Chemoselective catalytic conversion of glycerol as a biorenewable source to valuable commodity chemicals

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Received 8th October 2007
First published as an Advance Article on the web 22nd November 2007
DOI: 10.1039/b707343g

New opportunities for the conversion of glycerol into value-added chemicals have emerged in recent years as a result of glycerol's unique structure, properties, bioavailability, and renewability. Glycerol is currently produced in large amounts during the transesterification of fatty acids into biodiesel and as such represents a useful by-product. This paper provides a comprehensive review and critical analysis on the different reaction pathways for catalytic conversion of glycerol into commodity chemicals, including selective oxidation, selective hydrogenolysis, selective dehydration, pyrolysis and gasification, steam reforming, thermal reduction into syngas, selective transesterification, selective etherification, oligomerization and polymerization, and conversion of glycerol into glycerol carbonate.

1 Introduction

1.1 Industrial production of glycerol

The use of renewable feedstock is essential to the sustainable development of society. Much attention has been devoted to applying green catalytic processes to convert biorenewable feedstock to commodity chemicals and clean fuels. Glycerol (1,2,3-propanetriol) is widely available and is rich in functionalities. Glycerol can be found naturally in the form of fatty acid esters and also as important intermediates in the metabolism of living organisms.[1] Traditionally, glycerol is obtained as a by-product in four different processes: soap manufacture, fatty acid production, fatty ester production,[1] and microbial fermentation.[2] It can also be synthesized from propylene oxide.[1]

Glycerol can be obtained from biomass (including rapeseed and sunflower oil) *via* hydrolysis or methanolysis of triglycerides. The reactions for the direct transformation of vegetable oils and animal fats into methyl esters and glycerol have been known for over a century. However, it is only recently, following more than 10 years of research and development, that the transesterification of triglycerides, using rapeseed, soybean and sunflower oils, has gained significance for its role in the manufacture of high quality biodiesel fuel. (Scheme 1)[3–5] As a result, several chemical[6] and enzymatic[7] processes to produce fatty acid methyl esters from vegetable oil are now commercially available. Glycerol is normally generated at the rate of 1 mol of glycerol for every 3 mol of methyl esters synthesized; approximately 10 wt% of the total product.[6]

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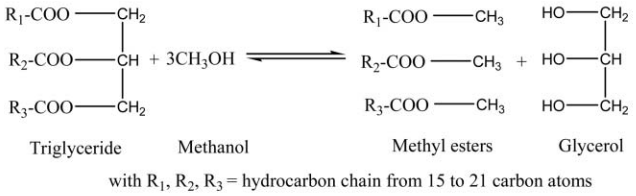


Scheme 1 Overall reaction for production of biodiesel through vegetable oils methanolysis.

Biodiesel has proved its value as a fuel for diesel engines,[7,8] being renewable and clean.[9,10] though its net energy balance is still disputable.[11] Recently, a European Union Directive stated that by the end of 2010, traffic fuels should contain at least 5.75% of renewable bio-components.[12] If the target of this directive is to be achieved, European biodiesel demand could increase to 10 million tons per year by 2010, producing about 1 million tons of glycerol as by-product.[13] In addition, if the United States replaces 2% of the on-road diesel with biodiesel in a B2 policy (2% biodiesel, 98% conventional diesel fuel) by 2012, almost 362.872 million kg of new glycerol would be added to the market.[14] Latest figures released from the US Department of Energy (DOE) on the current world feedstock availability of soybean, corn, trap grease and inedible tallow showed that 5.8 billion liters of biodiesel can be produced worldwide. Fig. 1 confirms the global projection estimates by Procter & Gamble on glycerol production until 2010.[15] On the other hand, biodiesel production from soy and palm oils can be cost effective for petroleum importing countries that shows a low GDP and poor balance of payment.

Markets have reacted strongly to an increased availability of glycerol. Although the global production of biodiesel is still limited, the market price of glycerol has dropped rapidly and could destabilize the free market of oleochemicals. Studies have shown that the glycerol commodity market is very limited and any increase in biodiesel production will cause a sharp decline of more than 60% of its current value by 2008. With the increased expansion of biodiesel and the sharp decrease of glycerol prices, glycerol is expected to become a major platform chemical and has been recently identified as an important building block for future biorefineries by the DOE.[16] This excess market-supply of glycerol could set the biodiesel industry backwards. Economic forecasts have demonstrated that the net production costs of B100 type biodiesel can be reduced from US$ 0.63 per liter to U$S 0.35 per liter by adding value to the glycerol by-product.[14,17]

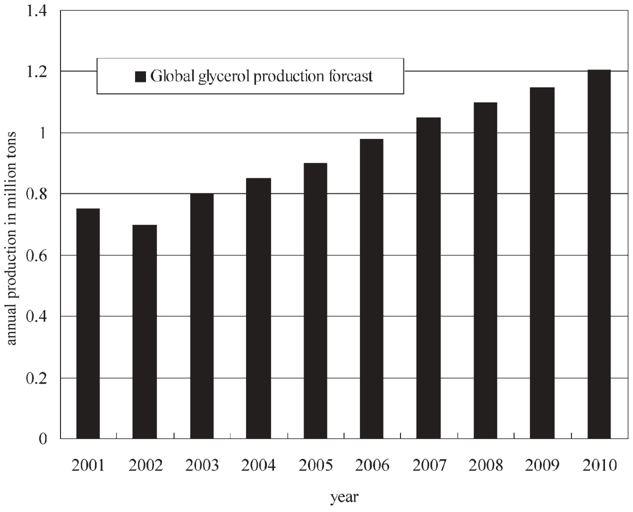


Fig. 1 The global projection estimates by Procter & Gamble of glycerol production to 2010[15]

1.2 Glycerol purification

In practice, the purity of by-product glycerol is a key economic and technological concern in conventional industrial biodiesel processes. Nowadays, most biodiesel plants use a homogeneous catalyst system operated in either batch or continuous mode utilizing typically base catalysts such as sodium hydroxide or other alkali metal hydroxides.[18,19] Glycerol resulting as a by-product during the transesterification process to biodiesel typically contains a mixture of methanol, water, inorganic salts (catalyst residue), free fatty acids, unreacted mono-, di- and triglycerides, methyl esters, and a variety of other organic materials in varying qualities, depending on the biodiesel process.[20,21] As such, crude glycerol with an estimated 50% purity has few direct uses and is of low value. Its disposal is also difficult as the methanol content of glycerol deems it as hazardous waste.

Further treatments for glycerol by-products generally involve neutralization and recycling to remove the excess methanol, the catalyst and soap.[21] One popular option is to use potassium hydroxide as the reaction catalyst and phosphoric acid for neutralization so that the potassium phosphate salt formed can be used as fertilizer. Following acidulation and separation of the free fatty acids, the methanol in the glycerol can be removed by evaporation using a vacuum flash process. Depending on the type of separation process used, the final glycerol purity is about 80–95%.[22] Such crude glycerol is typically sold to industrial glycerol refiners at a low cost.[14,16] Most (97%) of the glycerol used today is a highly refined product (97%+ purity) – the glycerol refining process can take the purity up to 99.5% to 99.7% using vacuum distillation or ion exchange processes.[23] However, these processes are expensive and small biodiesel plants usually discard the glycerol by-product as waste.

Di Serio *et al.*[24] have recently shown that using homogeneous Lewis acid catalyst metal salts reduces the cost of biodiesel with a higher quality of esters and glycerol, which can be promptly separated. In another development, the construction of a new 160000 tonnes per year biodiesel plant, based on the use of a heterogeneous catalyst developed by the French Institute of Petroleum (IFP) was recently announced.[25] Preliminary pilot plant experiments have shown that is it possible to produce biodiesel and a 98% pure glycerol that is limpid, free of any salt contaminants and colorless.[22]

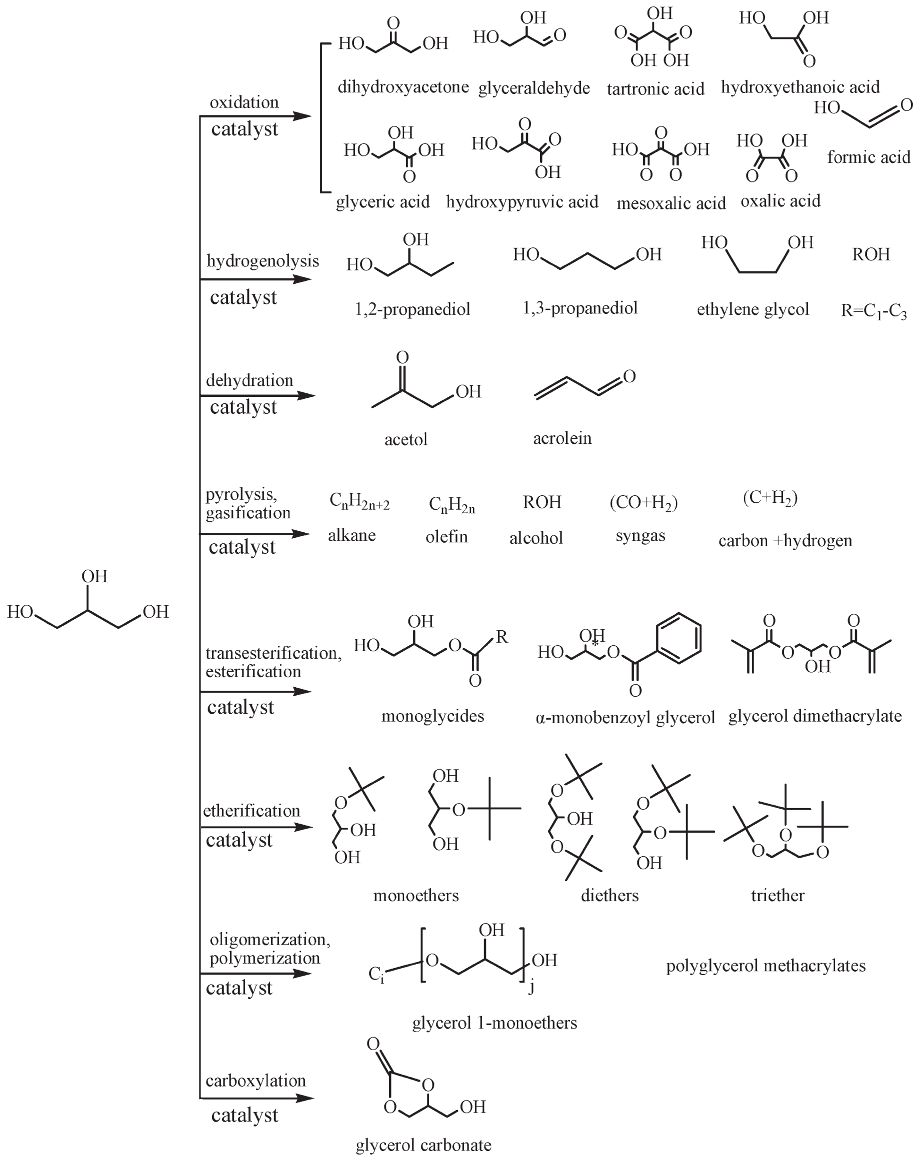
Despite these advances, the projected volume production of crude glycerol over the next 5 years will exceed the present commercial demand for purified glycerol, and consequently, purifying the by-product glycerol to be sold as commodity for traditional applications such as pharmaceutical, cosmetics and food industries, is not a viable option for the biodiesel industry. New high purity glycerol processes are needed, as high purified glycerol is the ideal feedstocks for chemoselectively catalytic conversion processes.

1.3 Glcerol conversion into valuable chemicals

Glycerol can also be commercially produced by the fermentation of sugars such as glucose and fructose, either directly[26] or as a by-product of the industrial conversion of lignocellulose into ethanol.[27] Technical and economic analyses show that the co-production of glycerol with ethanol lowers its production costs and increases profit margins.[28,29] Therefore, using glycerol for the synthesis of value-added chemicals is of great industrial importance, not only because glycerol can be formed in large amounts during the biodiesel process,[30] but also because glycerol is a nontoxic, edible, biosustainable and biodegradable compound.[1–3,21,22]

In the past, most products were based on unmodified glycerol or simple modifications to glycerol molecules as the production of more complex chemical compounds were too costly. Now, the lower cost of glycerol could open many significant new markets in polymers, ethers, and other fine compounds. From a technical standpoint, glycerol's multifunctional structure and properties can be tailored by several different reaction pathways as shown in Scheme 2. In the near future, the potential conversion of renewable resources into valuable commodity chemicals can facilitate the replacement of petroleum-based products. Furthermore, the conversion of glycerol to hydrogen or syngas can further contribute to the use of clean renewable energy sources. It is clear that a very large number of chemicals could be derived from glycerol. In this respect, catalysis represents a critical approach to green chemical technology in the activation and utilization of glycerol.

Recently, a series of novel catalytic conversion processes that transform glycerol into useful chemicals was reported in the literature. This review examines the most recent developments in chemoselectively catalytic conversion of glycerol to



Scheme 2 Processes of catalytic conversion of glycerol into useful chemicals.

promising commodity chemicals and fuels. Previous work has shown a great potential for the establishment of a variety of new catalytic processes and products from glycerol. As a result, new opportunities and challenges exist for research and industry to improve both the catalytic materials and technologies needed for the efficient transformation of glycerol into valuable chemicals.

2 Selective oxidation of glycerol

As glycerol is already a highly functionalized molecule compared to hydrocarbons, an advantageous alternative is to use it as feedstock for the production of valuable oxygenated derivatives. The oxidation of glycerol leads to a complex reaction pathway in which a large number of products such as dihydroxyacetone (DHA), glyceric acid (GLYAC), hydroxypyruvic acid (HYPAC), mesooxalic acid (MESAC), tartronic acid (TARAC), *etc.*, could be obtained. (Scheme 3).

