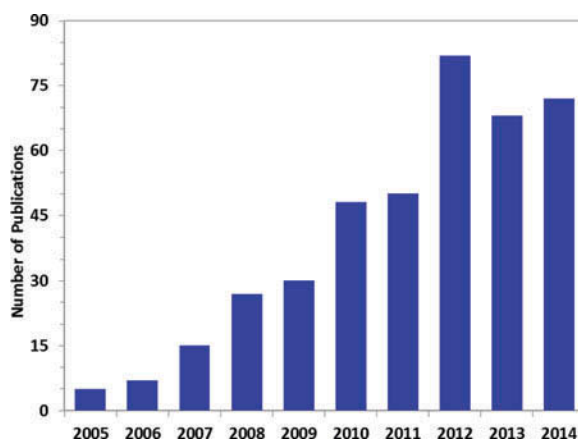
Figure 1. Annual number of publications (articles, patents and meeting abstracts) on the concept of glycerol hydrogenolysis (searched from database Scifinder as "glycerol" and "hydrogenolysis").
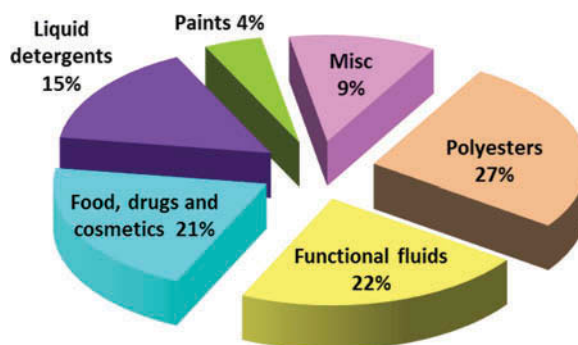

Figure 2. Applications of propylene glycol in different fields (6) (Misc: Tobacco humectants, flavors and fragrances, and animal feed).
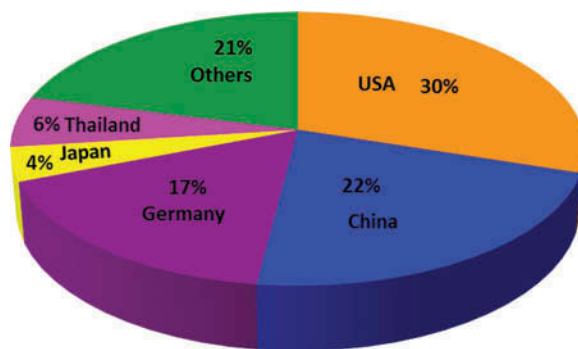
Figure 3. World scenario for the production of propylene glycol (7).

The conversion of glycerol to propylene glycol is usually carried out in presence of metallic catalysts and hydrogen either in a batch or a continuous-flow reactor. It is a selective hydrogenolysis process which proceeds via the removal of an oxygen atom by the addition of hydrogen. The challenging part of this process is the selective scission of one of the primary C-O bond over C-C or C-O (secondary) bonds. The latter cleavages result in the formation of degradation products (ethylene glycol, ethanol, methanol or methane) or 1,3-propanediol, respectively. The overall reaction is usually represented via two main steps (8,9). The first step is the glycerol dehydration step, leading to the formation of an intermediate enol, which is in tautomeric equilibrium with the hydroxyl acetone (acetol). The formation of acetol is thermodynamically more stable than the formation of 3-hydroxypropanal (intermediate formed by the elimination of the secondary alcohol during the synthesis of 1,3-propanediol). This step is endothermic in nature, hence a high temperature is required for the formation of acetol. The second step is the hydrogenation step where the acetol is hydrogenated to propylene glycol. An overall conversion process of glycerol to PG is summarized in Scheme 1.

Several reviews have been reported on the catalytic hydrogenation of glycerol to propylene glycol. Bogza et al. reviewed the effect of Cu, Ni, Co, and noble metal based catalysts on the conversion of glycerol to propylene glycol (10). The effects of reaction parameters (temperature, catalyst loading, hydrogen pressure, and glycerol concentration), reaction medium (acidic/alkaline),
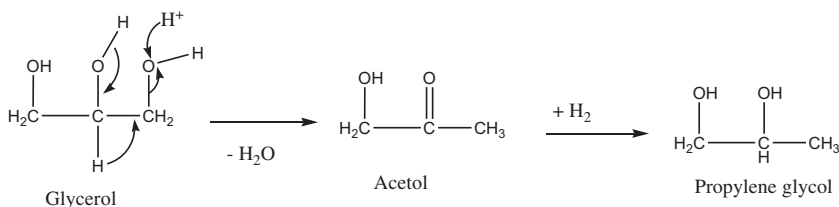
Scheme 1. The overall reaction process for the conversion of glycerol to propylene glycol.

role of promoters, and reaction mechanism have been reviewed (5,11). To overview the effects of different catalyst preparation and activation methods on the glycerol conversion and product selectivity, and performance of various types of reactor and catalysts, would not only complement the previous literature reviews but also help to optimize and scale-up the glycerol conversion processes.

In this article, recent advancements in the production of propylene glycol are reviewed. The developments in reactor systems, the effects of catalyst preparation and activation methods on catalytic activity and stability, and the performance of various catalysts are reported. The reaction mechanisms and the challenges of using crude glycerol as the feedstock for the glycerol hydrogenolysis reactions are also discussed.

2. Historical context

Propylene glycol was first synthesized by Wurtz in 1859 by the hydrolysis of propylene glycol diacetate as given in Scheme 2 (12). In the mid-1930s, DuPont produced propylene glycol as a by-product from the hydrogenation of coconut oil. However, it was first commercialized by Carbide and Carbon Chemical Corporation in 1931 using the chlorohydrine route from propylene (12).

The use of propylene glycol gained momentum during the World War II as it was used as a substitute for glycerol in pharmaceuticals, which led to opening of new production facilities by Dow Chemical in 1942 and Wyandotte Chemical Corp. in 1948 (12).

Conventionally, propylene glycol is produced from propylene oxide derived from petroleum resources. Currently, five different technologies are used in the commercial production of propylene oxide; namely (A) the styrene monomer process (LyondellBasel and Shell), (B) the anthraquinone process (Dow Chemical and BASF), (C) the tert-butyl alcohol process (LyondellBasel and Huntsman Corp.), (D) the cumene hydroperoxide process (Sumitomo Chemicals), and (E) the chlorohydrine process (Dow Chemical) (12). The reactions relating to these processes are shown in Scheme 3. The final product (propylene oxide) in all these processes is hydrolyzed to form propylene glycol.
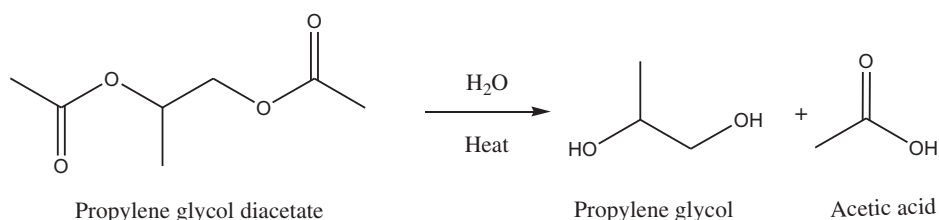
Scheme 2. Synthesis of propylene glycol from propylene glycol diacetate.
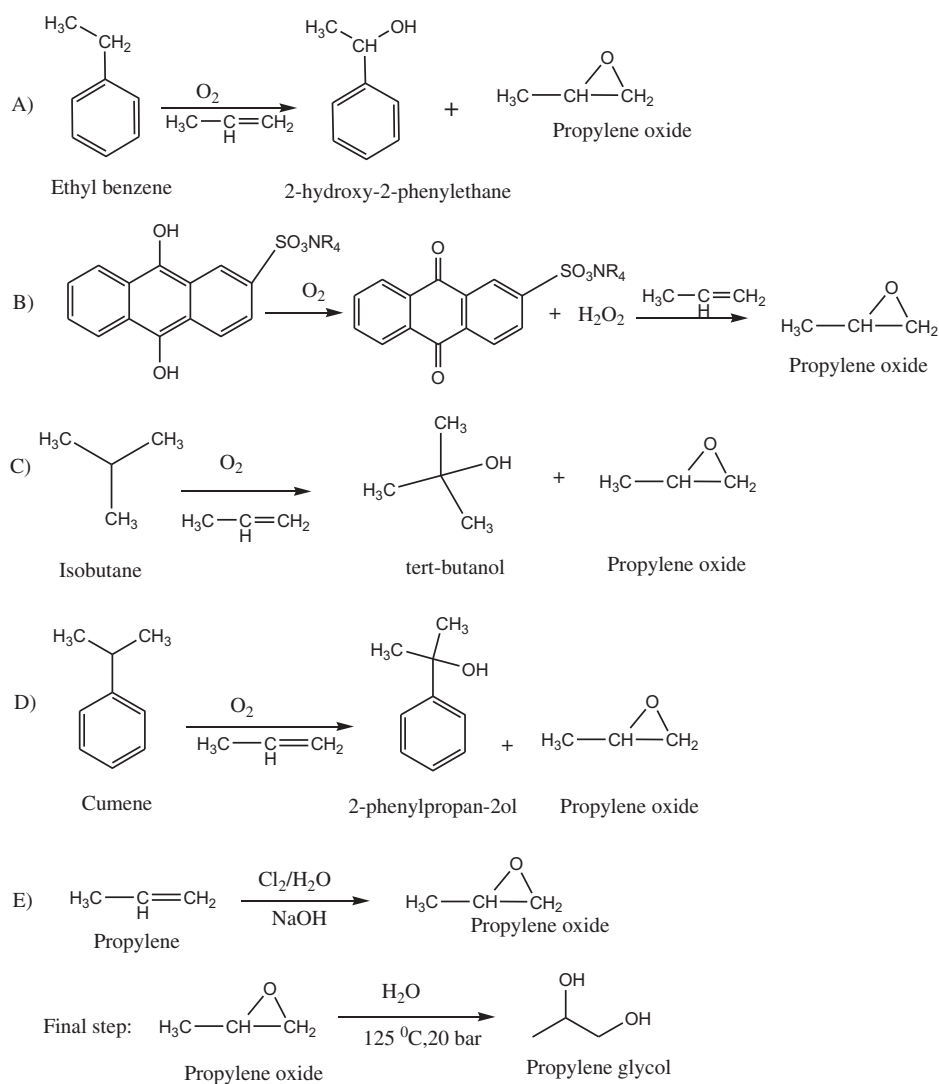
Scheme 3. Different processes for the production of propylene oxide – precursor for propylene glycol: (A) Styrene monomer process; (B) Anthraquinone process; (C) Tert-butyl alcohol process; (D) Cumene hydroperoxide process; (E) Chlorohydrin process.

The conventional methods for the production of propylene glycol from propylene oxide hydrolysis are normally non-catalytic processes at high temperature (150–250°C) and high pressure (>100 psi). A large excess of water is used in the process producing di-and tri-propylene glycol (Figure 4) as co-products (12, 13) which need to be separated making the process uneconomical (a drawback).

Thus, as a greener process, hydrogenolysis of glycerol—as an abundant and inexpensive industrial byproduct or waste to propylene glycol (PG) in an economical way is much more advantageous than the conventional processes described above.
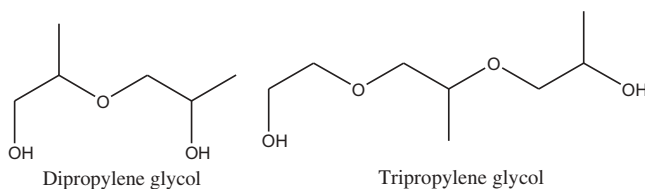
Figure 4. Structure of dipropylene glycol and tripropylene glycol.

3. Development in reaction processes

Traditionally, homogeneous catalysts have been used for the hydrogenolysis of glycerol to propylene glycol. Tessie patented a method for the catalytic production of propylene glycol from glycerol in aqueous solution using a homogeneous catalyst composed of a mixture of Rhodium complex and tungstic acid at reaction conditions of 4598 psi H_2 and 200°C (9, 14). During the reaction, PG (1,2-PDO) and 1,3-propanediol (1,3-PDO) were produced with yields of 23% and 20%, respectively (15). The use of homogeneous ruthenium iodocarbonyl complex catalyst species $[Ru(CO)_3I_3]^-$ has been reported for the hydrogenolysis reaction of polyols (16). A process using a palladium-based homogeneous catalyst in a water-sulfolane mixture was developed by Shell Oil in which the yields of n-propanol, PG, and 1,3-PDO, after a 10 h reaction period, were found to be in the weight ratio of 47:22:31 (15, 17).

The hydrogenolysis of glycerol via homogeneous catalytic processes however, has some apparent shortcomings including corrosion, separation/recovery of the catalyst from the product stream and the use of expensive/toxic solvents in the reaction, which raises environmental and economic concerns for these processes. Therefore, heterogeneous catalysts were sought to address these problems. The use of heterogeneous catalysts such as Ni, Ru, Rh, Cu, Re, Pd, etc. over different support materials is to be reviewed in the next sections.

Synthesis of PG from glycerol in a batch reactor using either homogeneous or heterogeneous catalysts has been extensively studied (18–22). However, these processes have some major disadvantages including long reaction times, high labor cost per unit of production, difficulty in scale up and commercialization, and long down times for reactor cleaning, etc. (23, 24). To overcome some of these issues and to enhance the PG production, Torres et al., studied the hydrogenolysis of glycerol in a batch-slurry reactor using a bimetallic Ru-Re catalyst over carbon support (25). The reactor system was made up of a parallel array of six autoclave reactors that could be operated simultaneously at different temperatures and pressures using computer control. The authors reported a maximum glycerol conversion of 58% with a PG selectivity of 37% at 220°C and 1000 psi H_2. A similar multiple slurry reactor was used by Roy et al. for aqueous phase hydrogenolysis of glycerol, as shown in Fig. 5 (26). In their study, an admixture of 1 wt%:1 wt% of 5wt% Ru/Al_2O_3
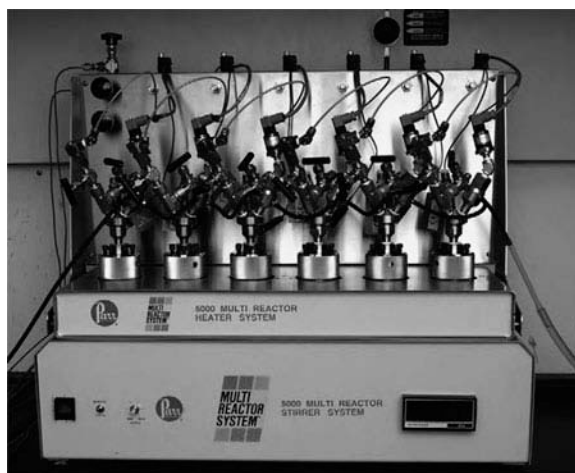
Figure 5. Multiple slurry reactor used for the hydrogenolysis of glycerol (25) (adopted with copyright permission).

and 5 wt% Pt/Al_2O_3, respectively, was used to obtain glycerol conversion of 50% with PG selectivity of 47% after 6 h at 220°C and 595 psi without external hydrogen (or using internally generated hydrogen from glycerol steam reforming) and a glycerol loading of 3 g. In 2012, Checa et al. investigated the hydrogenolysis of glycerol in a slurry phase reactor using Pt, Pd, Rh, and Au supported on ZnO in the absence of external hydrogen (27). They observed that the activity of the catalysts for glycerol conversion under similar reaction conditions followed the sequence of Pt > Rh > Pd > Au. Although hydrogenolysis of glycerol using slurry reactor moved the process one step closer towards commercialization, it has some concerns including difficulty in process design, generation of fine particles during the process (having the potential to plug-up the reactor), difficulty in sampling, and higher catalyst consumption (hence poorer economics) (28).