These products, particularly tartronic and mesoxalic acids, are potentially valuable chelating agents that can be used as intermediate compounds for the synthesis of fine chemicals and novel polymers. For example, in a lower market price situation, DHA could be more widely used as a tanning structural unit in organic synthesis and as building blocks of new degradable polymers.[31,32] To date, these products have a limited market because they are either produced using costly and polluting stoichiometric oxidation processes (*e.g.* potassium permanganate, nitric acid or chromic acid) or low-productivity fermentation processes.[33,34]

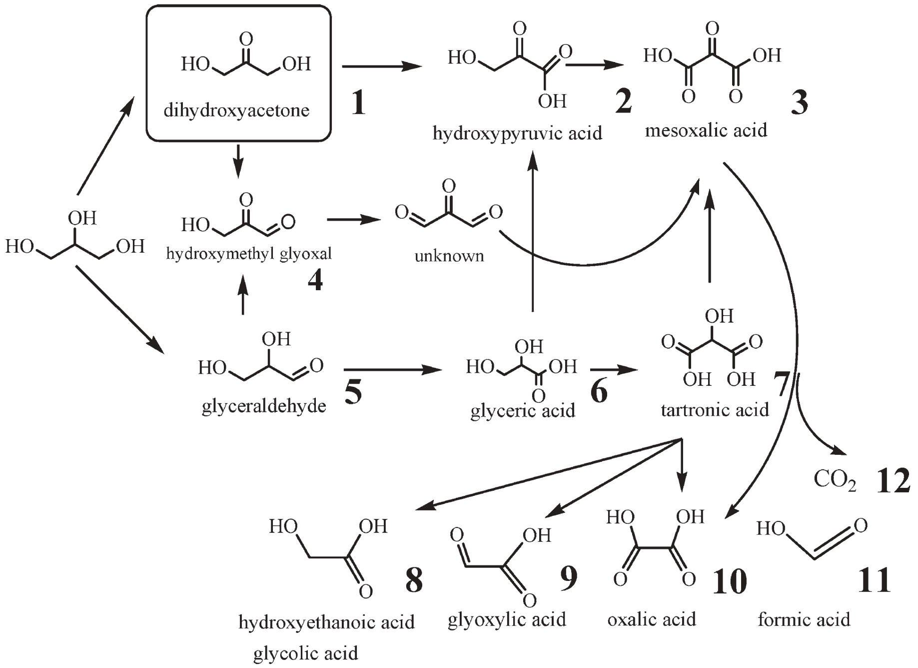
Glycerol's unique structure makes it possible to conduct the heterogeneous catalytic oxidative reaction using inexpensive clean oxidizing agents such as air, oxygen, and hydrogen peroxide, instead of costly stoichiometric oxidants, leading to an environmentally friendly alternative. Combining these inexpensive oxidizing agents with inexpensive glycerol will allow the economic production of a new class of chemical derivatives.

2.1 Chemoselective catalytic oxidation of glycerol

As shown in Scheme 3, seven potential C_3 oxygenated products – dihydroxyacetone, hydroxypyruic acid, mesoxalic acid, glyceraldehydes (GLYALD), glyceric acid, tartronic acid and hydroxymethyl glyoxal, together with C_2 (oxalic acid, hydroxyethanoic acid) and C_1 products (formic acid, CO_x) – can be obtained from the oxidation reaction of glycerol. Selective *versus* nonselective oxidation is, therefore, the big challenge associated with these catalytic oxidation reactions. The first important step in the industrialization of these new processes requires the design of new, effective heterogeneous catalysts to control the chemoselective orientation of the glycerol oxidation reaction towards either the oxidation of the primary alcohol functions, to give glyceric acid, or the oxidation of the secondary alcohol function, to produce dihydroxyacetone and hydroxypyruvic acid.

An increasing number of studies dealing with the chemoselective catalytic oxidation of glycerol, mainly using supported noble-metal-nanoparticles such as Pd, Pt, Au as catalysts, have been reported. Given its high boiling point, the selective oxidation of glycerol with air or oxygen is normally carried out in the liquid phase using water as the solvent. Table 1 lists some typical results of catalytic oxidation of glycerol reported by several groups.

Their results showed that when using palladium and platinum catalysts in a basic medium, glyceric acid was obtained as the main product with tartronate and oxalate as the main over-oxidation by-products. Glyceric acid oxidation proceeded rapidly to give high yields of hydroxypyruvic acid. Earlier, Kimura *et al.*[35,36] showed that adding bismuth to



Scheme 3 Possible reaction pathways to oxygenated derivatives of glycerol.

Table 1 Some typical results of catalytic oxidation of glycerol investigated by several groups

Catalysts	Oxidants	pH	Other reaction conditions	Glycerol conversion	Selectivity or yield	Researchers and year	Ref.
Pt/charcoal	air (0.1 MPa)	2–4	10% GLY, 323 K, 4 h	37%	4% (Y_{DHA})[b]	Kimura, 1993	35,36
Bi–Pt charcoal	air (0.1 MPa)	2–4	10% GLY, 323 K, 4 h	30%	20% (Y_{DHA})	Kimura, 1993	35,36
Pt–Bi/charcoal[a]	air (0.1 MPa)	—	50% GLY, 323 K, O_2/GLY = 2 (mol/mol)	80%	80% (S_{DHA})	Kimura, 1993	35,36
5% Pd/C	air (0.1 MPa)	11	10% GLY 333 K, 30% NaOH, 5 h	100%	8% (S_{DHA}), 70% (S_{GLYAC})	Garcia *et al.*, 1995	37
Bi–Pt/C	air (0.1 MPa)	2	10% GLY, 333 K, 5 h	75%	50% (S_{DHA})	Garcia *et al.*, 1995	37
5%Bi–5%Pt/C	O_2 (0.02 MPa)	5.5	8 mmol GLY/60 ml H_2O, 338 K, 3 h	—	25% (Y_{DHA}),20% (Y_{HYPAC})	Abbadi *et al.*, 1996	40
Ti–Si co-gel	H_2O_2(10% w/v)	7	10 g GLY, 353 K, 24 h	22%	37% (S_{GLYALD})	McMorn *et al.*, 1999	68
1%Au/charcoal	O_2 (0.3 MPa)	basic	12 mmol GLY/20 ml H_2O 333 K, 3 h, 12 mmol NaOH	56%	100% (S_{GLYAC})	Carrettin *et al.*, 2002	54
5%Pt/C	Air (0.1 MPa)	11	1 M GLY, 333 K, 21 h, 30% NaOH	60%	47.5% (S_{GLYAC})	Carrettin *et al.*, 2003	55
1% Au/C	O_2 (0.3 MPa)	basic	0.3 M GLY, NaOH/GLY = 4 (mol/mol), 303 K, 20 h	100%	92% (S_{GLYAC})	Porta *et al.*, 2004	57
1% Pd/graphite	O_2 (0.3 MPa)	basic	0.3 M GLY, NaOH/GLY = 4 (mol/mol), 50 °C, 1 h	90%	62.4% (S_{GLYAC})	Dimitratos *et al.*, 2005	58,60
1% (Pd + Au)/ graphite	O_2 (0.3 MPa)	basic	0.3 M GLY, NaOH/GLY = 4 (mol/mol), 323 K, 2 h	100%	39.1% (S_{GLYAC})	Dimitratos *et al.*, 2005	58,60
1% (Au@Pd)/ graphite	O_2 (0.3 MPa)	basic	0.3 M GLY, NaOH/GLY = 4 (mol/mol), 323 K, 2 h	100%	45.5% (S_{GLYAC})	Dimitratos *et al.*, 2005	58,60
1% Pt/C	O_2 (0.3 MPa)	basic	0.3 M GLY, NaOH/GLY = 4 (mol/mol), 50 °C, 4 h	81.6%	50% (S_{GLYAC})	Dimitratos *et al.*, 2006	61
1%(Au + Pt)/C	O_2 (0.3 MPa)	basic	0.3 M GLY, NaOH/GLY = 4 (mol/mol), 323 K, 4 h	69.3%	58.3% (S_{GLYAC})	Dimitratos *et al.*, 2006	61
Au/C	O_2 (0.1 MPa)	12	1.5 M GLY, NaOH/GLY = 2 (mol/mol), 333 K, 3 h	30%	75% (S_{GLYAC})	Dimirel, 2005	63
Au/C	O_2 (0.1 MPa)	12	1.5 M GLY, NaOH/GLY = 2 (mol/mol), 333 K, 1.5 h	50%	26% (Y_{DHA}), 44% (Y_{HYPAC})	Dimirel *et al.*, 2007	63
Au-Pt/C	O_2 (0.1 MPa)	12	1.5 M GLY, NaOH/GLY = 2 (mol/mol), 333 K, 1.5 h	50%	36% (Y_{DHA}), 30% (Y_{HYPAC})	Dimirel *et al.*, 2007	63

[a] Fixed bed reactor. [b] Selectivity to the product given in parentheses.

platinum catalysts greatly improves the selectivity towards the secondary alcohol. Moreover, this reaction mainly depends upon both reaction conditions and the catalyst nature. The products of glycerol oxidation seem to also depend on the type of reaction vessel employed: a batch reactor working at pH 11 appears to produce more DHA than a fixed-bed reactor. However, a 20% yield in DHA was obtained in a batch reactor at 30% glycerol conversion using a 1%Bi–5%Pt/C catalyst, and a 30% DHA yield at 40% glycerol conversion was obtained in a fixed-bed catalytic reactor with a 0.6%Bi–3%Pt catalyst supported on granular charcoal. The results suggested that, on a fixed bed reactor loaded with Bi/Pt/C catalyst, glycerol conversion and DHA yield increases. Referring to the effect of catalyst, they postulated that bismuth blocks Pt(111), controlling the glycerol orientation towards DHA formation.

When the oxidation of the secondary alcohol functions of glycerol was carried out at an acidic pH on bismuth-promoted platinum catalysts, an 80% initial selectivity to DHA was found, but as reaction time progressed the catalyst deactivated due to the increase in the number of strongly adsorbed acids on the surface.[37–39] Aldehydes were formed rapidly but their rates of oxidation were much faster than those of alcohols so that they cannot normally be detected in the reaction medium. In addition, Abbadi *et al.*[40] found that over a bismuth-modified platinum catalyst, and using air as the main oxidant, glycerol was not a suitable starting material for the preparation of β-hydroxypyruvic acid, as it mainly yields oxalic acid.

In general, Abbadi, Gallezot, Kimura and co-workers[44–49] found Pd to be more selective for the formation of glyceric acid than Pt. When using a basic reaction solution, the oxidation of the primary alcohol function is promoted, whereas acidic conditions promoted the oxidation of the secondary alcohol function.[41–43] An improvement in the activity, selectivity and stability can be achieved in the presence of a second p-electron metal, particularly the heavy metal atoms of Group IV (*e.g.* lead) and V (*e.g.* bismuth). Therefore, the nature of the individual metal could promote the reaction selectivity towards dihydroxyacetone and glyceraldehydes.[28–33] The pH of the solution could govern the nature of the complex formed between the promoter and the substrate, which constitutes the basis of the selectivity of the bismuth-modified platinum catalyst.[44]

Interestingly, Kimura *et al.*[45,46] also reported that Pt supported on CeO_2, catalyzes the oxidation of both primary alcohols giving a 40% yield of tartronic acid. These differences in selectivity can be exploited to catalytically synthesize ketomalonic acid (*i.e.* MESAC) using a 2-step aerobic process, converting glycerol first to tartronic acid over a Pt/CeO_2 catalyst, and then tartronic acid to ketomalonic acid by using the PtBi/C catalyst. In contrast, when a single multifunctional supported BiPtPd/CeO_2 catalyst is used either under basic[47] or acidic[48] conditions, glycerol can be directly converted to poly(ketomalonate) in a one-pot oxidative polymerization process leading to a high molecular weight polycarboxylate. The polymerization possibly proceeds by an ether bonding mechanism.

The main disadvantage of supported Pt and Pd catalysts generally used for polyol oxidation is their deactivation at increasing reaction time. In particular, catalysts that are based on the platinum group metal suffer oxygen poisoning that is proportional to the oxygen partial pressure.[49,50] This is the principal reason that, when using this type of catalyst, a low partial pressure of oxygen must be used to limit oxygen dissolution. However, gold catalysts appear to be more resistant to oxygen poisoning than platinum-based catalysts, allowing the use of higher oxygen partial pressure.[51] Biella *et al.* even found that pure oxygen at 0.3 MPa pressure can be present during reaction without any sign of catalyst deactivation.[52]

Hutchings and co-workers[53–55] recently reported that a 100% selectivity of glyceric acid can be obtained from the oxidation of glycerol under mild conditions (333 K, 3 h, under 0.3–0.6 MPa of O_2, water as solvent) over 1% Au/charcoal or 1% Au/graphite catalysts. The selectivity of the reaction toward glyceric acid appears to be conversion dependent, decreasing from 100% at half glycerol conversion to 86% at 72% glycerol conversion. Further catalyst characterization using TEM reveals that active catalytic sites have fairly broad-size distributions between 5–50 nm diameter for the gold nanoparticles, although most are *ca.* 25 nm in diameter, whereas an inactive Au/graphite catalyst displays significantly larger particle diameters (>50 nm) with a narrower size distribution. These results indicate that there may be an optimum particle size for the desired selective catalysis. Characterization using cyclic voltammetry of active Au/graphite catalysts carried out in the presence of NaOH solutions reveals the existence of an oxide species that may be responsible for the observed catalytic behavior.[56]

Porta *et al.*[57] recently found that catalyst preparation techniques, particle size, and reaction temperature had an important effect on the catalytic conversion and selectivity of glycerol oxidation. For example, noble-metal catalysts prepared using sol–gel immobilization techniques performed better than catalysts prepared by impregnation or incipient wetness methods.[57] Consequently, the overall selectivity of the reaction derives from a combination of factors such as initial selectivity of the catalyst, base-catalyzed interconversion, and stability of the products. As a result, the optimum reaction condition was found to be at 92% glycerate selectivity and 100% glycerol conversion. Furthermore, Dimitratos *et al.* showed that by using bimetallic catalysts (Au–Pd, Au–Pt) supported on carbon the distribution of the products could be controlled. Moreover, bimetallic catalysts were more active than monometallic catalysts[58] and selectivity could be tuned by using different preparation methods.[59] The addition of Au to Pd or Pt metals also enhanced the resistance to oxygen or by-product poisoning with respect to monometallic catalysts.[60]

More recently, Dimitratos *et al.* stated that the particle growth and nature of the Au and Pt metals can be significantly affected during the reduction step when using reducing agents such as H_2 and $NaBH_4$.[61] Single-phase Pd–Au bimetallic catalyst supported on activated carbon was prepared in a two-step reduction process limiting the available Pd species by decreasing the reduction rate of the palladium salt.[62] The resulted single-phase Pd–Au catalyst exhibited higher performance during the selective oxidation of glycerol when compared with the monometallic Pd/AC, Au/AC and the physically mixed Pd–Au catalyst. This behavior can be attributed to the synergistic effect of the metal alloy formation, as the change in interatomic metal distance on the surface could have both geometric and electronic effects on the catalytic behaviors.