Recently, a submerged catalysis and membrane filtration reactor for the semi-continuous hydrogenolysis of glycerol over Cu-ZnO has been reported (29). In this reactor, a ceramic membrane was fixed and sealed inside the autoclave and connected to the liquid outlet valve to separate the catalyst from the product stream. The authors reported a poor glycerol conversion (21%), though high propylene glycol selectivity (88%) was maintained for 8 catalytic cycles.

In order to make glycerol hydrogenolysis processes more efficient and economical, a variety of efforts have been made in developing flow reactors (30–35). It is obvious that the production of PG in a continuous-flow reactor using heterogeneous catalysts is advantageous as the process has advantages of both high heat and mass transfer efficiency, ease of scale-up from laboratory to industrial scale, and high surface to volume ratios (36). Moreover, the

concept of "Novel Process Windows" with respect to temperature, pressure and reactant concentration can be exploited and the intrinsic kinetics of the reaction can be enhanced in flow processes to improve the yield of the desired products (37–39). Zhou et al. used a flow reactor to study the kinetics of th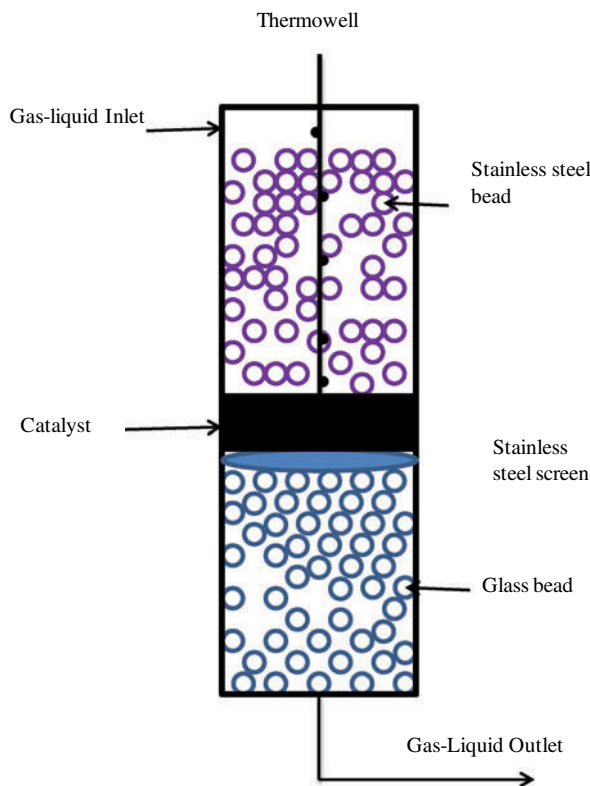e hydrogenolysis conversion of glycerol over ZnO-Al$_2$O$_3$ catalyst (40). A similar type of reactor was used for the vapour phase hydrognolysis of glycerol (41, 42). The details of this reactor are given in Fig. 6. In this set up, an aqueous or vaporized glycerol solution (80 wt%) was first passed through a pre-heated zone to reduce the viscosity of the solution before feeding it into the reactor. Hao and co-workers developed a flow reactor for the hydrogenolysis reaction in presence of Cu-H$_4$SiW$_{12}$O$_{40}$/Al$_2$O$_3$ without the use of a pre-heater, but using a 10 wt% glycerol aqueous solution for the reaction (43). Very good results were achieved in this reactor system, with 90% PG selectivity at 90% glycerol conversion. Similar fixed-bed reactors have been reported in literature (44–47).

Xi and co-workers developed a kinetic and mass transfer model for glycerol hydrogenolysis over carbon-supported metals (2.5 wt% Co, 0.5 wt% Pd, and 2.4 wt% Re) using a trickle-bed reactor with a volume of 40 cm^3 (48). The schematic of the reactor is illustrated in Fig. 7. In this reactor, the catalyst was sandwiched between a layer of 2 mm diameter glass beads at the bottom of the bed and 2 mm diameter stainless steel beads at the top of the bed to facilitate liquid distribution and preheating prior to reaction. The authors showed that the model predictions agreed well with experimental data and accurately predicted the trends in reactor performance indicating the possible commercialization of this reaction system.
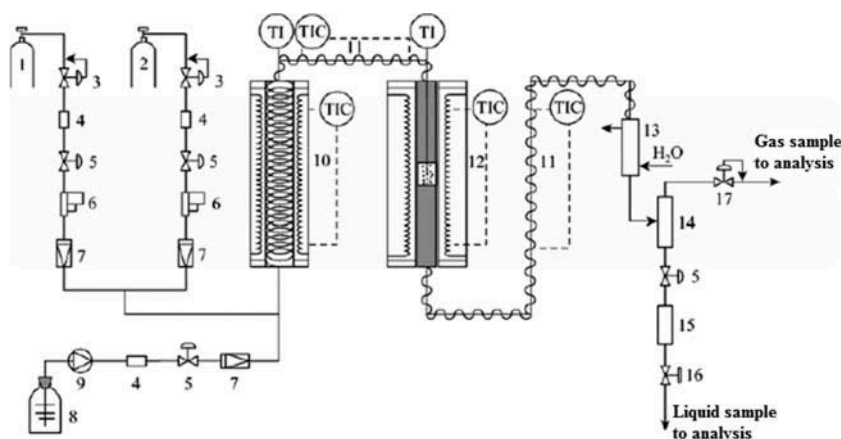
Figure 6. Schematic diagram of the flow reactor set-up (39) (adopted with copyright permission). (1: Nitrogen; 2: Hydrogen; 3: Pressure regulator; 4: Filter; 5: Ball valve; 6: Mass flow controller; 7: Check valve; 8: Liquid feed; 9: Metering pump; 10: Pre-heater; 11: Heater and thermal insulator; 12: Reactor; 13: Condenser; 14: Gas-liquid separator; 15: Sampling pipe; 16: Needle valve; 17: Back-pressure regulator).

Thermowell

Gas-liquid Inlet

Stainless steel
bead

Catalyst

Stainless
steel screen

Glass bead

Gas-Liquid Outlet

Figure 7. Schematic diagram of the trickle-bed reactor developed by Xi and co-workers (47).

This section provides information on the evolution of the process from a homogeneous system (with or without organic solvent) to a heterogeneous system using water as solvent, as well as from batch processes in the heterogeneous system to batch-slurry, semi-continuous, plug-flow and trickle-bed processes. In the following section, the performance of various types of catalysts in the conversion of glycerol to propylene glycol will be further discussed.