Nano-sized gold particles supported on different carbons (*i.e.* carbon black, activated carbon and graphite) and oxides (TiO_2, MgO and Al_2O_3) were active for the heterogeneously catalyzed liquid-phase oxidation of glycerol under atmospheric pressure conditions.[59,63] For the same reaction conditions and using comparable gold particle size, the carbon supported gold catalysts showed high activity for the liquid phase oxidation of glycerol. Further experiments using Au/C catalysts containing gold particle sizes in the range from 2 to 45 nm confirmed that the reaction is structure-sensitive. Moreover, the selectivity of the Au/C catalyst depends on the base concentration and the reaction time. They also showed that the presence of Pt as a promoter increases not only the catalyst activity but also the selectivity to DHA from 26% (Au/C) to 36% (Au–Pt/C).

Under alkaline conditions the intrinsic catalyst selectivity was influenced by the nature of the catalyst (metal,[28–30] particle dimensions,[53,54] and support[64]). At the same time, the stability of the reaction intermediates and their interconversion was found to be influenced by experimental conditions such as temperature and base concentration. Although Au appears to be an active catalyst dependent upon the particle size,[65] the problem is that the presence of a base leads to an intermediate product interconversion that can mask the true selectivity of the catalyst and allow only the production of the salt of glyceric acid. As a matter of comparison, supported Pd/C and Pt/C always gave other C_3 and C_2 products in addition to glyceric acid and, in particular, some C_1 by-products can be obtained. The supporting effect of graphite makes it a suitable catalyst support to be used for gold during glycerol oxidation.[47–50]

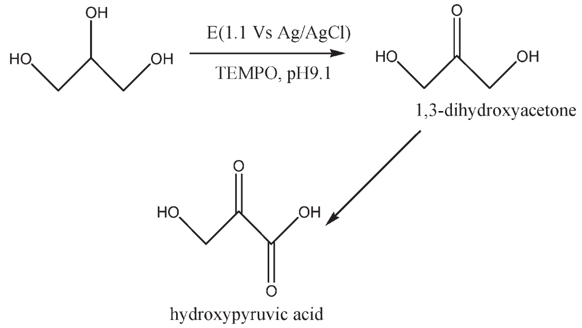
The role that NaOH plays during the catalytic glycerol oxidation is considered essential for the start of the reaction.[47–49,66] Normally, the first step of alcohol oxidation consists of the dehydrogenation of the alcohol function followed by the oxidation of the formed intermediate.[67] Kimura also reported that the type and concentration of the base plays a major role in the course of the reaction.[45] Hence, in the presence of the base, the H readily abstracted from one of the primary hydroxyl groups of glycerol overcomes the rate limiting step for the oxidation process. However, it is still difficult to explain why both the selectivity to glyceric acid and the formation of tartronic acid *via* consecutive oxidation of glyceric acid and glycerol are very dependent upon the glycerol/NaOH ratio. Therefore, a precise control of the preparation method and reaction conditions is still needed in order to obtain active and selective catalysts towards the desired products.

In addition to using noble metal supported catalysts, McMorn *et al.*[68] studied glycerol oxidation employing a range of transition-metal-containing silicates and aluminophosphate catalysts in the presence of hydrogen peroxide as oxidant. The results revealed that variations in reaction conditions (extent of conversion, temperature, glycerol/hydrogen peroxide ratio) or catalysts (silicalite containing Ti, V, Fe or AlPO-5 containing Cr, V, Mn, Co) did not lead to the formation of partial oxidation products of glycerol. Formic acid and a mono-formate ester of glycerol were observed to be the major products together with a complex mixture of acetals. Accordingly, they found that increasing the pore size from *ca.* 0.5 nm to 15 nm on a titania–silica co-gel catalyst significantly increased the formation of partial oxidation products of glycerol, namely glyceraldehyde, dihydroxyacetone and glyceric acid. McMorn *et al.* also suggested that under the same reaction conditions used in their study, the diffusion of products within the narrow pores possibly leads to their facile over-oxidation, resulting in the formation of formic acid. As the pore size increases, the diffusion limitations decrease and the products of partial oxidation can be easily observed. It is therefore clear that, for the oxidation of glycerol, it is important to use only macroporous catalysts to overcome any diffusion-related problems, which result in the products of non-selective oxidation.

2.2 Electrocatalytic oxidation of glycerol

Glyceric acid could be prepared by anodic oxidation of glycerol using a silver oxide electrode.[69,70] It was recently reported that stable organic nitroxyl radicals of the TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) family are increasingly being used for the catalytic oxidation of alcohols to carbonyl and carboxyl compounds due to their pronounced selective activity and versatility of the oxidant species. The catalysts were easily regenerated *in situ* using a variety of primary oxidants under mild conditions, either in water, organic solvents or using biphasic systems.[71] Ciriminna *et al.*[72] have also shown that glycerol can be selectively converted to ketomalonic acid in a one-pot reaction at pH 10 using NaOCl as a regenerating oxidant at 275 K in the presence of a catalytic Br^- together with the radical TEMPO. Thus, they can also demonstrate that the reaction can be conducted to yield ketomalonic acid with low amounts of 1,3-DHA and tartronic acid as intermediate by-products if microporous sol–gel silica glasses doped with TEMPO were used. These are stable heterogeneous catalysts that can be easily separated from the reaction mixture and recycle stream. Considering the stability and versatility of such doped glasses, these materials show real promise as reusable metal-free catalysts for the conversion of a readily available and renewable glycerol into a highly valued compound.

In a more recent work, Ciriminna *et al.*[73] also reported that a simple one-pot, waste-free oxidation of glycerol to DHA at the anode can be achieved by simply applying a small electric potential (1.1 V *vs* Ag/AgCl) to a glycerol solution (0.05 M) in water buffered with bicarbonate (0.2 M) at pH 9.1 in the presence of 15 mol% TEMPO. After 20 h, an optimal yield of 25% DHA was obtained that is comparable to that from the fermentation process, while providing a product of high purity. Noteworthy is that extending the reaction time causes over-oxidation of DHA and an increase in the amount of hydroxypyruvic acid (HYPAC) (Scheme 4). Hence, after 200 h a 35% yield of HYPAC was present in solution along with 30% of DHA. It is also surprising that no over-oxidation to carboxylic acid was observed even after prolonged reaction times, showing that at the chosen potential (1.1 V) both carbonyl products (DHA and HYPAC) are stable. Hydration of aldehydes is usually fast in water at pH 9.1, and the formation of the acid is similarly rapid in the presence of a chemical oxidant such as hypochlorite. The electro catalytic process does not require traditional chemical oxidants as shown in Scheme 4. The reason that glycerol is preferentially oxidized at secondary hydroxyl to yield DHA is still not clear. However, this clean one-pot oxidation process could find commercial use as an alternative to conversion of biomass-derived glycerol.



Scheme 4 Electrochemical oxidation of glycerol mediated by TEMPO in water affords DHA and, after longer reaction times, HPA. (After scheme from ref. 73 with permission from Elsevier. © 2006 Elsevier.)

3 Selective hydrogenolysis of glycerol

Hydrogenolysis is a catalytic chemical reaction that breaks a chemical bond in an organic molecule with the simultaneous addition of a hydrogen atom to the resulting molecular fragments. Through the selective hydrogenolysis of glycerol in the presence of metallic catalysts and hydrogen, 1,2-propanediol (1,2-PD), 1,3-propanediol (1,3-PD), or ethylene glycol (EG) could be obtained. Therefore, catalytic hydrogenolysis of glycerol is another alternative route to increase the profitability of biodiesel production plants as the products of glycerol hydrogenolysis can easily replace the chemical compounds, which at present are industrially produced mainly by using non-renewable sources.

Propylene glycol, *i.e.* 1,2-PD, a three-carbon diol with a stereogenic center at the central carbon atom, is an important medium-value commodity chemical with a 4% annual growth in the market size. It is used for polyester resins, liquid detergents, pharmaceuticals, cosmetics, tobacco humectants, flavors and fragrances, personal care, paints, animal feed, antifreeze, *etc*. Traditionally, it is produced by the hydration of propylene oxide derived from propylene by either the chlorohydrin process or the hydroperoxide process. There has been a rapid expansion of the market for 1,2-PD as antifreeze and de-icing agents because of the growing concern over the toxicity of ethylene glycol-based products to humans and animals. 1,3-PD is also a high-value specialty chemical that is mainly used in specialty polyester fibers, films, and coatings. 1,3-PD is copolymerized with terephthalic acid to produce the polyester SORONA® from DuPont, or CORTERRA® from Shell, which has unique properties in terms of chemical resistance, light stability, elastic recovery, and dyeability.[74,75] 1,3-PD is currently catalytically produced from petroleum derivatives such as ethylene oxide (Shell route) or acrolein (Degussa-DuPont route). The low conversion efficiency of the acrolein process, as well as the hazardous nature of acrolein, has spurred a great deal of interest in producing 1,3-PD from other chemical sources, especially glycerol. Another important diol, ethylene glycol, mainly derived from ethylene, is also a raw material for synthetic fibers and explosives, *etc.*[76]

The different pathways of the hydrogenolysis of glycerol are shown in Scheme 5. The hydrogenolysis of the two primary hydroxyl groups yields 1,2-PD, then 2-propanol (2-P), and eventually propane. 1,3-PD could be formed first, and then the consecutive removal of the remaining OH yields 1-propanol (1-P) and propane. Whether the primary or secondary hydroxyl group is more easily reduced depends on different catalyst systems and reaction conditions. Catalytic –OH cleavage with noble metals under reductive conditions usually favors reduction of primary hydroxyl groups over secondary groups. Tertiary hydroxyls are cleaved faster than secondary hydroxyls, but most likely because of differing mechanisms (*e.g.*, unimolecular nucleophilic substitution – S_N1). The alternating primary–secondary–primary hydroxyl reduction pathway is obviously unlikely to occur.

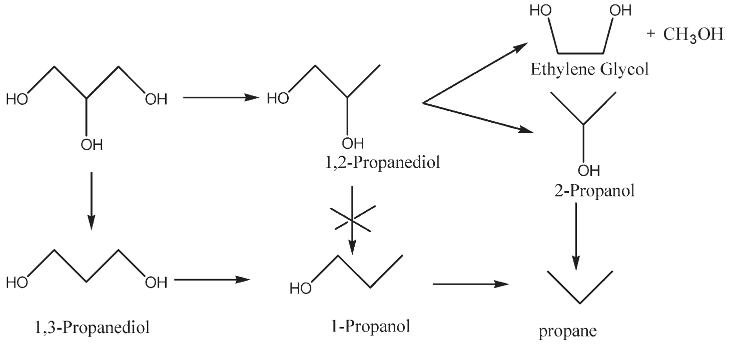
Traditional practices of hydrogenation (addition of hydrogen to molecules) have indicated that the alcohol groups are stable and do not readily react at normal hydrogenating reaction conditions. Moreover, the alcohols are also known as excellent resistant solvents for the hydrogenation reaction. Hence conventional hydrogenation catalysts such as nickel, ruthenium, and palladium are not very effective when used for hydrogenation and catalytic –OH cleavage, *i.e.* hydrogenolysis of glycerol.

Earlier, Che[77] patented a one-step process for the catalytic hydrogenolysis of glycerol in water solution using syngas at 473 K and 32 Mpa pressure in the presence of a homogeneous rhodium complex catalyst ($Rh(CO)_2(acac)$) and tungstic acid. During the reaction, 1,3-PD and 1,2-PD were produced with 20% and 23% yield, respectively. Braca *et al.*[78] reported the catalytic hydrogenolysis in an aqueous solution of polyols catalyzed by Ru homogeneous complexes. Schlaf *et al.*[79] also described the catalytic hydrogenolysis of glycerol in sulfolan catalyzed by a homogeneous complex of ruthenium. The reaction proceeded under milder conditions (5 MPa, 383 K) but very low yields of 1,2-PD and 1,3-PD were achieved (<5%). Recently, the Shell Oil Company developed a process that uses homogenous palladium complex in a water–sulfolane mixture containing methane sulfonic acid. After a 10 h reaction, 1-propanol, 1,2-propanediol and 1,3-propanediol were detected in a ratio of 47 : 22 : 31.[80]

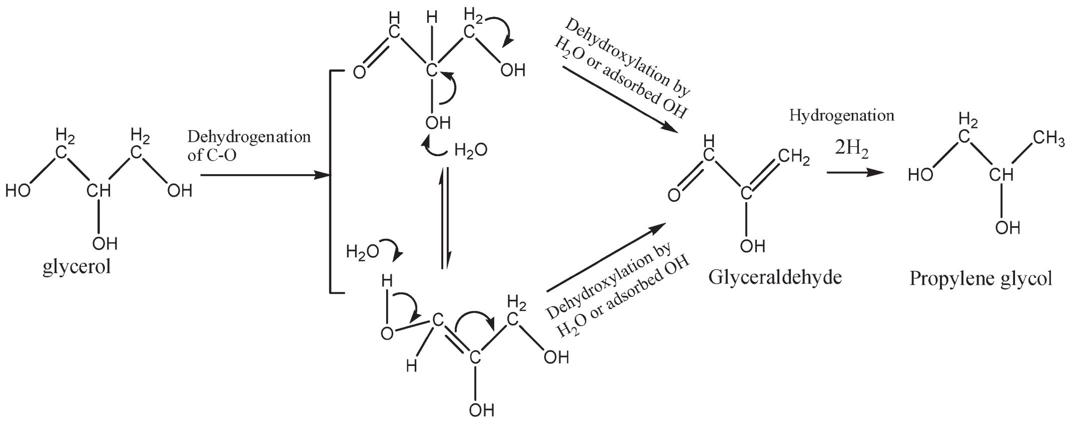
Therefore, if the catalytic hydrogenolysis of glycerol can be carried out over solid catalysts without the presence of dangerous solvents, it would become economically and environmentally attractive. Montassier *et al.*[81] carried out the hydrogenolysis of glycerol at 30 MPa H_2 at 533 K in the presence of Raney Ni, Ru, Rh and Ir catalysts. They found that mainly methane was produced, but when Raney Cu was used as a catalyst, 1,2-PD was the main reaction product. Raney Cu is known for its poor hydrogenolytic activity towards C–C bond but it is an efficient catalyst for C–O bond hydrogenation and dehydrogenation. Furthermore, experimental results using Raney Cu, Cu/C,[82] Cu–Pt and Cu–Ru bimetallic catalysts[83] at 1.0–4.0 MPa and 493–513 K have also been reported. A reaction mechanism for conversion of glycerol to 1,2-PD proposed by Montassier *et al.*[84,93] is shown in Scheme 6.