4. Performance of various catalysts

4.1. *Effect of catalyst preparation and activation methods*

The catalyst preparation methods for the hydrogenolysis of glycerol have significant effects on the glycerol conversion and product selectivity. It has been reported that the catalyst preparation and activation methods strongly affect the structural and physicochemical properties such as metal dispersion and stabilization of the catalyst (44, 49–51). A proper catalyst preparation and activation method enhances the reducibility of the metal and minimizes the metal sintering during reduction, calcinations, and reaction steps. It also

helps to reduce the adsorption rate of water on the catalyst surface during the reaction that inhibits the product formation. A wide variety of methods including impregnation (IM), adsorption, ion-exchange (IE), sol-gel (SG), (co)precipitation (CP), hydrothermal treatment (HT), solid fusion (SF), and carbon-microsphere-templating (CT) have been reported in the preparation of catalysts (41, 44–46, 49). The effects of the different catalyst preparation methods on glycerol conversion and PG selectivity are given in Table 1.

Huang et al. reported glycerol hydrogenolysis using a highly dispersed silica-supported copper catalyst (Cu/SiO_2) prepared by gel-precipitation and compared the activity of this catalyst to a reference Cu/SiO_2 catalyst prepared by impregnation (52). A very high selectivity (>98%) towars PG was observed with both catalysts, however, the catalyst prepared by gel-precipitation demonstrated much higher activity at each given temperature as compared to the impregnated catalyst. For example, at 160°C, 1305 psi H_2 with 80% aqueous glycerol solution, the glycerol conversion and propylene glycol selectivity for gel-precipitation catalyst was 19% and 98% respectively, whereas for the impregnated catalyst it was 2% and 99%, respectively. Moreover, the gel-precipitation catalyst demonstrated better long term stability over impregnated catalyst (200 h vs. 12 h). The authors attributed the higher activity of the gel-precipitation catalyst to the smaller crystalline size (5.7 vs. 20.7 nm) and higher metal dispersion than the impregnated catalyst. The large size of the impregnated catalyst was due to inhomogeneous agglomeration of the active species at grain boundary of the support, resulting in sintering of Cu species. Bienholz et al. compared the activity of CuO/ZnO catalysts prepared by co-precipitation and oxalate-gel (OG), and found that the catalyst prepared by the oxalate-gel method exhibited higher glycerol conversion (46% vs. 17%) and space-time yield (9.8 $g_{propylene\ glycol}$/g_{Cu}/h vs. 0.8 $g_{propylene\ glycol}$/g_{Cu}/h) than the co-precipitation catalyst (53). In order to find the reason for different conversions of glycerol, the authors carried out N_2O chemiosorption of both the catalysts at 330 °C. A larger copper surface area (30 vs. 17 m^2/g), higher dispersion (17% vs. 9%) and smaller average particle diameter (6 nm vs. 12nm) was observed for OG–catalyst than CP-catalyst.

In 2013, Li et al. investigated the performance of zinc incorporated copper catalysts over alumina support ($Cu-ZnO/Al_2O_3$) prepared by impregnation and co-precipitation (46). In their work, the $Cu-ZnO/Al_2O_3$–CP catalyst demonstrated higher glycerol conversion (86%) and PG selectivity (85%) than the $Cu-ZnO/Al_2O_3$ –IM (conversion: 64% and selectivity: 68%). Similar trend has been reported by Kim et al. using a Cu/Cr_2O_3 catalyst (51), Yuan et al. using CuO/MgO catalyst (54), and Balaraju et al. using Ru/TiO_2 catalyst (55) (Table 1). Almost in every study, the catalysts prepared by co-precipitation method demonstrated better performance than those prepared by impregnation method. The authors attributed the high

Table 1. Effect of catalyst preparation methods on glycerol conversion and propylene glycol selectivity.

Catalyst	Method	Surface area (m²/g)	Reactor type and reaction conditions	%C glycerol	%S (1,2PD)	Ref
Cu-Al₂O₃	CP	57	Batch reactor 20 wt% aq glycerol, 0.01 g/mL cat, 493K, 5.2 MPa H₂, 5 h	58	88	(49)
	SF	127		5	74	
Cu-SiO₂	IM	38.6 (Cu)	Batch reactor 80% aq glycerol, 453 K, 6 MPa, 4 g cat, 12 h	83	99	(52)
	PG	198.9		50	98	
CuO-ZnO	OG	30.1 (Cu)	Batch reactor 140 mL pure glycerol, 473 K, 3 g cat, 5 MPa H₂, 7 h	46	90	(53)
	CP	16.7		17	87	
Cu-Cr₂O₃	IM	15.1	Batch reactor 50 g glycerol, 1 g cat, 8 MPa, 493 K	32	41	(51)
	Pre	19.3		80	85	
CuO/MgO	CP	26.2	Batch reactor 75wt% aq glycerol 8.0 mL, 1.0 g cat, 3.0 MPa H₂, 453 K, 20 h	72	98	(54)
	IM	N.D		30	93	
Ru-TiO₂	IM	2.4	Batch reactor 20 wt% aq glycerol, 6 MPa H₂, 453 K, catalyst loading 6wt% of solution, 8 h	31	59	(55)
	CP	7.2		44	58	
Cu-ZnO/Al₂O₃	IM	145	Flow reactor 80 wt% aq glycerol, 523K, 3.2 MPa H₂, 2.8 h⁻¹	100[a]	95[a]	(46)
	CP	182		20[a]	76[a]	
	SG	175		76[a]	78[a]	
Ni-ZnO	IM	5	Flow reactor 10 wt% aq glycerol, W_{cat}=0.5 g, 508K, 3.1 MPa H₂, 6 h	45	44	(45)
	CP	11		80	46	
	HT	24		84	50	
	CT	32		88	55	
Cu-ZnO/Al₂O₃	IM	25	Flow reactor 80 wt% aq glycerol, 523K, 0.05h⁻¹, 0.1 MPa	64	68	(44)
	CP	75		86	85	

[a]After 12 h on-stream.

performance of the CP catalysts to their larger surface area and higher dispersion of the Cu metal than the IM catalysts. Moreover, the authors observed a higher total acidity of the reduced CP catalysts than the IM catalysts which enhanced the dehydration of glycerol to acetol before hydrogenation. In contrast to these results, Panyad et al. compared the activity of Cu-ZnO/Al$_2$O$_3$ catalysts prepared by impregnation, co-precipitation and sol-gel methods and found the order of catalytic activity and stability (after 12 h) to be: IM > CP > SG (44). In this case, the higher activity and stability of the IM catalysts was ascribed to decreased levels of coke deposition (IM= 2.3%, SG= 3.9%, and CP= 5.5%).

Hydrogenolysis of glycerol over Ni/ZnO catalysts prepared by impregnation, co-precipitation, hydrothermal treatment, and carbon microsphere hard-template methods was investigated by Hu et al. (45). The authors carried out the reaction in a flow reactor by reacting 10 wt% glycerol aqueous solution at 235°C under 450 psi of H$_2$ over a catalyst loading of 0.5 g. The process was an integration of reforming and hydrogenolysis reaction. The activity of different catalysts, at any given WHSV tested (reaction conditions: 235°C, 450 psi Ar, 0.5 g catalyst, and 6 h on-stream), was found to increase as follows: impregnation (IM) < co-precipitation (CP) < hydrothermal treatment (HT) < carbon microsphere hard-template (CT), which was attributed to the large surface area (IM= 5 m^2/g; CP= 11 m^2/g; HT= 24 m^2/g; CT= 32 m^2/g) and high Ni dispersion (IM= 4 %; CP= 7%; HT= 10; CT= 11%). The large surface area and high Ni dispersion of the Ni/ZnO-CT sample, also responsible for the higher reducibility (H$_2$-TPR analysis) among other catalysts, were ascribed to the decomposition of metal carbonates to carbon microspheres in the catalyst. In 2012, Mane et al. also published their work on the effect of preparation methods on the activity of the catalysts meant for the hydrogenolysis of glycerol (49). They prepared Cu/Al$_2$O$_3$ catalysts using the co-precipitation (CP) and solid state fusion (SF) methods. The best results were obtained at 220°C, 754 psi of H$_2$ using a 20 wt% aqueous glycerol solution and 0.01 g/mL of catalyst. Under these conditions, glycerol conversion and PG selectivity for Cu/Al$_2$O$_3$-CP were 58% and 88%, respectively, whereas the conversion and selectivity for Cu/Al$_2$O$_3$-SF catalyst were 5% and 74%, respectively. One of the main issues in this work was the large particle size (and correspondingly smaller surface area) of the catalyst prepared by solid state fusion.