Casale and Gomez explained the hydrogenolysis of glycerol at 15 MPa of pressure and between 513–543 K temperatures using copper and zinc catalyst[85] as well as sulfided ruthenium supported on an activated carbon catalyst.[86] In contrast, Ludvig and Manfred[87] studied the production of propanediols using a catalyst containing cobalt, copper, manganese, molybdenum, and an inorganic polyacid that achieved a 95% yield of 1,2-PD at 25 MPa and 523 K. Haas *et al.*[88] reported a two-stage process for simultaneous production of 1,2-PD and 1,3-PD from gaseous glycerol solutions at a temperature of 573 K. It involves: (a) dehydration of a gaseous 10–40% glycerol–water mixture at 523 K to 613 K over a solid acid catalyst, and (b) catalytic hydrogenation of the reaction mixture to yield 1,2-PD and 1,3-PD. In another work, Werpy recently filed a patent for the hydrogenolysis of glycerol and other polyols over Ni/Re catalyst. After reaction for 4 h at 503 K under 8 MPa H_2 pressure, 44% of 1,2-PD and 5% of 1,3-PD were obtained together with 13% of ethylene glycol.[89]

Analyzing the above cases we found that in order to obtain optimum selectivity values, very complex conditions and catalytic systems were needed. A more preferable technology would convert crude natural glycerol at moderate



Scheme 5 Theoretical pathways for catalytic hydrogenolysis of glycerol. (After scheme from ref. 96 with permission from the American Chemical Society. © 2005 American Chemical Society.)

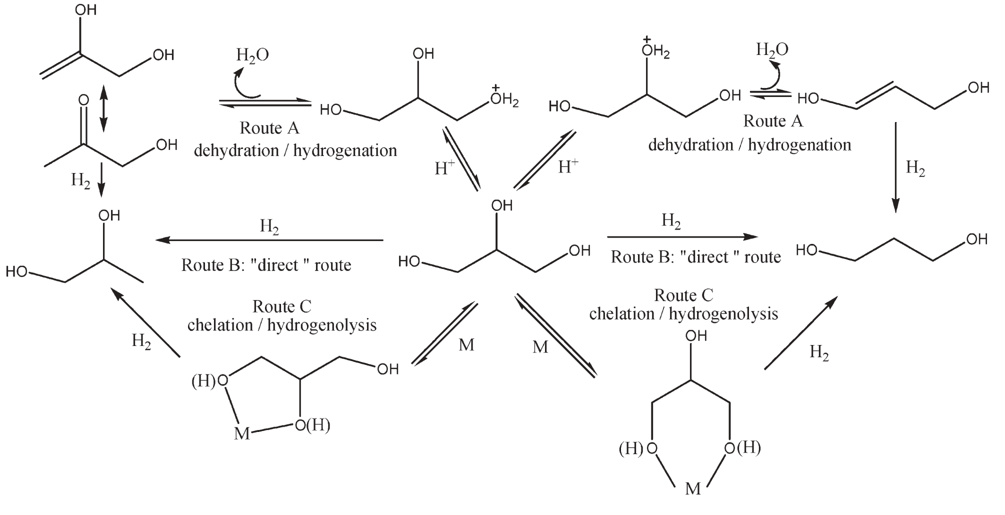


Scheme 6 Reaction mechanism for conversion of glycerol to propylene glycol proposed by Montassier *et al.* (After schemes from ref. 84 and 93 with permission from Elsevier. ©1988 and 2005 Elsevier.)

temperatures and pressures. Hydrogen pressures of around 6–10 MPa and reaction temperatures of 453–513 K for glycerol hydrogenolysis have been reported using supported metal catalysts.[85–91]

Chaminand *et al.*[92] addressed the complexity of using heterogeneous Cu, Pd, and Rh catalysts supported on ZnO, C, and alumina for the hydrogenolysis of glycerol carried out at 8 MPa pressure and at 453 K in the presence of solvents (H_2O, sulfolane, dioxane). Additives such as tungstic acid (H_2WO_4) that act as a modifier to improve the selectivity toward 1,3-PD were added to the reaction medium. Therefore, during the hydrogenolysis of glycerol in water, a 100% selectivity to 1,2-PD can be obtained when using CuO/ZnO catalysts. Regarding the addition of solid acid to metal catalysts, it has been reported that H_2WO_4 was effective in enhancing the glycerol conversion. The authors also demonstrated that the addition of H_2WO_4 to Rh/C increased the 1,3-PD selectivity (1,3-PD/1,2-PD = 2) in sulfolane compared with previous systems. On the other hand, it was noted that the presence of iron dissolved in the reaction medium can improve the selectivity to 1,3-PD. In view of these results, Chaminand *et al.* (Scheme 7) proposed a general mechanism. The figure shows that tungstic acid can favor the dehydration route (route A, *E*1-like mechanism) *via* protonation of the hydroxyl groups with loss of water. The keto group formed as an intermediate can be easily reduced under these reaction conditions. However, when using acid (*i.e.* HCl) a low conversion was obtained, suggesting that the acidity of H_2WO_4 does not have a dominant effect over the reaction mechanism. At the same time, the formation of a Rh–W alloy can not be excluded and can affect the selectivity and the activity of the glycerol hydrogenolysis reaction. Furthermore, Chaminand *et al.* show that the addition of a second metal (Fe or Cu) to the reaction medium reduces the activity of the Rh due to a poisoning effect. Moreover, iron can be chelated by a diol and consequently modifies the selectivity of the hydrogenolysis (route C). From the findings, we conclude that further work is still needed to establish the exact reaction mechanism and to optimize the reaction pathways.

Dasari *et al.*[93] used commercially available catalysts for low-pressure hydrogenolysis of a concentrated glycerol solution into 1,2-PD (Table 2). A copper chromite was identified as the



Scheme 7 Possible reaction routes for catalytic hydrogenolysis of glycerol proposed by Chaminand *et al.* (After scheme from ref. 92 with permission of the Royal Society of Chemistry. © 2004 The Royal Society of Chemistry.)

Table 2 Summary of conversion of glycerol, yield and selectivity of propylene glycol from glycerol over various metal catalysts (After table from ref. 93 with permission of Elsevier. © 2005 Elsevier.)

Catalyst Supplier	Description	Conversion (%)	Yield (%)	Selectivity (%)
Johnson Matthey	5% Ru/C	43.7	17.5	40.0
Johnson Matthey	5% Ru/alumina	23.1	13.8	59.7
Degussa	5% Pd/C	5	3.6	72.0
Degussa	5% Pt/C	34.6	28.6	82.7
PMC Chemicals	10% Pd/C	8.9	4.3	48.3
PMC Chemicals	20% Pd/C	11.2	6.4	57.1
Grace Davision	Raney nickel	49.5	26.1	52.7
Grace Davision	Raney copper	48.9	33.8	69.1
Sud-Chemie	Copper	53	21.1	39.8
Sud-Chemie	Copper chromite	54.8	46.6	85.0
Johnson Matthey	Ni/C	39.8	27.3	68.6
Alfa-Aesar	Ni/silica-alumina	45.1	29.1	64.5

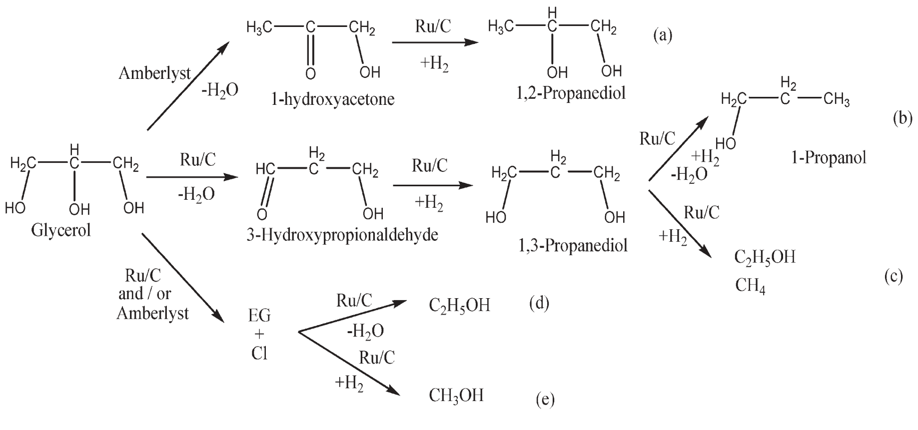
[a] Reactions were carried out using 80% glycerol solution at 473 K and 1.38 MPa (200 psi) hydrogen pressure for 24 h.

most effective catalyst, yielding 73% of 1,2-PD at moderate reaction conditions of 1.4 MPa and 473 K. This result provides a very distinctive competitive advantage over traditional processes that use more severe reaction conditions. The authors proposed a novel two-step reaction mechanism for the conversion of glycerol to 1,2-PD for the copper chromite catalyst. The first step carried out at atmospheric pressure involves the formation of 1-hydroxyacetone by the dehydration reaction while the hydrogenation second step requires a hydrogen partial pressure.

Recently Tomishige *et al.*[94,95] demonstrated that when active Ru, supported on carbon is used in combination with a cation exchange resin such as Amberlyst 15, it can exhibit higher activity in glycerol hydrogenolysis under mild reaction conditions (393 K and 4 MPa or 8.0 MPa H_2) than other metal–acid bifunctional catalyst systems such as zeolites, sulfated zirconia, H_2WO_4, and liquid H_2SO_4. The Ru/C catalyst showed higher conversion than Rh/C, Pd/C and Pt/C. However, the selectivity of cracking products was rather high over Ru/C, with the dehydration of glycerol to 1-hydroxyacetone being catalyzed by the acid catalysts. The subsequent hydrogenation of 1-hydroxyacetone on the metal catalysts gives 1,2-propanediol. Thus the addition of solid acid catalysts to Ru/C was effective in increasing the conversion and hydrogenolysis selectivity. A proposed reaction scheme for the hydrogenolysis of glycerol is shown in Scheme 8. During the hydrogenolysis reaction, the activity of the metal catalyst when combined with the cation exchange resin can be related to that of 1-hydroxyacetone hydrogenation over the metal catalysts. In addition, the OH group on Ru/C can also catalyze the dehydration of glycerol to 3-hydroxypropionaldehyde, which ultimately can be converted into 1,3-PD and other degradation products through subsequent hydrogenation. From these results Ru/C + H_2SO_4 showed lower activity than combined Ru/C+Amberlyst, suggesting that the solid acid was more effective for the hydrogenolysis of glycerol.

More interestingly, Perosa *et al.*[96] showed that Raney Ni is an active catalyst for the hydrogenolysis of glycerol at low hydrogen pressure (1 Mpa) when the reaction is conducted in the presence of liquid phosphonium salt and without added solvents. Selectivity toward 1,2-PD is high, with the only by-products being ethanol and CO_2. The reaction does not require solvents, promoter or harsh conditions. But the addition of a liquid phosphonium salt, at the reaction temperature, improved the reaction rate and selectivity to a small extent but did not facilitate the separation of the final reaction mixture. Kinetic analysis of the hydrogenolysis of glycerol to glycols using a Langmuir–Hinshelwood-type model was developed by Lahr *et al.*.[97] Using a batch reactor system, they also studied the effects of temperature between 478–613 K and the effect of sulfur loading for 0–1.0 mol S/Ru using Ru supported on carbon catalysts.[98] It was found that due to competitive adsorption, the relative degradation rates of the glycols were independent of temperature. Sulfur modification of the ruthenium catalysts did not change the activation energy of the degradation reactions, but did dramatically suppress the reactions. They postulated that the hydrogenolysis of glycerol to 1,2-PD may occur on the catalyst surface and not just in solution. These results suggest that selectivity for 1,2-PD relative to ethylene glycol and degradation products can be enhanced if the catalyst is active for dehydration.