Yu and co-workers investigated the role of activation processes on the performance of Ni/AC (activated carbon) catalysts (56). They prepared Ni/AC catalyst by incipient wetness impregnation. Samples of the as-prepared catalyst (Ni/AC) were subjected to carbothermal and hydrogen reduction in a tubular furnace with 90 min ramp and 180 min hold at 450°C under flow N$_2$ and H$_2$, respectively. The samples were designated Ni/AC-C and Ni/AC-H, respectively, as shown in Table 2. Samples of Ni/AC-C and Ni/AC-H were

Table 2. Effect of catalyst activation process on glycerol conversion and propylene glycol selectivity.

Catalyst	Activation process	Reactor type and reaction conditions	%C glycerol	%S (PG)	Ref
Ni/AC	C	Batch reactor, 25wt% aq glycerol, 0.693 g Ni,	7	18	(56)
	H	5 MPa H_2, 473 K, 6 h	6	32	
	CB		43	76	
	HB		11	64	
Cu-Al$_2$O$_3$	C	Batch reactor,	13	38	(50)
	C-r	80% aq glycerol, 0.8 g catalyst, 2.4 MPa H_2,	14	75	
	C-r-o	493 K, 8h reaction	19	35	
	C2		19	25	
	C2-r		23	37	
	C2-r-o		30	34	
Cu-SiO$_2$	Air (stag)	Batch reactor,	33	94	(57)
	NO	40 vol% alcoholic solution glycerol, 8 MPa H_2, 513K, 5 h	51	95	
Cu-SBA	Air (flow)		52	97	(57)
	NO		49	96	
	Air		52	96	
Cu-SBA 900C	NO		37	96	(57)
	Air (flow)		20	92	

treated with KBH_4 in 0.2 M NaOH. These catalysts were designated Ni/AC-CB and Ni/AC-HB, respectively. The Ni/AC-CB was found to be the most active (63% conversion with 77% PG selectivity) in the hydrogenolysis of glycerol among others. The authors attributed the high activity of the Ni/AC-CB catalyst to the synergistic effects of hydrogen center and acidity generated from the processes.

The research group of Vila also published an article on glycerol hydrogenolysis over Cu/γ-Al$_2$O$_3$, where the effects of activation processes including calcination, reduction and re-oxidation were investigated (50) (Table 2). In this work, the Cu-Al$_2$O$_3$ catalyst was prepared by the impregnation method. The catalyst was then dried at 120°C for 12 h. Three samples of this material were taken and pretreated as follows (i) calcination at 400°C under 20 vol% O_2 in Ar at a flow of 100 mL/min with a heating rate of 10°C/min for 0.5 or 2 h (ii) reduction in 5 vol% H_2/Ar flow at 300°C for 1 h (iii) re-oxidation in N_2O/N_2 flow at 80°C for 0.25 h. It was reported that the glycerol conversion rate for the catalysts calcined for 2 h was higher (19%) than that calcined for 0.5 h (13%) under same reaction conditions (220°C, 348 psi, and 80% glycerol for 8 h). Irrespective of the calcination time, the selectivity of the reduced catalyst was significantly higher than those measured with the calcined and re-oxidized catalysts. However, significant differences in PG selectivity were observed for the reduced catalysts, indicating that other factors such oxidation states of Cu species ($Cu°/Cu^+/Cu^{+2}$) and their surface concentration may also be relevant. Moreover, Vasiliadou et al. studied the effect of activation processes on the activity of glycerol hydrogenolysis catalysts (57). They observed that the

conversion of glycerol using Cu/SiO_2 catalysts that were calcined in flowing air or NO was higher (~50% conversion) compared to catalysts calcined under stagnant air (33%) (Table 2). For the SBA and SBA900C-supported catalysts, the different calcination atmosphere (air or NO flow) also influenced catalytic activity. The effect of calcination atmosphere was more pronounced with in SBA900C-supported catalysts. The samples calcined in NO resulted in higher glycerol conversion (37%) compared with those calcined in air (20%). They observed that the air-calcined catalysts presented almost empty pores with large copper particles on the exterior of the support, which could have affected the performance of the catalysts.

In brief summary, the glycerol conversion and PG selectivity mainly depends on the catalyst preparation and activation methods. Among other preparation methods, impregnation method was found to be least efficient resulting in high agglomeration and low dispersion of metals. Activation processes such as calcination and reduction, the activation environment (stagnant air, air flow, NO flow, or H_2 atmosphere), and duration of activation period greatly influenced the structural and physicochemical properties of the catalyst. The catalyst calcined for a long period followed by reduction in a flow environment (air/H_2) has comparatively higher active sites for hydrogenolysis of glycerol.

4.2. Noble metal-based catalysts

Noble metals are well known for their ability to adsorb hydrogen and facilitate hydrogenation reactions. To exploit this behavior, Montassier et al. used Rh and Ru (also sulfur modified Ru) catalysts for hydrogenolysis of glycerol and found that at 210°C and 870 psi H_2, Ru/C mainly gives ethylene glycol (EG selectivity: 50%), ethane (25%), and PG (12%) (58). Interestingly, under these conditions, sulfur poisoning of the Ru surface increased the selectivity of PG to 79%. Chaminand et al. provided an insight into the hydrogenolysis of glycerol with Rh and Pd catalysts by using different solvents (water, sulfolane, and dioxane) over C, Al_2O_3, and Nafion supports at 180°C, and 1160 psi H_2 (59). 21% glycerol conversion with 70% PG selectivity over Rh/C in water solvent was reported. Miyazawa and co-workers investigated the use of Ru, Rh, Pd, and Pt over carbon support and observed that Ru/C has the highest activity in terms of glycerol conversion (4%) and propylene glycol selectivity (26%) at 140°C and 1160 psi of H_2 among other catalysts (60).

The activities of different noble metal catalysts such as Ru/C, Pd/C, Ru/Al_2O_3, and Pt/C, etc. were also studied in a batch reactor by Dasari et al. (9). At 200°C, 200 psi and after 24 h of reaction, Pd/C showed the least activity with glycerol conversion of 5% and PG yield of 3.6% (Ru/C: 44% conversion, 40% selectivity; Pt/C: 35% conversion, 83% selectivity, Ru/Al_2O_3: 23%

conversion and 60% selectivity). In another study, Pt/C demonstrated greater PG selectivity than Ru/C (61). Furicado's research group studied the activity of Rh, Ru, Pt, and Pd supported on C, SiO_2 or Al_2O_3 in the hydrogenolysis of glycerol at a low temperature (120°C) (62). The Pd and Pt catalysts, regardless of support, exhibited extremely low activity (<1% conversion). For Ru catalysts, activated C was found to be a better support (3.5% conversion) than either SiO_2 (0.2% conversion) or Al_2O_3 (0.3% conversion). Among all the catalysts, Rh/SiO_2 exhibited the highest glycerol conversion of 7.2% with PG selectivity of 38% at this low reaction temperature.