Despite several research efforts, the potential importance of the glycerol hydrogenolysis reaction is limited to the

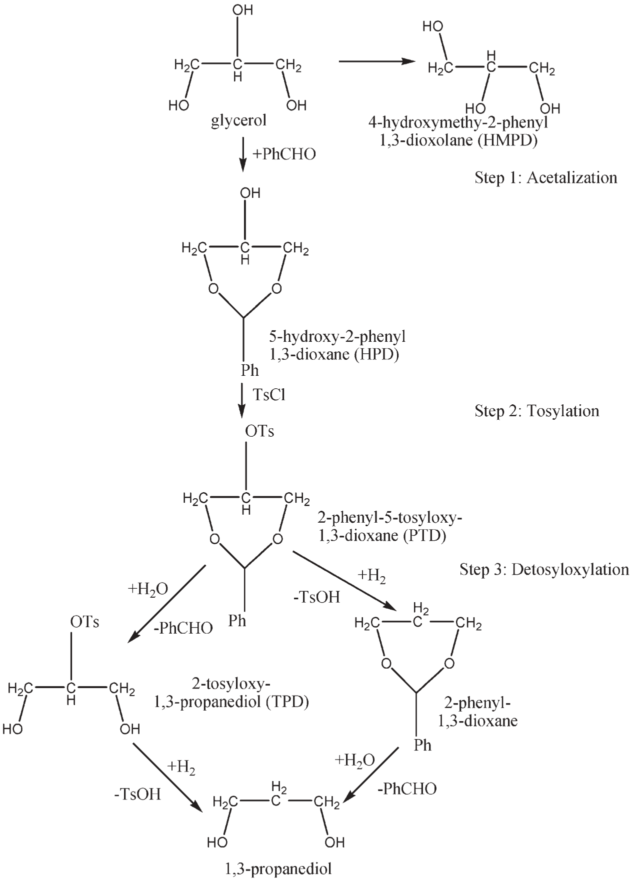


Scheme 8 Reaction scheme for glycerol hydrogenolysis and degradation reactions proposed by Miyazawa *et al.* (After scheme from ref. 95 with permission of Elsevier. © 2006 Elsevier.)

laboratory scale as the common drawbacks of high temperature and pressure, dilute solutions and the low selectivity towards propylene glycol still require further investigation. Interestingly, Wang *et al.*[99] described a new approach to the selective production of 1,3-PD from glycerol. (Scheme 9). The idea is to selectively transform the second hydroxyl group of glycerol into a tosyloxyl group (tosylation) and then to remove the transformed group by catalytic hydrogenolysis (detosyloxylation). This new approach involves three steps, namely, acetalization, tosylation, and detosyloxylation. A 1,3-PD yield as high as 72%, roughly taken as the overall yield of this new glycerol hydrogenolysis process, was achieved for 2-phenyl-5-tosyl-1,3-dioxane(PTD) detosyloxylation reaction.

4 Catalytic dehydration of glycerol

Acrolein is an important and versatile chemical intermediate for the production of acrylic acid esters, super absorber polymers or detergents. A sustainable and cost effective acid dehydration of glycerol to acrolein could offer an alternative for the currently commercial catalytic petrochemical process based on propylene oxide over a Bi/Mo-mixed oxide catalyst. Scheme 10 shows a schematic reaction path for catalytic dehydration of glycerol.

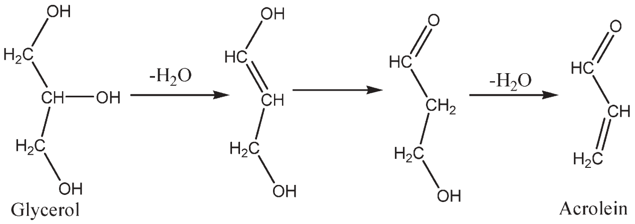


Scheme 9 Conversion of glycerol to 1,3-propanediol *via* selective dehydroxylation in three steps. (After scheme from ref. 99 with permission of the American Chemical Society. © 2003 American Chemical Society.)

In 1950, Waldmann and Frantisek[100] obtained 13.5 g of acrolein, distilled from a reaction mixture of 50 g glycerol, 100 g phthalic anhydride and 3 g benzenesulfonic acid. Ramayya *et al.*[101] also reported that an 84% acrolein selectivity can be obtained at 40% conversion of glycerol by adding 5 mM H_2SO_4 into water at 573–623 K and 34.5 MPa. Antal *et al.*[102] showed that a high reaction temperature is needed for the dehydration of glycerol in water. A low 1% glycerol conversion was only obtained without the presence of acrolein when the reaction was conducted at 523 K and 34.5 MPa pressure. There are several patents concerning the gas phase dehydration of glycerol. Scheering–Kahlbaum AG[103] reported an acrolein yield up to 80 mol% using phosphates of Cu or Li as catalysts at a temperature of 573–873 K. A more recent patent by Degussa AG[104] claimed that the reaction can be conducted at 513–623 K in the presence of an acid catalyst. On the other hand, Biswas *et al.*[105] suggested the use of pervaporation, a membrane-based separation technique, as a potential replacement process for the vacuum distillation process, which is normally used for the dehydration of glycerol–water mixtures.

As discussed in the previous section, solid acid catalysts (*i.e.* Amberlyst ion-exchange resin) can catalyze the dehydration of glycerol, while Ru/C catalyst can play an important role in the reaction selectivity to 3-hydroxypropionaldehyde, which can be converted to 1,3-propanediol through subsequent hydrogenation and other degradation products, according to a reaction mechanism proposed by Miyazawa *et al.*[88]

Sub- and supercritical water (SCW) reactions can be used for the production of acrolein from glycerol. Bühler *et al.*,[106] using flow compressed water (HCW) equipment, found only low glycerol conversions (31 mol%) and low acrolein selectivity (S = 37 mol%) in pure water when the system operated at a temperature range from 573–747 K and pressure from 25–45 MPa with a residence time in the range of 16–100 s. With initial glycerol concentration changing from 0.19–0.57 M, the authors suggested that the glycerol reactions in HCW progress competitively through both ionic and radical reaction mechanisms. The predominance of the ionic or radical mechanisms could be controlled by temperature and pressure: the ionic reaction preferred subcritical water below the critical temperature (liquid state) and the reaction *via* radical formation was favored at the supercritical region. The kinetic model also indicated that glycerol dehydration into acrolein mainly occurred through ionic reactions, whereas the other dehydration reaction led to allyl alcohol with the bond scission reaction forming into acetaldehyde and formaldehyde through radical reactions. In addition, Watanabe *et al.*[107] revealed that the yield of acrolein can be enhanced using a higher



Scheme 10 A schematic reaction path for catalytic dehydration of glycerol.

concentration of glycerol and H_2SO_4 in combination with higher pressure. Approximately 80% selectivity of acrolein was obtained at 90% conversion of glycerol on an acid catalyst in supercritical condition (673 K and 34.5 MPa). The rate constant of acrolein decomposition was always higher than that of acrolein formation in the absence of an acid catalyst, but the rate constant of acrolein formation could overcome that of acrolein decomposition by the addition of an acid in supercritical condition.

In another interesting work, Ott *et al.*[108] found that zinc sulfate is an effective catalyst for the acrolein synthesis from glycerol in HCW (573–663 K, 25–34 MPa, 10–60 s), achieving an acrolein selectivity of 75% at 50% of glycerol conversion. It turned out that the addition of zinc sulfate causes a decrease of the activation energy from 150 kJ mol^{-1} to (140 ± 2) kJ mol^{-1}.

Previous research results by Ramayya, Bühler, Ott and their coworkers [101,106,108] confirmed that the formation of acrolein from glycerol was controlled by ionic species (such as proton) and can be increased by the presence of an acid and HCW conditions. However, the current use of SCW is only promising if acid is added. But as water itself under these conditions induces corrosion, the presence of an acid compound intensifies the corrosive effect, with a salt catalyst having the same corrosion potential in SCW as mineral acids.[109] As such, another less corrosive anion more stable under these reaction conditions is needed if the acrolein synthesis from glycerol is expected to become an attractive commercial process in the near future.

Recently, Nimlos *et al.*[110] investigated the dehydration of neutral and protonated glycerol using quantum mechanical calculations (CBSQB3). Calculations of the dehydration of glycerol by the neutral mechanisms indicate that these processes can only occur at relatively high temperatures such as are found in pyrolysis or combustion. They suggested that the addition of acids will allow substantially lower dehydration temperatures.

5 Pyrolysis and gasification of glycerol

The pyrolysis process yields liquid fuels at low temperatures (673–873 K) and gaseous products at high temperatures (>1023 K). Gasification is a process related to pyrolysis, but the major difference between both processes is that gasification is conducted in the presence of oxygen, in the form of air or steam.

Earlier, Stein *et al.*,[111] using a laminar flow reactor operated at 0.1 MPa with temperatures ranging from 923 to 973 K and residence times below 0.13 s, studied the pyrolysis of glycerol in the presence of steam. Major gaseous reaction products included CO, H_2, C_2H_4, and CH_4 (in decreasing order of yields). Almost no CO_2 was detected. These results have also shown that the initial products of decomposition were CO, acetaldehyde and acrolein. Acetaldehyde and acrolein further decomposed to produce primarily carbon monoxide, ethylene, methane and hydrogen.

$$C_3H_8O_3 \rightarrow 3CO + 4H_2 \qquad (1)$$

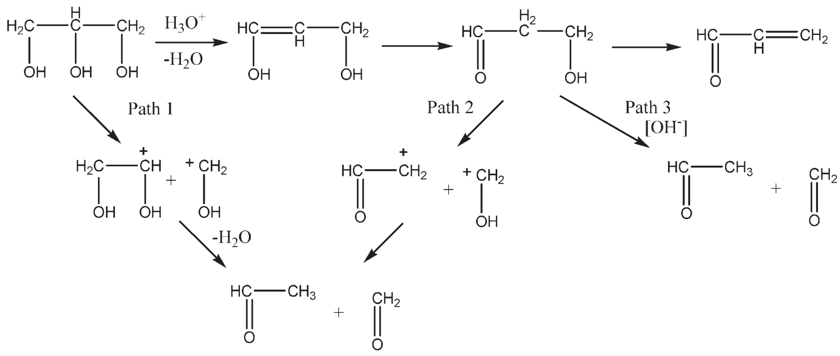
$$C_3H_8O_3 + 3H_2O \rightarrow 3CO_2 + 7H_2 \qquad (2)$$

Another possible solution is the use of glycerol as a source of hydrogen (eqn (1)), and, in this regard, steam reforming of glycerol could be a suitable reaction (eqn (2)). Xu *et al.*[112] showed that glycerol is easily and completely gasified to a hydrogen-rich gas in supercritical water without a catalyst after 44 s at 873 K and 34.5 MPa. The presence of the catalyst has little effect on the gas composition. During their experimentation they observed a very low CO yield in contrast with a high H_2 yield. These results may be in disparity with those observed by Stein *et al.*[111] Evidently, the supercritical condition results in considerably different gasification chemistry than that observed at atmospheric pressure.

Using a tubular reactor system in the temperature range of 622–748 K, with pressures of 25, 35, or 45 MPa, and reaction times from 32 to 165 s, Bühler *et al.*[106] investigated the decomposition of glycerol at different initial concentrations using near- and supercritical water. A conversion between 0.4 and 31% was observed with the main products of the glycerol degradation being methanol, acetaldehyde, propionaldehyde, acrolein, allyl alcohol, ethanol, formaldehyde, carbon monoxide, carbon dioxide, and hydrogen. A non-Arrhenius behavior of the overall degradation, as well as the pressure dependence of the reaction rate was found. The product distribution indicates the occurrence of two competing reaction pathways as depicted in Scheme 11,[101,106,113] (1) ionic reaction steps, which are preferred at higher pressures and/or lower temperatures and (2) a free radical degradation that dominates at lower pressures and/or higher temperatures.

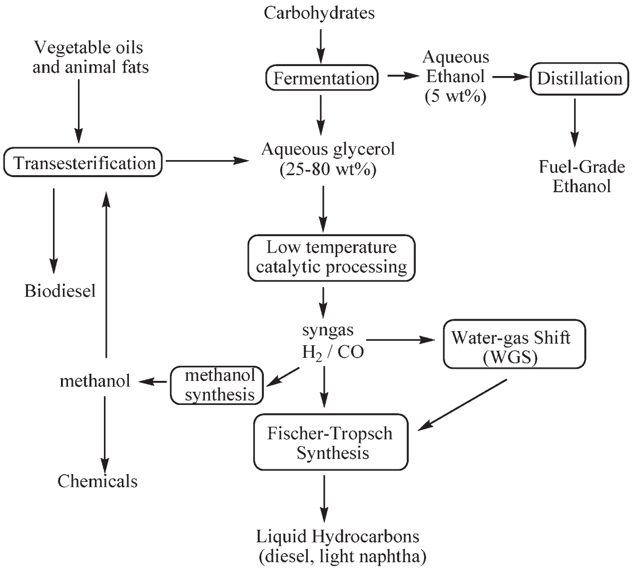
Shabaker *et al.*,[114] using Raney–NiSn catalysts at temperatures of 498 K for the aqueous-phase reforming of sorbitol, glycerol and ethylene glycol solutions, produced an effluent gas stream composed of 66 mol% H_2, 30 mol% CO_2, and 4.2 mol% methane alkanes (dry basis). Although the advantages of low catalyst deactivation have been reported for the aqueous phase reaction, it is unavoidable that the reforming of glycerol must be conducted under high pressure. On the other hand, reforming in the gas phase can be conducted under atmospheric pressure with a conventional fixed-bed flow reactor. Dauenhauer and co-workers[115] reported studies of the autothermal reforming of pure glycerol under water solutions over platinum- and rhodium-based catalysts supported on alumina foams at a contact time of ~10 minutes. They found that rhodium catalysts, with the addition of ceria on a γ-Al_2O_3 washcoat layer, exhibited the best combination of high fuel conversion and high selectivity to H_2 near equilibrium. On the other hand, steam addition increased selectivity of H_2 to 79%. We believe their results occur primarily through a surface reaction mechanism initiated by adsorption on metals through hydroxyl oxygen lone pairs to form surface alkoxides, which decompose almost exclusively to H_2 and C_1 carbon compounds. Hirai *et al.*[116] developed a novel efficient 3 wt%Ru/Y_2O_3 catalyst for glycerol steam reforming in the gas phase. The Ru/Y_2O_3 catalyst displayed very high activity in a prolonged run and is considered to be resistant to the deactivation caused by carbon deposition.

More recently, Soares *et al.*[117] investigated a low-temperature catalytic route for converting glycerol into H_2/CO gas mixtures that are suitable for combination with Fischer–Tropsch and methanol syntheses. The conversion of glycerol



Scheme 11 Formation of acetaldehyde, acrolein and formaldehyde as suggested by Antal *et al.* (After scheme from ref. 106 with permission of Elsevier. © 2002 Elsevier.)

into CO and H_2 takes place according to eqn (1). Interestingly, the authors proposed that the endothermic enthalpy change of this reaction (350 kJ mol^{-1}) corresponds to about 24% of the heating value of the glycerol (-1480 kJ mol^{-1}). The heat generated by the Fischer–Tropsch conversion of the CO and H_2 into liquid alkanes such as octane (-412 kJ mol^{-1}) corresponds to about 28% of the heating value of the glycerol (eqn (2)). Thus, combining these two reactions results in an exothermic process, with an enthalpy change (-63 kJ mol^{-1}) that is about 4% of the heating value of the glycerol. The process pathways that can generate liquid fuels and chemicals from glycerol are outlined in Scheme 12. Accordingly, Soares and co-workers designed Pt–Ru and Pt–Re alloy catalysts that possess the catalytic properties of Pt with respect to selective cleavage of C–C *versus* C–O bonds, but that have less exothermic enthalpy changes for CO adsorption. The results have shown that the percentage conversion of glycerol and the product-gas ratios remained constant for at least 72 h time-on-stream at these low temperatures. The main condensable organic compound in the effluent streams of the reaction was unconverted glycerol, with smaller quantities of ethylene glycol, methanol, hydroxypropanone, and ethanol.