It was observed that the use of noble metals without an acidic or basic additive have low selectivity to PG (63). The use of Ru/C along with Amberlyst-70 was reported by Miyazawa et al. (64) where the presence of the acidic co-catalyst was found to increase the reaction rate as well as PG selectivity. Balaraju i investigated the hydrogenolysis of glycerol in the presence of Ru/C with different inorganic solid acids including niobia- and zirconia-supported tungstophosphoric acid at 180°C, and observed glycerol conversion of 63% with PG selectivity of 67% with the co-presence of niobia acid (65). Hydrogenolysis of aqueous glycerol using a ruthenium-incorporated acidic hetero-polysalt ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$) catalyst was reported and a high PG selectivity of 96% was obtained at 150°C. However, the glycerol conversion in the process was low (21%) (66).

The activity of Ru over different support materials (SiO_2, γ-Al_2O_3, NaY zeolite, C, and TiO_2) was investigated by Feng et al. who found Ru/TiO_2 to be the most active catalyst (90% glycerol conversion) but, at the same time, the least selective for PG (47%) (67). Hydrogenolysis of glycerol over Ru/TiO_2 in the presence of different bases including LiOH, NaOH, KOH, Li_2CO_3, Na_2CO_3, and K_2CO_3 at 170°C has been reported in literature (68). The addition of LiOH and NaOH enhanced glycerol conversion as well as PG selectivity. The highest glycerol conversion (90%) and PG selectivity (87%) was obtained using Ru/TiO_2 with LiOH. Maris and Davis compared the activity of Ru/C and Pt/C with the activity of a base-incorporated catalyst, and noticed that the presence of 0.8 M NaOH or CaO enhanced the rate of glycerol hydrogenolysis over the control catalyst (Ru/C or Pt/C) (61). Yuan and co-workers investigated the hydrogenolysis of 20 wt% glycerol aqueous solution over different solid base supported Pt catalysts (20). They noticed that Pt/MgO and Pt/hydrotalcite catalyst exhibit higher glycerol conversion (50% and 92%) and PG selectivity (82% and 93%) than Pt/C catalyst incorporated with NaOH (7% conversion and 82% selectivity).

Shinmi et al. modified Rh/SiO_2 catalyst with Re, Mo, and W as a promoter and observed a significant improvement in catalytic activity for hydrogenolysis of glycerol at a Re/Rh ratio of 0.5 (69). The Rh-ReO_x/SiO_2 (Re/Rh= 0.5) catalyst exhibited a higher glycerol conversion (80%) than the Rh/SiO_2 catalyst. The authors also noted that metal-oxide modified noble metal

catalysts appear to be suitable for the selective synthesis of 1, 3-PDO. The improvement in the activity of the Rh-ReO$_x$/SiO$_2$ catalyst was attributed to the presence of low-valent ReO$_x$ clusters covering the surface of the Rh particles, which enhanced the C-O hydrogenolysis activity of Rh metal and suppressed C-C hydrogenolysis activity.

4.3. 3D transition metal-based catalysts

The cheap availability of 3D transition metal-based catalysts is one of the main reasons to gain more interest over the noble metal catalysts in a wide variety of processes including the hydrogenolysis process. Montassier et al. reported the hydrogenolysis with 85% glycerol conversion and 66% PG yield at 240°C and 435 psi of hydrogen (70). Chimanand et al. achieved 100% selectivity to PG over CuO/ZnO at 180°C and 1160 psi of hydrogen in a batch reactor, but the activity of the catalyst was so low that it took 90 h to reach 20% glycerol conversion (59). A similar result of high selectivity (>93%) of PG but low glycerol conversion (12%) using Raney Ni was reported by Perosa and Tundo (71). Wang and Liu showed that smaller Cu particles are very active for the synthesis of PG (72).

In order to reduce the process and capital costs, Dasari et al. investigated the hydrogenolysis of a 80% glycerol solution in a batch reactor at lower temperatures and pressures and reported glycerol conversion of 65% with PG selectivity of 90% after 24 h at 200°C, and 300 psi using a copper-chromite catalyst (9).

Recently, copper catalysts have attracted much attention for the conversion of glycerol to PG because of their intrinsic ability to selectively cleave the C-O bonds in glycerol rather than the C-C bonds. To increase the activity of Cu metal, Cu-based catalysts such as Cu-Cr, (34, 51, 73, 74) Cu-Al, (50) Cu-Mg (54, 75) have been developed to promote the hydrogenolysis reaction. Bienholz et al. prepared a highly dispersed silica-supported copper catalyst (Cu/SiO$_2$) using an ion-exchange method and achieved 100% glycerol conversion with 87% PG selectivity at optimum conditions of 5 mL/h of 40 wt% aqueous glycerol solution, 255°C, and 300 mL/min of H$_2$ at 218 psi (41).

Zhu and co-workers studied the promoting effect of boron oxide on Cu/SiO$_2$ catalyst for hydrogenolysis of glycerol (76). They observed that the Cu/SiO$_2$ catalyst exhibited glycerol conversion of 62% with PG selectivity of 90% at the reaction conditions of 200°C, 725 psi, 10 wt% glycerol aqueous solution, H$_2$/glycerol of 123:1 (mol/mol) and WHSV of 0.075 h^{-1}. The incorporation of 3 wt% boron to the above catalyst improved glycerol conversion to 100% with PG selectivity of 98% under same reaction conditions. The effect of precipitation agents (NaOH, Na$_2$CO$_3$, NH$_4$OH, and NH$_4$HCO$_3$) and rare earth additives (La, Ce, Y, Pr, and Sm) on the catalytic performance of Cu/SiO$_2$ catalyst was investigated by Huang et al. (77). The authors observed that the incorporation of

precipitation agents and/or rare earth additives had a detrimental effect on glycerol conversion due to decrease in BET surface area, increase in Cu particle size, and difficulties in CuO reduction. However, the additives maintained the propylene glycol selectivity, thermal stability, and long-term stability of the Cu-SiO$_2$ catalyst.

Marnoiu et al. studied the synthesis of PG from glycerol in a batch reactor using a Ni/SiO$_2$-Al$_2$O$_3$ and observed a high selectivity to PG (98%) at 30% glycerol conversion under moderate conditions: 200°C, 290 psi of H$_2$, 5 wt% loading of catalyst and reaction time of 8 h (78). Searching for reusable and green catalysts for the hydrogenolysis reaction, Guo and co-workers used a CoAl alloy as a catalyst and observed 100% glycerol conversion with 70% selectivity to PG in a batch reactor at 160°C, 580 psi H$_2$, 1 g catalyst in 30 mL of 10% aqueous glycerol solution (79).

Ni/SiO$_2$ is well known for its mild activity in hydrogenolysis reactions. Huang et al. incorporated phosphorus (P) to Ni/SiO$_2$ in an attempt to improve its catalytic activity in hydrogenolysis of glycerol (80). They noted a significant improvement in the glycerol conversion (95% vs. 73%) and PG selectivity (86% vs. 50%) by P-loading. The authors ascribed the improvement in the catalytic activity to the electronic effect in which electrons transferred from Ni to P resulting in a lower electron density in the Ni comprising the Ni$_2$P phase as compared to metallic Ni. Also, P increases the Ni-Ni distance. These factors reduce the activity of Ni$_2$P/SiO$_2$ for the cleavage of C-C bonds.

The effects of different kinds of zeolite (γ-Al$_2$O$_3$, HY, 13X, HZSM-5, Hβ) as support materials on the performance of Cu for hydrogenolysis of glycerol were studied by Guo et al. (81). The order of activity followed the sequence: Cu/Al$_2$O$_3$ > Cu-Hβ > Cu-HY > Cu-HZSM ≈ Cu-13X. Alumina is a well-known support for dehydration reactions; it is obvious that alumina could possess an appropriate acidity to catalyze the dehydration of glycerol to form acetol. Similar results were reported by Sato et al. (82). The failure of other acidic supports was attributed to the formation of acrolein instead of acetol. Zhao's group also studied the effects of different support materials (NaMOR zeolite, NaZSM-5 zeolite, NaA zeolite, NaX zeolite SiO$_2$, and γ-Al$_2$O$_3$) on the performance of metallic Ni catalyst (83). In a batch reactor at 200°C, 870 psi of H$_2$, 16 g of 25 wt.% glycerol aqueous solution, 2.0 g catalyst and 10 h reaction, glycerol conversion followed the order Ni/Al$_2$O$_3$ (97%, 40% selectivity towards PG) > Ni/NaX (95%, and 72% selectivity towards PG) > Ni/SiO$_2$ (57%) > Ni/NaZSM-5 (48%) > Ni/NaMOR (14%) > Ni/NaA(10%). The high conversion and selectivity of Ni/NaX catalyst was attributed to its acidity and the ability of NaX to adsorb glycerol molecules and increase their concentration on the surface of the catalyst.

4.4. Combination of noble and 3D-transitional metal-based catalysts

Recently, the selective hydrogenolysis of glycerol has been studied using mixed metal catalysts including oxides of Cu, Zn, Cr, and Zr. These mixed metal catalysts have attracted much interest because it is possible to obtain the desired catalytic performance by varying the proportions of the different metals in the catalyst, to achieve glycerol conversion of 100% with PG selectivity of >97% in a batch reactor at reaction conditions of 240°C, 580 psi H_2, 100 g of 80% glycerol solution, with 3.0 g of catalyst for 10 h (84). Wu et al. investigated hydrogenolysis of glycerol over carbon nanotube-supported Cu-Ru catalyst at 200°C and observed 100% glycerol conversion with PG selectivity of 87% (85). The high activity of the catalyst was ascribed to the high dispersion of Ru clusters on the external surface of the Cu particles. These Ru clusters generated active hydrogen sites that were transferred to the Cu surface via hydrogen spill-over enhancing the hydrogenolysis reactions. Similar hydrogen spill-over phenomena with glycerol conversion more than 88% and 100% PG selectivity was reported by Xia et al. and Kim et al. using $Pd_xCu_{0.4}Mg_{5.6-x}Al_2(OH)_{16}CO_3)$ and $Pd-CuCr_2O_4$ catalysts, respectively (86, 87). Recently, Liu's group studied the glycerol hydrogenolysis over Ru-Cu catalysts supported on different support materials including SiO_2, Al_2O_3, NaY zeolite, TiO_2, ZrO_2, and HY zeolite (88). The best activity was observed for Ru-Cu/ZrO_2 with 100% glycerol conversion and 84% PG selectivity. The high activity of this catalyst was attributed to the synergistic effect of Ru in the catalyst related to hydrogen spill-over as discussed above.

In conclusion, all these results suggest that noble metals are more expensive and less active in comparison to 3D transition metal-based catalysts, hence being unfavorable for the glycerol hydrogenolysis reaction. Among the transition metal based catalysts, Cu-based catalysts have demonstrated their potential with almost complete glycerol conversion and 100% selectivity towards propylene glycol (PG), implying that Cu-based catalysts may be promising in scaling-up and commercialization of the process.

4.5. Catalyst deactivation

As discussed previously, there are a number of very effective catalysts discovered for the hydrogenolysis of glycerol. However, these catalysts tend to be unstable under the reaction conditions and exhibit decreased activity over time. The deactivation of the catalysts could be due to poisoning, coking, fouling, sintering, or leaching of the metal(s).

Bienholz and co-workers investigated the deactivation of CuO/ZnO catalyst in a batch reactor (reaction conditions: 200°C, 725 psi H_2, 140 mL pure glycerol, 3 g catalyst and for 7 h) (53). Fresh catalyst exhibited glycerol conversion of 46% with PG selectivity of 90%, however, when the

catalyst was used in a subsequent run under the same conditions only 10% glycerol conversion was observed (but high PG selectivity was maintained, i.e., > 95%). The authors attributed the reduction in catalyst activity to increased CuO and ZnO particle size due to sintering during the reaction and/or the presence of water in the reaction medium leading to a decrease in the active surface area of the catalyst. Similar observations were reported by Vasiliadou and co-workers for Cu-based catalysts, where the authors observed that the deactivation of the catalyst was mainly due to coke deposition and sintering (57). Panyad et al. investigated the deactivation of alumina supported Cu-ZnO catalyst (44). They observed that the catalysts prepared by impregnation method have longer stability (14 h) than sol-gel (6 h) and co-precipitation (2 h) catalysts. Moreover, irrespective of the catalyst preparation methods (co-precipitation, wet impregnation, and sol-gel), all the spent catalysts have lower BET surface area and pore volume as compared to respective fresh catalysts. This was attributed to the sintering of the active metals and the residual coke deposition which plugged the pore mouths. In addition, the compositional analysis of the catalysts (prepared by co-precipitation method) by X-ray flouroscence analyzer (XRF) and atomic absorption spectrometer (AAS) indicated the leaching of Cu during the reaction contributing to a significant loss of activity (~35) (44).

Recently, Wang et al., investigated the deactivation of Cu-ZnO catalyst at 220°C, 725 psi H_2, and 20 g/L of glycerol concentration in a batch reactor (29). The authors found that the activity of the catalyst gradually decreased from cycle 1 (conversion 50%) to cycle 8 (conversion 20%). After comparing the XRD of fresh and spent catalysts, it was observed that CuO crystallite diffraction peaks disappeared while Cu crystallite phase structure appeared in the spent catalyst suggesting that CuO was completely converted to metallic copper during the reaction. Moreover, the intensities of Cu and ZnO crystallite diffraction peaks appeared much stronger after several experimental cycles of the spent catalyst, indicating the worse dispersion as well as larger crystallite size due to agglomeration of Cu and ZnO during the reaction. The reusability of Ce promoted Cu-Mg catalyst was investigated by Mallesham and co-workers (89). The authors performed 4 cycles using the same catalyst at 200°C, 870 psi H_2, 50 g of 20 wt% aqueous glycerol, 1 g reduced catalyst for 10 h reaction time. After each cycle the separated catalyst was washed with methanol, dried at 120°C for 12 h followed by reduction at 300°C for 3 h. It was found that the BET surface area and pore volume were reduced from 209 m^2/g and 0.57 cm^3/g in fresh catalyst to 51 m^2/g and 0.26 cm^3/g, respectively, in the spent catalyst (4th cycle), indicating the agglomeration and coking of catalyst as the cause for catalyst deactivation. Similar deactivation of Titanium supported Ru-Cu catalyst due to coking has been reported by Salazar et al. (90).
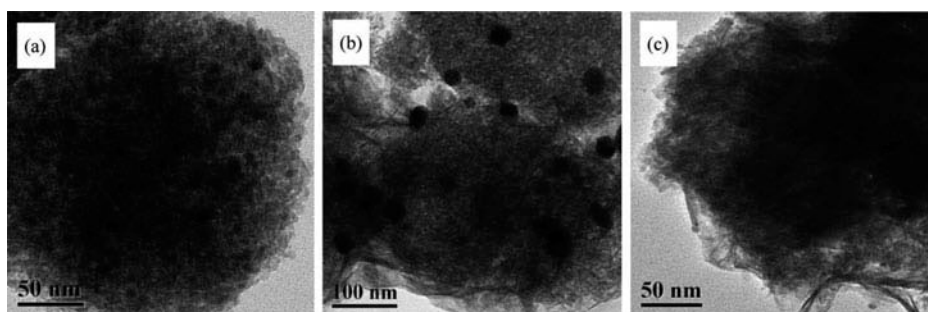
Figure 8. TEM micrographs of Ag/Al$_2$O$_3$ catalyst: fresh (a), spent (b), and spent-washed-calcined (c) (90) (adopted with copyright permission).