Scheme 12 Schematic of liquid fuel and chemical production *via* catalytic processing of glycerol. (After scheme from ref. 117 with permission from Wiley-VCH. © 2006 Wiley-VCH.)

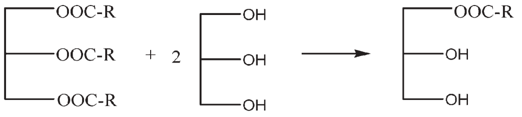
Generally, the generation of H_2 and CO by liquid-phase reforming at low temperatures is accompanied by selectivity challenges, as the reaction of H_2 with CO or CO_2 to form alkanes (C_nH_{2n+2}) is highly favorable at these low temperatures. Thus, an effective catalyst for the production of H_2 by aqueous-phase reforming of glycerol must break C–C, O–H, and C–H bonds in the reactant, and the catalyst must facilitate the water-gas shift to remove adsorbed CO from the surface. However, breaking C–O bonds leads to alkane formation and the degradation of hydrogen production. Aqueous-phase reforming can also lead to the formation of oxygenated intermediates by several reactions, including dehydration and isomerization.[118] Therefore, an efficient catalyst for the steam reforming of glycerol still needs to be found.

In other unrelated work, Du *et al.*[119] reported that carbon anions with diameters ranging from 60 to 90 nm were successfully synthesized *via* thermal reduction of glycerol with magnesium in a stainless steel autoclave at 923 K as shown in eqn (3). X-ray diffraction (XRD) and Raman spectroscopy results confirmed that the carbon material has graphite and polycrystalline structure. This reaction is similar to that reported by Qian and co-workers, who synthesized carbon nanotubes and carbon cones using the reactions of ethanol and butyl alcohol with magnesium, respectively.[120] The mechanism to form the carbon anions needs to be studied further.

$$3Mg + C_3H_8O_3 \xrightarrow{923K} 3MgO + 3C + 4H_2 \qquad (3)$$

6 Selective glycerol transesterification and esterification

Monoglycerides (MG) and polyglycerol esters (PEG) consist of a hydrophilic head and a hydrophobic tail, which give them detergent characteristics. It is very well known that monoglycerides and their derivatives have wide applications as emulsifiers in food, pharmaceutical, and cosmetic industries.[121] Projects are under way to convert glycerol into ester or ether derivatives that can be processed into new marketable products, *e.g.*, biodegradable surfactants.[122] The monoglycerides are generally obtained by: (I) the hydrolysis of triglycerides, (II) the glycerolysis of triglycerides, *i.e.*, the transesterification of glycerol with fatty methyl esters, a base-catalyzed transesterification of triglycerides with glycerol at elevated temperature (*e.g.*, 528 K) (eqn (4)), or (III) the direct esterification of glycerol with fatty acids (eqn (5)).



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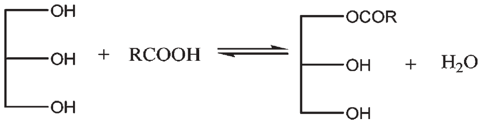


(5)

However, as the three hydroxyl groups in glycerol do not strongly differ in reactivity, the product of the direct esterification or transesterification of glycerol with acid and/or base catalysis is a mixture of mono-, di- and some triglyceride, and dissolved glycerol, which typically contains 40–60% monoglyceride and 35–45% diglyceride. Furthermore, the proportion of 2-acyl or β-monoglyceride remains below 10% at low temperature but increases with the reaction temperature. In order to lower the reaction temperature for the direct esterification of glycerol with fatty acids, normally an acid catalyst is required, *e.g.*, sulfuric acid, phosphoric acid, or organic sulfonic acids such as Twitchell-type reagents.

Traditionally, basic catalysts such as KOH and $Ca(OH)_2$, can be industrially used during the transesterification processes. After reaction, they should be neutralized with phosphoric acid, and then the formed salts must be removed. Therefore, a lot of undesired waste chemicals can be obtained. Furthermore, these processes suffer from another drawback – the requirement of high temperature. In parallel, techniques for purification of monoglycerides, *e.g.*, distillation, are limited to food applications as such process steps are expensive.

It is therefore highly desirable to find a greener catalytic process that can improve the yield of desired products (*e.g.* monoester yield) using more economic reaction conditions on an appropriate solid catalyst suitable to regeneration. The basic features of these processes and some progress of modifying classical process using solid catalysts have been previously reviewed.[123,124]

Solid basic materials such as metal oxides MgO, CeO_2, La_2O_3 and ZnO; Al–Mg hydrotalcites; Cs-exchanged sepiolite; and mesoporous MCM-41 have been tested as potential catalysts for the glycerol transesterification with triglycerides.[125,126] Table 3 summarizes some recent typical results of synthesis of monoglycerides over various solid catalysts. Researchers found that, due to the negative influence of the low solubility of the hydrophilic glycerol in the fat phase, the use of organic solvents would have a beneficial effect on the overall reaction but, for safety reasons, it is avoided when producing monoglycerides that are then used as food additives (Table 3).[127] Recently, Bancquart *et al.*[126] investigated the transesterification of glycerol with basic solid catalysts in the absence of solvents in order to reduce the waste formation and extraction steps and permit an easier removal of the catalyst. A comparison of several basic solids (MgO, CeO_2, La_2O_3 and ZnO) has shown that when the intrinsic basicity is significant, the catalyst becomes more active. It was found that MgO prepared by hydration followed by calcination of a commercial raw material was the most active catalyst. The reaction rate was similar to that obtained in the presence of homogeneous catalysts. However, the monoglycerides selectivity was rather similar with an observed distribution of mono/di/tri glycerides close to 50%/40%/10%, respectively. In other work, Barrault

Table 3 Typical results of synthesis of monoglycerides over various solid basic or acidic catalysts

Catalysts	Reactants	Glycerol/ fatty comp. (molar ratio)	Solvent	Reaction temp (K)	Time/h	Conversion[a] (%)	Monoglyceride selectivity (%)	Ref.
ZnO	glycerol + methyl stearate	1	no	493	6	18	80	126
MgO	glycerol + methyl stearate	1	no	493	6	83	42	126
La_2O_3	glycerol + methyl stearate	1	no	493	6	97.0	28	126
CeO_2	glycerol + methyl stearate	1	no	493	6	4	100	126
ZnO	glycerol + stearic acid	1	diglyme	160	16	63.3	82.5	127
ZnO	glycerol + lauric	1	diglyme	433	16	56.1	73.3	127
ZnO	glycerol + oleic	1	diglyme	433	16	45.1	90.7	127
MgAl-MCM-41	glycerol + lauric acid	3	no	493	20	80	70	128
ZnO	glycerol + myristic	3	no	493	33	80	62	128
ZnO	glycerol + stearic acid	3	no	493	44	80	50	128
Calcined Al–Mg hydrotalcite	glycerol + methyl stearate	6	No	473	8	95	67	129
Calcined-rehydrated(12 h) Al–Mg hydrotalcite	glycerol + methyl stearate	6	No	473	8	98	80	129
KF/Al_2O_3	glycerol + methyl stearate	6	no	473	2	68	69	129
USY (Si/Al = 14.2)	glycerol + oleic acid	1	no	373	24	8.2	55	144
Beta (Si/Al = 13)	glycerol + oleic acid	1	no	373	24	8.8	64	144
Al-MCM-41 (Si/Al = 15)	glycerol + oleic acid	1	no	373	24	5.8	96	144
MCM-41-F[b]	glycerol + oleic acid	1	no	373	24	10.9	68	144
MCM-41-C[b]	glycerol + oleic acid	1	no	373	24	24.2	69	144
Phenyl-MCM-41	glycerol + oleic acid	1	No	393	8	25	67	144
Methylsulfonic/ phenylsulfonic-MCM-41	glycerol + oleic acid	1	no	393	8	39	69	144

[a] Conversion of fatty aids or fatty acid monoesters. [b] Where MCM-41-F means post-synthesis functionalization of sulfonic acid and MCM-41-C stands for co-condensation procedure.

et al.[128] reported the conversion of monoglycerides from lauric (C_{12}), myristic (C_{14}) and stearic (C_{18}) acid methyl esters and glycerol using several MCM-41 magnesium-containing catalysts. Over a Mg–MCM-41 catalyst (interreticular distance d_{100} of 3.4 nm), glycerol monolaurate was obtained with selectivity and yield of about 80%. More recently, Corma *et al.*[129] studying the transesterification of oleic acid methyl ester with glycerol solid found that Brønsted base catalysts have a higher activity and a higher specific rate than the Lewis basic hydrotalcite catalyst. The selectivity to monoglycerides of the former is higher because of the lower deactivation of the catalyst, which allows the transesterification of diglycerides to occur at longer reaction times. Calcined Li–Al hydrotalcites result in higher activity than MgO or Al–Mg hydrotalcites because of the stronger Lewis basicity of the former. All of the solid Lewis basic catalysts, regardless of the base strength, have the same selectivity to monoglyceride, which is lower than that of Brønsted basic solid catalysts.

In contrast, a variety of solid acids such as 12-membered-ring structures, like faujasite,[130] USY[131–133] and zeolite beta;[134] 10-membered-ring structures, like ZSM-5, or unidirectional 12-membered rings materials like mordenite,[135,136] have also been tested for the catalytic esterification of glycerol with fatty acids. The authors stated that, in the presence of porous zeolites, the relatively small pore opening of these materials would have the potential to reduce the formation of the bulky di- and triesters, therefore increasing the selectivity to monoglycerides. However, as di- and even traces of triglycerides are still readily observed at conversions higher than 10%, a significant contribution of the external surface to the overall reaction cannot be totally excluded. Even if such catalysts exhibit high monoester selectivity, the activity and consequently monoglyceride yield were still low. In order to avoid the effect of the pore-size constraints of the zeolite materials on the reaction, cross-linked porous polymers, like ion-exchange resins containing sulfonic acid groups, have been used as catalysts for the esterification of glycerol with fatty acids.[137]

Mesoporous silicas are easily accessible for large reactants such as fatty acids and their esters and offer the possibility to overcome the pore-size limitation characteristic of traditional zeolite materials. Unfortunately, the strength of the acid sites present in conventional MCM-41 materials is much lower than microporous zeolites,[138] and, consequently, their activity and monoglycerides selectivity is low.[139,140] They should be frequently modified in order to obtain specific properties, *e.g.*, in acidity or basicity. Bossaert *et al.*,[141,142] has shown that glycerol can be esterified with an unspecified amount of lauric acid to monolaurin using zeolites, sulfonic resins, and sulfonic mesoporous materials (silica gel, MCM-41, HMS) as catalysts. The latter were obtained by immobilization of 3-mercaptopropyl groups and oxidation with H_2O_2. When using silica gel coated with propylsulfonic acids, high reaction rates are coupled to high monoglyceride yields, *e.g.*, 53% mono yield for a 1 : 1 glycerol : lauric acid ratio. Minimizing the autocatalytic contribution of the fatty acid reactant is a critical issue. The best mesoporous sulfonic catalysts offer a unique combination of high activity and selectivity, which is not obtained with homogeneous or traditional heterogeneous catalysts. Pérez-Pariente and coworkers recently investigated the behavior of mesoporous materials containing R–SO_3H groups in the esterification of glycerol with fatty acids.[143–149] The catalytic activity of Al-MCM-41 (Si/Al = 15) in the esterification of glycerol with oleic acid is much lower than that of zeolites USY with similar Si/Al ratios (Table 3), whereas the selectivity to mono-olein increases substantially. Nevertheless, the activity of this material is still too low. A strategy to increase the catalytic activity while keeping the benefits of the large pore diameter could be to introduce, in a controlled manner, new acid groups on the catalyst surface. The superior performances of mesoporous materials containing organosulfonic functional groups synthesized by co-condensation over those obtained *via* silylation of the calcined materials were found for esterification of glycerol with oleic acid (Table 3). The higher activity of the sample synthesized by co-condensation is most probably due to its higher content of sulfonic acid.

Recently Díaz *et al.*[150] studied the catalytic activity and selectivity for the esterification of glycerol with lauric and oleic acids using newly synthesized materials such as HSO_3-ethyl-MCM-41, HSO_3-ethyl/methyl-MCM-41 and HSO_3-methyl-MCM-41. By comparing their results with HSO_3-phenyl/methyl-MCM-41 and HSO_3-propyl/methyl-MCM-41, the authors were able to demonstrate that an optimum balance exists among parameters such as the nature of the organic group, which supports the sulfonic acid (aromatic or alkyl, length of the alkyl chain), distance between the sulfonic group and the silica surface, average pore size of the material. As a consequence the newly synthesized materials have also strong influence on improving the catalytic properties during the course of the esterification reaction.

Despite improvements in the selectivity of monoglyceride when using mesoporous acid catalysts, a monoglyceride yield of at least 90% is still needed to avoid the costly molecular distillation of the ester mixtures.

Among different alternatives, the use of glycerol-based additives to improve properties of biodiesel is being explored. For instance, Melero *et al.*[151] recently described the esterification of glycerol with acetic acid to yield these glycerine acetates, such as diacetylglycerol (DAG) and triacetylglycerol (TAG, also called triacetin), which have shown to be valuable petrol fuel additives leading to either enhanced cold and viscosity properties when blended with diesel fuel or anti-knocking properties when added to gasoline. The activities and selectivities achieved using sulfonic acid functionalized mesostructured materials (SBA-15) as catalysts are comparable or even superior to those displayed by conventional acid catalysts, providing values up to 90% of glycerol conversion and over 80% of combined selectivity toward DAG and TAG after 4 h of reaction. Within the studied range, optimal conditions were found at a temperature of 125 °C and an acetic acid to glycerol molar ratio of 9 : 1. The acid strength of the sulfonic acid site has also been found to be an important factor affecting the catalytic performance of these materials.

7 Selective etherification of glycerol

7.1 Selective etherification of glycerol to fine chemicals

Although glycerol itself could be burnt as a fuel, it could also be processed through selective etherification into more valuable fuel additives or solvents with suitable properties. It can be converted into branched oxygen-containing components by catalytic etherification with either alcohols (*e.g.* methanol or ethanol) or alkenes (*e.g.* isobutene). Among these, *tert*-butyl ethers have potential to be used as diesel fuel additives in gasoline and offer an alternative to oxygenates such as methyl *tert*-butyl ether (MTBE) and ethyl *tert*-butyl ether (ETBE), which are currently added to fuels.[152] As a consequence, a market need for *tert*-butyl ethers from glycerol with a high content of di-ethers and especially tri-ethers is expected to grow significantly in the next 5 years.[153,154] Scheme 13 showed the different reactions involved.[161]

The etherification of glycerol can be catalyzed by acidic homogeneous catalysts (*e.g.* *p*-toluene sulfonic acid and methane sulfonic acid) and preferentially by heterogeneous acid catalysts such as zeolites. It is worthwhile to evaluate strong acid ion exchange resins as suitable catalysts for the production of commercial ethers from glycerol.[155–158] Klepacova *et al.*[159,160] studied the etherification of glycerol by isobutylene or by *tert*-butyl alcohol over commercial strong acid ion-exchange resins and they compared their results with two large-pore zeolites H–Y and H-Beta. When comparing the conversions and selectivity of glycerol to di- and tri-*tert*-butyl ethers using macroreticular and gel type ion-exchange resins, they found that acid macroreticular resins in a dry form are very active catalysts for the etherification reaction with isobutylene because of a large pore diameter. It was also stated that *tert*-butyl alcohol as an alkylation agent is not suitable because it deactivates the catalysts as consequence of the formation of water. The use of zeolites and gel type polymer catalysts are not effective for this etherification reaction as they have small pore diameter. The best results at 100% conversion of glycerol *tert*-butylation using isobutylene with selectivities to di- and tri-ethers larger than 92% were obtained over strong acid macroreticular ion-exchange resins. Karinen *et al.*[161] have also reported that for the liquid phase etherification of glycerol with isobutene in the presence of the acidic ion exchange resin catalyst, up to five product ethers were obtained and, as a side reaction, isobutene reacted to give C_8–C_{16} hydrocarbons. The authors reported that the optimal selectivity conditions for ether formation were found to be at an isobutene/glycerol molar ratio of 3 at 353 K. They also showed that the extent of the etherification reaction, and, thus the main ether products, can be changed by varying the reaction conditions. Kinetic study experiments at constant operating conditions (363 K, feed ratio isobutene : glycerol, 2 : 1) have been performed using a batch reactor.[162]

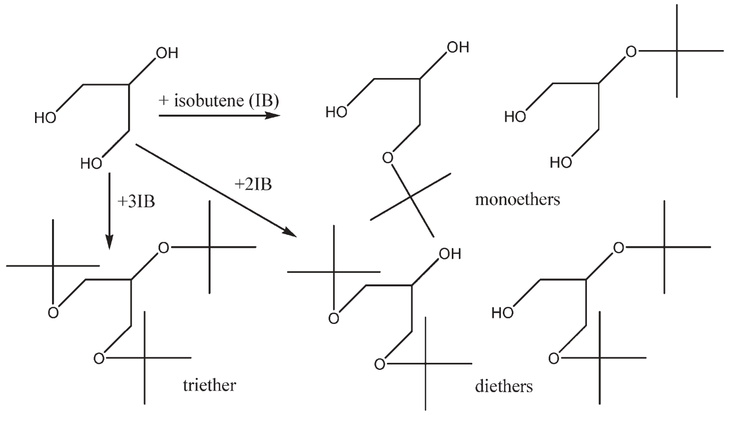
7.2 Selective etherification of glycerol to polyglycerols

Glycerol has traditionally played a role in the production of several types of polymers, some of which are available commercially. Selective etherification reactions can convert glycerol into polyglycerol (PG) and polyglycerol esters, which have been suggested to be used as biodegradable surfactants, lubricants, cosmetics, food additives, *etc.*[163–165] The polyglycerols, ethers, have many of the properties of glycerol. The polyglycerols offer greater flexibility and functionality than glycerol. For example, polyglycerol and polyglycerol methacrylates are used as treatments for wood to improve its stability.[166] In comparison, glycerol based polymers offer additional benefits including lower amounts of leachability into the environment.[167] This application would compete with the more widely used polyethyleneglycols.

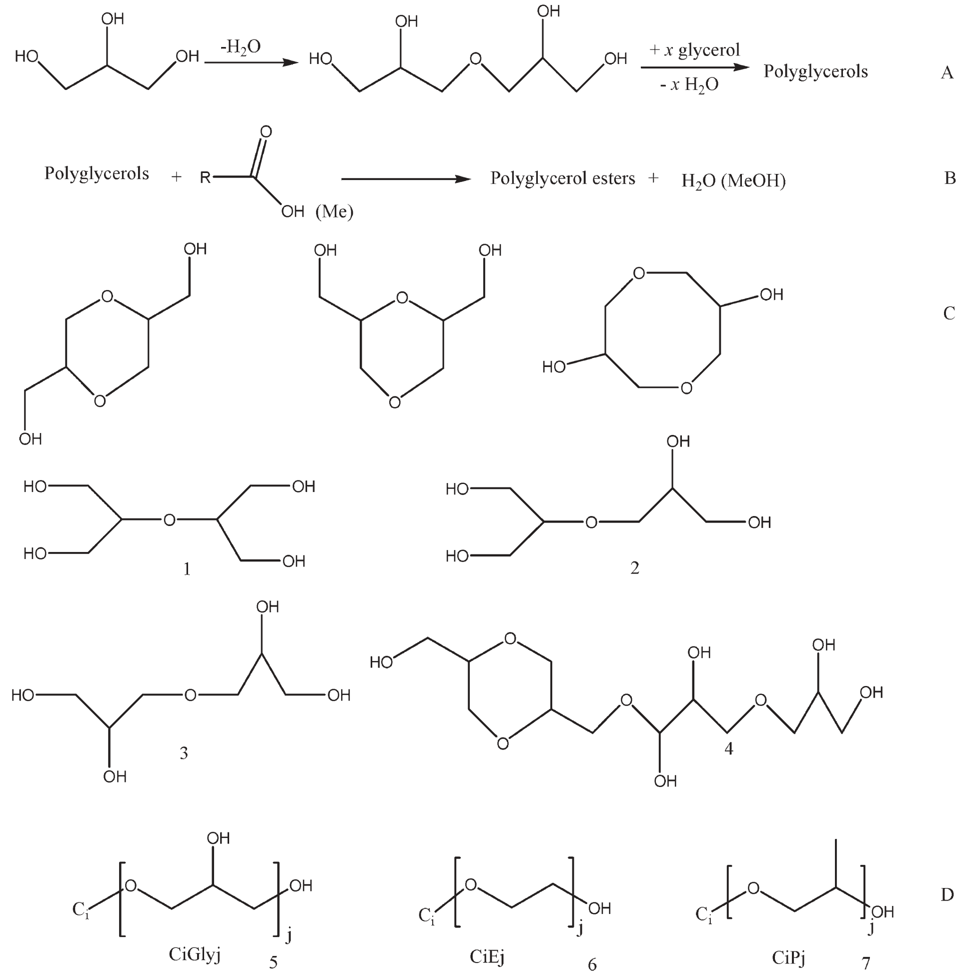
Polyglycerols and polyglycerol esters are obtained from the oligomerization of glycerol and the esterification or transesterification of the oligomers with fatty acids or methyl esters. Normally, the reactions are performed in the presence of homogeneous catalysts so that a mixture of polyglycerols (Scheme 14) as well as a mixture of esters can be synthesized. In addition to linear polyglycerols, branched polyols as well as oxygenated heterocyclic compounds can be obtained from cyclization reactions of glycerol and acrolein by glycerol dehydration (Scheme 11).

The mixtures are obtained using either solid catalysts such as zeolites[168,169] or alkaline catalysts such as calcium hydroxide,[170] sodium carbonate.[171]

Several bases have been tested as catalysts, including hydroxides, carbonates and oxides of several metals.[172] It has been found that the carbonates are more active than hydroxides, despite the weaker base character of the former. This is attributed to the better solubility of carbonates in the glycerol and in the polymeric product at elevated



Scheme 13 Reaction scheme for the etherification of glycerol with isobutene. (After scheme from ref. 161 with permission of Elsevier. ©2006 Elsevier.)



Scheme 14 (A) glycerol oligomerization, (B) polyglycerol esterification, (C) some samples of di- and triglycerol isomers (1,2 and 3 being the linear diglycerol isomers, (D) glycerol 1-monoethers (CiGlyj) (6,7 being the ethylene glycol ethers (CiEj) and propylene glycol ethers (CiPj), respectively. ((A)–(C) and (D) after schemes in ref. 184 and 190 with permission of Springer and the Royal Society of Chemistry. © 2004 Springer and 2006 The Royal Society of Chemistry, respectively.)

temperatures. Oxides like MgO, CaO and ZnO are less active because of lack of solubility. The condensation reaction of glycerol and glycidol catalyzed by acids has been claimed to render polyglycerols of high degree of polymerization with low color values.[173–175] Practically, the use of different filtration steps as well as neutralization and purification steps to eliminate solvents and homogeneous catalysts are necessary.[162] Over sodium hydroxide at a temperature of 503 K, only a 12.5% weight fraction of diglycerol is obtained.[176] Two distillation steps (under vacuum) are necessary to obtain 98% purity of diglycerol. Development of novel catalysts with high selectivity is still a high priority to lower processing costs.

Lemke[170] found that a high proportion of linear polyglycerols and polyglycerol with a reduction in the formation of cyclic polyglycerol esters can be obtained if a calcium containing compound, such as calcium hydroxide, is added in place of potassium or sodium hydroxide for the polymerization of glycerol during the etherification reaction.

The results reported by Harris *et al.*[168] show that the fraction of the diglycerol and triglycerol is below or equal to 65% over sodium zeolites and sodium silicate. They suggested that there is no shape selectivity effect over these catalysts and presumably the outer surface of the catalyst plays an important role in the case of NaA zeolite sample. One Japanese patent claimed that when using Na_2CO_3 as an homogeneous catalyst, a 76.4% of selectivity to diglycerol and triglycerol with 87% of glycerol conversion was observed, while another patent by Eshuis *et al.*[169] stated that when zeolite beta is used as catalyst at the laboratory scale, a 90% of selectivity to diglycerol and triglycerol with 100% of glycerol conversion can be produced. However, the precise analysis of the products proved to be difficult and it is not clearly reported in these patents. Recently, Castle and Debaig *et al.*[177,178] efficiently synthesized a variety of linear, branched and cyclic oligomers of glycerol, with well-defined structures and degrees of polymerization.. These works showed that most of the main isomers or groups of isomers were detectable with high precision.

Theoretically, porous solid catalysts could exert some shape-selective effect on the course of the polymerization reaction. Nevertheless, reports on such catalysts are extremely scarce. As discussed above, zeolites NaX, NaA[168,179] and zeolite beta[169] have been used as catalysts for the selective production of diglycerol. In another work, Cottin and coworkers[180] found that acid catalysts (benzene sulfonic, ion exchange resins) favor the dehydration of glycerol to acrolein while Na_2CO_3 is more active than a hydroxide or an oxide but the selectivity to diglycerol or triglycerol is very low. On the contrary the NaX and CsHY zeolites, which are less active at the beginning of the reaction, favor the formation of di- and triglycerol without any formation of acrolein. Indeed, the selectivity to diglycerol is higher than 90% over a CsHY or a NaX zeolite. In this particular case, it seems that the pore size of the catalyst slightly increases the selectivity of the reaction, especially when glycerol conversion is less than 80%. Furthermore, they showed the effect of alkaline elements on the activity and selectivity; the best results were obtained with the most basic promoter. When using Cs-exchanged zeolite X a 70% glycerol conversion was obtained with high selectivity to di-(62%) and triglycerol (33%), and only a 4% of tetraglycerol. In contrast, medium-pore Cs-containing zeolites like ZSM-5 are less active and selective.

The influence of pore size and the basicity of the catalysts on the polymerization reaction are evidenced by the use of basic MCM-41 catalysts.[163,181] Earlier, Kloetstra *et al.*[182] prepared and modified new mesoporous basic solids by impregnation of different elements in the MCM-41 type mesoporous materials. Their goal was to selectively obtain diglycerol or a mixture of (di- + tri-) glycerol by direct etherification of glycerol without the use of solvents and without the formation of acrolein, which is mainly produced by double dehydration of glycerol over acidic sites. Barrault *et al.*[183] working without the presence of solvents discovered that, if well chosen, basic mesoporous materials can be quite selective catalysts for the direct synthesis of di- and triglycerol from glycerol. In comparison to their previous experiments,[180] conducted with homogeneous systems, resins or zeolites, they found that when basic mesoporous materials are used there is a significant increase in the selectivity and yield of di, tri-glycerols without formation of cyclic compounds or acrolein. The Cs-impregnated material provided the best results, whereas Mg- and La-containing catalysts favored glycerol dehydration and the formation of acrolein. The selectivity of these mesoporous catalysts approaches that of the Cs-exchanged faujasite X. In the presence of lanthanum or magnesium containing catalysts, the glycerol dehydration to acrolein is significant, whereas this unwanted product is not formed when caesium is used as a promoter during the impregnation step. Barrault *et al.*[184] further showed that the impregnation method results in the highest activity. Concerning the selectivity of the modified mesoporous catalysts, the best values to di- and tri-glycerol (>90%) are obtained over solids prepared by the impregnation or grafting methods. The caesium-impregnated catalysts can be reused without loss of selectivity to the (di- + tri-) glycerol fraction. Moreover, when compared to homogeneous catalysts, the mesoporous solids induce a different regio selectivity. Finally, as far as the catalyst leaching and stability is concerned, the best results are obtained with the grafted solids, which retain their structure and their specific area after the promoter addition to the solid support. Such property is not observed over impregnated catalysts.