Vanama and co-workers studied the stability of 1–6 wt% Ru incorporated MCM 41 catalysts at 230°C, 140 mL/min H$_2$ flow and 2.09 h^{-1} WHSV (42). The results demonstrated that 3Ru/ MCM 41 has the higher conversion (62%) and better long term stability (>10 h) among others. The faster deactivation of other catalysts was attributed to the carbon deposition and agglomeration during the reaction.

The deactivation of Ag/Al$_2$O$_3$ in the hydrogenolysis process was studied by Zhou *et al.* in a batch reactor at 220°C and 217 psi initial H$_2$ pressure for 10 h (91). In this process, glycerol conversion using the spent catalyst dropped drastically from 46% (in the fresh catalyst) to 21%. A tremendous increase in the Ag particle size was observed in TEM (Fig. 8) of the spent catalyst (10 nm in fresh catalyst vs. 30 nm in the spent catalyst). The authors regenerated the catalyst by washing it with deionized water followed by calcinations at 400°C for 3 h in air. There was negligible difference in glycerol conversion using the regenerated catalyst (44%) vs. the fresh catalyst (45%), implying that the main causes of catalyst deactivation in the process were sintering and coking.

In conclusion, a majority of the studies reported that the deactivation of catalyst is due to fouling, coking or sintering. The reduced activity of catalysts caused by coking or fouling can be recovered to some extent by combustion (calcination) of the used catalysts at a relatively higher temperature followed by reduction. However, the heat treatment is not sufficient enough to regain the activity of catalysts if deactivated by sintering (44). More investigation on the regeneration of deactivated catalyst is necessary for commercial applications of the catalysts.

5. Use of crude glycerol as feedstock

The use of crude glycerol as a feedstock for the synthesis of propylene glycol is an important concept for the economical production of propylene glycol and sustainability of biodiesel industry. However, as mentioned earlier, crude glycerol contains various impurities derived from the biodiesel production

processes, including water, sodium, or potassium hydroxides, esters, fatty acids, and alcohols. When crude glycerol is used as a feedstock for the conversion reaction, the impurities would cause operating problems by either deactivating the catalyst or plugging the reactors. Hosgün and co-workers used crude glycerol as feedstock for the synthesis of propylene glycol over Raney Ni catalyst in a batch reactor and compared the results with that of pure glycerol (92). The authors reported almost equal glycerol conversion (~77%), and propylene glycol selectivity (~25%) under similar reaction conditions (20 wt% aq. glycerol, 230°C and 580 psi H_2) for both type of feedstock (pure glycerol and crude glycerol). The authors attributed the unexpected positive performance of crude glycerol to the presence of alkali impurities that acted as co-catalysts to enhance the conversion and product selectivity.

In another study by Sharma et al., a Cu:Zn:Cr:Zr-based catalyst was used for selective hydrogenolysis of glycerol to PG again in a batch reactor (84). It was observed that incorporation of zinc and zirconium in the Cu:Cr catalyst matrix improved glycerol conversion and propylene glycol selectivity, due to increases in acidity and Cu dispersion in the catalyst matrix. The liquid phase reaction was carried out with 80 wt% of glycerol solution at 240°C, with 580 psi of hydrogen pressure and 3 wt% catalysts loading. The selected catalyst Cu:Zn:Cr:Zr with the elemental molar ratio of 3:2:1:3 gave 100% of glycerol conversion and 97% of propylene glycol selectivity when using pure glycerol as the feedstock. Whereas when a simulated crude glycerol with 80% purity (remaining 20% contains mono, di, and tri-fatty acid ester) was used, the yield of propylene glycol decreased to 90% under the same conditions as described above, suggesting slight deactivation of the catalyst. However, real crude glycerol normally contains various impurities derived from the biodiesel production processes, which may seriously deactivate the catalysts for hydrogenolysis of glycerol, and cause reactor plugging when the reaction is operated in a flow reactor. There is not much research carried so far on hydrogenolysis of real crude glycerol in a flow reactor, so more work is needed in this regard.

6. Conclusions

The recent boom in biodiesel production has resulted in the generation of large volumes of glycerol as a byproduct (or waste stream). Therefore, the use of this waste stream from the biodiesel industry as a renewable feedstock to produce high-value chemicals such as propylene glycol, as reviewed in this chapter, is of great significance for better economics and sustainability of the biodiesel industry. This article has outlined the advancements in catalytic conversion of glycerol into propylene glycol. Some key conclusions are summarized below.

(1) Hydrogenolysis of glycerol to propylene glycol has been widely conducted in batch reactors, and various types of flow reactors including slurry

phase and trickle bed reactors as well as continuous-flow tubular reactor. The use of continuous-flow reactors with water as a green solvent demonstrates a great potential for commercialization of the process.

(2) The use of heterogeneous catalysts is economical (easy recovery) and environmentally benign, thus more preferable than using homogeneous catalysts.

(3) The methods of catalyst preparation were found to have significant effects on the activity and stability of the catalyst. Catalysts prepared by co-precipitation have larger active surface areas as compared to catalyst prepared by impregnation, leading to higher glycerol conversion and propylene glycol selectivity. Catalyst activation steps such as calcination, reduction, and re-oxidation, as well as the duration and treatment environment have also been shown to affect the formation of active hydrogen sites on the catalyst surface.

(4) Different types of catalysts including noble metal-based catalysts, transition metal-based catalysts, and mixed metal catalysts have demonstrated high activity and selectivity in hydrogenolysis of glycerol to propylene glycol. Very high propylene glycol yields have been achieved using transition metal-based catalysts, particularly Cu-based catalysts over silica or alumina supports, with yields in the range of 80–100%. Nevertheless, the main problem in the process is the rapid deactivation of these catalysts due to coke deposition and sintering.

(5) The use of crude glycerol as a feedstock for the synthesis of propylene glycol is an important concept for the economical production of propylene glycol and sustainability of biodiesel industry. Nevertheless, real crude glycerol usually contains various impurities such as water, sodium, or potassium hydroxides, esters, fatty acids, and alcohols, which may seriously deactivate the catalysts for hydrogenolysis of glycerol, and cause reactor plugging when the reaction is operated in a flow reactor. There is not much information is available for the hydrogenolysis of real crude glycerol in a flow reactor, so more research work is needed in this regard.

"The use of hydrogen is essential in the hydrogenolysis process of glycerol. Currently, hydrogen is dominantly originated from fossil fuels, either by gasification of coal or petroleum coke or by reforming natural gas or heavy oil, which is energy intensive and unsustainable (93, 94, 95). Different synthesis routes for hydrogen production from renewable resources have been reported. Currently, processes such as alkaline water electrolysis, photocatalytic water splitting, biological hydrogen production, and thermocatalytic production of hydrogen from biomass are the most attractive processes for bio-hydrogen production (96, 97). Although there are several challenges such as energy consumption, cost, reliability, durability and safety of these processes, it is expected that in near future bio-hydrogen from these processes could be competently available for the hydrogenolysis of glycerol".

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