It is still rather difficult to selectively obtain one type of polyglycerol or to control the mixture and the quality of the product. If an individual polyglycerol (ester) needs to be obtained, new catalytic methods or novel catalysts need to be found.[178] Product distribution of polyol is important as the polyglycerol moiety of the ester should meet some specifications to be used as food additive. For example, according to European Union regulations, the majority of the content should be di-, tri- and tetraglycerol, whereas the content of polyglycerols equal to or higher than heptaglycerol must be low.[185] Food and Drug Administration regulations allow the use of polyglycerols up to and including decaglycerol.[186] Theoretically, low amounts of catalyst (<1 mol%) and relatively short reaction times are required to exert some control on the polymerization degree in order to favor a mixture of products having, on average, a low polymerization degree.

Noteworthy is that the development of solvosurfactants derived from glycerol are an opportunity to take advantage of this abundant resource. Although polyglycerol based surfactants are already well known and common,[179,187] especially in the food and cosmetic industries,[188,189] low molecular weight glycerol derivatives have been almost totally ignored during the last century. Only a few of them are used, *e.g.* to deliver drugs, or for degreasing and detergent use. Very little work has focused on their physico-chemical properties and phase behavior. Recently, Queste *et al.*[190] (2006) described the synthesis of short chain glycerol 1-monoethers ($CiGly_1$, $4 \leqslant i \leqslant 6$; Scheme 14 (D)) and their aqueous phase behavior, which is compared with those obtained from ethylene glycol and propylene glycol. Unfortunately, no efficient direct synthesis of glycerol 1-monoethers from glycerol and an alcohol or an alcohol derivative is known today. Usually, an initially protected or modified glycerol is preferred to the use of glycerol itself, which gives rise to mixtures of various mono- and polyethers that are difficult to purify.

8 Carboxylation of glycerol to glycerol carbonate

Glycerol carbonate is a new and interesting material in the chemical industry. It has been investigated as a novel component of gas separation membranes, polyurethane foams,[191] a surfactant component,[192] a nonvolatile reactive solvent for several types of materials, a component in coatings, paints and detergents. Inexpensive glycerol carbonate could serve as a source of new polymeric materials for the production of polycarbonates and polyurethanes.[193]

A reaction with phosgene and an exchange reaction with a dialkyl carbonate are known as a conventional method of preparing glycerol carbonate from glycerol. A method of reacting glycerol with carbon monoxide and oxygen at a high pressure in the presence of a catalyst is also known.[194] A less expensive, simpler method using a highly safe material, however, is desired. It is therefore attractive either to conduct the reaction with a catalyst that can be easily separated or without the presence of a catalyst.

One method for the synthesis of glycerol carbonate described in the literature is the *trans*-esterification of ethylene carbonate (EC) or propene carbonate (PC). Either homogeneous or heterogeneous catalysts are used, with a mass ratio of 1 : 1 with respect to glycerol. Mouloungui *et al.*[195] patented a process for the manufacture of glycerol carbonate by reacting glycerol with cyclic organic carbonate (ethylene or propylene carbonate) in the presence of organic carbonates or mixture of carbonates as solvents, and adding an anionic, bicarbonated or hydroxylated macroporous resin, or a three dimensional X- or Y-type zeolites as catalysts. They postulated that the diol radicals are formed on the basic sites of the catalysts. Such technology is not completely appropriate because EC and PC can be prepared by carboxylation of ethene oxide or propene oxide that is formed by the epoxidation of the relevant olefin. Therefore, finding a new direct route to glycerol carbonate would be very welcome, as it would avoid multi-step processes reducing energy and waste.

One possible method for the synthesis of glycerol carbonate is by the direct reaction of glycerol with urea in the presence of a metal oxide catalyst such as zinc oxide, an alkaline earth metal oxide, *e.g.* magnesium oxide, or performing the reaction in the absence of any catalyst.[196] More specifically, the reaction is preferably carried out at a temperature between 373 K and 393 K, in the presence of a dehydrating agent such as anhydrous magnesium sulfate, anhydrous sodium sulfate, anhydrous calcium sulfate or a molecular sieve with a preferred amount of catalyst in the range of 0.001 to 10 wt% based on glycerol weight. It is also preferable to feed urea at 0.2 to 2.0 times moles equivalent to glycerol.

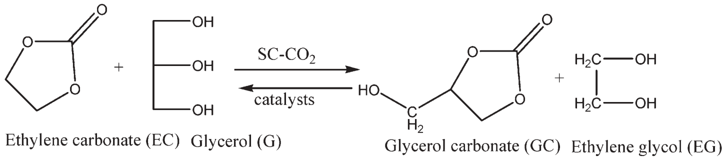
Direct production of glycerol carbonate from glycerol and carbon dioxide under supercritical conditions has also been reported.[197] Vieville *et al.* showed that under these conditions an organic carbonate such as ethylene carbonate was required as a starting material. It is possible that the carbonation of glycerol in the presence of ethylene carbonate can be enhanced using carbon dioxide as a co-source of carbonate for synthesis of glycerol carbonate. The zeolite Purosiv or 13X as well as a strongly basic resin catalyst such as Amberlyst A26 in hydroxyl form effectively enhanced the reactivity of glycerol adsorbed onto the solid catalyst and the ethylene carbonate dissolved in sc-CO_2. The reaction is represented in Scheme 15.

Aresta *et al.*[198,199] investigated the direct carboxylation of glycerol with CO_2 (5 MPa) at 450 K using transition metal alkoxides (Sn-catalysts *n*-$Bu_2Sn(OMe)_2$, *n*-Bu_2SnO or $Sn(OMe)_2$), *via* either glycerol or tetraethylene glycol dimethyl ether (TEDMG) as the reaction medium. *n*-$Bu_2Sn(OMe)_2$ was the most active catalyst tested as demonstrated during the conversion into *n*-Bu_2Sn(glycerol-2H) upon reacting with glycerol and with elimination of MeOH. As such, monomeric *n*-Bu_2Sn(glycerol-2H) was proposed to be the active species. These results demonstrated that if, after the first catalytic cycle, an oligomer that did not contain glycerol is formed, both the reactivity of the complex towards CO_2 and the activity of the catalyst are slowed down. $Sn(OMe)_2$ was able to uptake CO_2 but was not able to promote the carboxylation of glycerol. *n*-$Bu_2Sn(OMe)_2$ and *n*-Bu_2SnO also promoted the transesterification of dimethylcarbonate (DMC) with glycerol to afford glycerol carbonate, but at a lower rate than the direct carboxylation of glycerol. This fact seems to rule out that the carboxylation of glycerol may proceed through the preliminary formation of DMC and its subsequent transesterification. The carbonate was formed with an appreciable rate until a 1.14 : 1 molar ratio of carbonate to the catalyst was reached. The assumed mechanism is shown in Scheme 16. The direct carboxylation of glycerol (Scheme 16) is an interesting process that would convert two wastes into a valuable product.

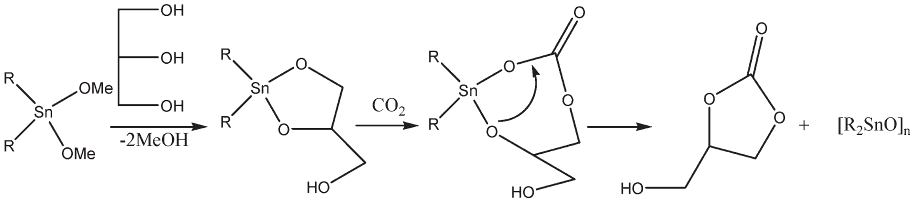
Additionally, the high yield preparation of glycidol from glycerol carbonate, and thus, from glycerol, has also been reported, suggesting that low cost glycerol could be used to produce low cost glycidol and its family of products.[200] Small scale production of these highly branched glycidol polymers has been commercialized in Europe by Hyperpolymers (Germany).

9 Prospects and concluding remarks

The utilization of glycerol for the synthesis of value-added chemicals is a topic of great industrial interest because glycerol



Scheme 15 The carbonatation of glycerol with ethylene carbonate (EC) to glycerol carbonate. (After scheme from ref. 197 with permission of Springer. © 1998 Springer.)



Scheme 16 Reaction mechanism of formation of glycerol carbonate from glycerol and CO_2 under *n*-$Bu_2Sn(OMe)_2$ catalysis. (After scheme from ref. 199 with permission of Elsevier. © 2006 Elsevier.)

can be formed in large amounts during the production of biodiesel from natural triglycerides, and represents a waste that must be used. Its effective utilization will be a key factor that can promote biodiesel commercialization and further development. As a biomass-derived chemical feedstock, its utilization is also a part of the global challenge aiming at the production of marketable chemicals *via* the catalytic transformation of biosustainable resources employed as substitutes for fossil fuels and fine chemicals.

This review presents many possible processes for the conversion of glycerol into useful chemicals and materials. Some new processes such as oxidation of glycerol have been extensively studied in recent years, especially in academic research institutions. In most cases, good selectivity to the desired products at high glycerol conversion is still difficult because of the extensive functionalization of the triol glycerol molecule with hydroxyl groups of similar reactivity, and because of a lack of optimal catalysts or unknown reaction conditions. Comparatively, much research has been carried out on the oxidation, transesterification and esterification of glycerol to more valuable products, while less is being focused on the novel processes such as hydrogenolysis and carboxylation of glycerol to glycerol carbonate. Some processes have been used industrially for decades, such as fatty esters of glycerol, but the catalysts used are generally homogenous. For catalytic dehydration of glycerol to acrolein, mineral acid or its salts are also used as catalysts in homogeneous catalytic processes. These homogenous catalytic processes still cause severe pollution, corrosion and high production costs. New solid catalysts stable under the reaction conditions are highly desirable in the future.

So far there have been extensive studies and some encouraging results in the development of new catalytic processes for glycerol conversion, though only a small number of catalysts have been tested and the reaction conditions have not yet been fully optimized over specific catalysts. Many challenges for increasing selectivity and yield present excellent opportunities for researchers in catalysis and nanomaterials to find specifically high activity catalysts for glycerol conversion to specific useful products. Careful design of the catalyst to control the selectivity to the desired product is highly desired. Homogeneous catalysts need to be replaced or substituted to avoid problems arising from product separation and purification.

In addition, alternative value-adding chemicals such as glycidol can be particularly interesting as this chemical has been conventionally synthesized from epichlorohydrin – a product from the chlorination of allyl alcohol. Glycerol to glycerol carbonate conversion is a significant alternative route to economically producing glycidol. This would have enormous implications for low cost glycidol and its family of products[201] Epichlorohydrin, which in the past was used to produce glycerol, can now be produced from glycerol (*e.g.* Epicerol™)).[6]

Traditionally the high price of glycerol limited the economic viability of such transformations, except for products used in the high value niche markets; *i.e.* cosmetic additives, tanning agent components, amino acid precursors, or selective metal chelants. As the price of glycerol decreases, new products, especially polymers, will be increasingly derived from glycerol. Oxidation-assisted polymerization of glycerol would open a new field of polymerization in aqueous media assisted by oxidation and will be applied to general polyhydroxy compounds. This will open up a new system of chemistry in developing modern oleochemistry using fats as renewable resources. Other selective oxidation products may find applications as structural analogs of polylactic acid[202] and new types of nylons.[203]

Furthermore, conversion of glycerol to fuels would also be expected to grow. For example, converting glycerol into H_2 or syngas by steam reforming is very promising. The use of glycerol-based additives to improve petrol fuel properties is also one of the possibilities currently being explored to utilize this renewable feedstock. Using glycerol to produce fuel additives, *e.g.* *tert*-butyl ethers of glycerol and acetylated glycerol derivatives as diesel fuel or gasoline additives, could also offer an important market for biomass resources.

Finally, we note that a crucial issue in both current and future biodiesel production is economic viability, specifically enhanced by the profitable use of glycerol by-products and waste streams.[204,205] Subsequently, one of the real challenges is that glycerol obtained as a by-product from the biodiesel industry is crude and impure. Facing the large quantity of crude glycerol produced by current processes, four new challenges for its commercialization appear: 1) new application and products based for directly using crude glycerol need to be found; 2) cost-effective purification processes need to be developed to purify raw glycerol from biodiesel processes, 3) a combination of separation of crude glycerol with catalytic conversion, and 4) direct biocatalytic conversion using crude glycerol should be investigated and developed to make it economically practical.

As discussed above, the improvement of the economic viability of the biofuels industry through new applications of crude glycerol seems unclear. However, a heterogeneous catalyzed continuous process is an alternative to obtain a higher quality of glycerol rather than using the homogeneous catalyzed continuous process. This will prove a better possibility by converting it to value-added chemicals and energy.[22,206] and ideally, will provide a more economically viable alternative to biofuel producers.[207]

It is prudent to point out, though, in most chemoselectively catalytic processes, it is difficult to directly use crude glycerol with high levels of contaminants. In this case, biological transformations could help circumvent the disadvantages of chemical catalysis (*e.g.* low product specificity, use of high pressure and/or temperatures, inability to use crude glycerol with high levels of contaminants, *etc.*), while offering the opportunity to synthesize a large array of products and functionalities. At its low prices, even glycerol is very competitive with sugars and carbohydrates in the production of chemicals and fuels *via* microbial fermentation.[208,209] Therefore, both a novel catalytic process for production of biodiesel that can improve the purity of by-product crude glycerol and a cost effective method for refining and converting glycerol needs to be developed.

Acknowledgements

The authors wish to acknowledge the financial support from the ARC Centre of Excellence for Functional Nanomaterials and the financial support for visiting academic CH Zhou by the China Scholarship Council (CSC, No2004833117) and NSF of China (No. 20773110, 20541002), the NSF of Zhejiang Province (No.Y405064) during the preparation of this review.

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