ROYAL SOCIETY OF CHEMISTRY

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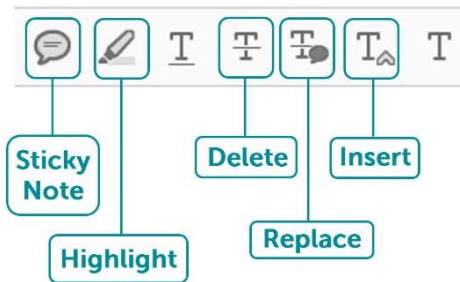
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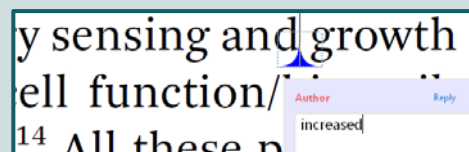
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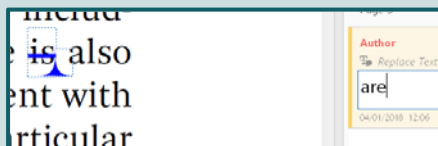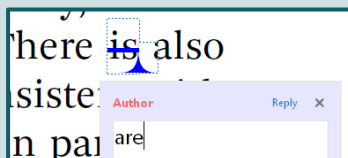
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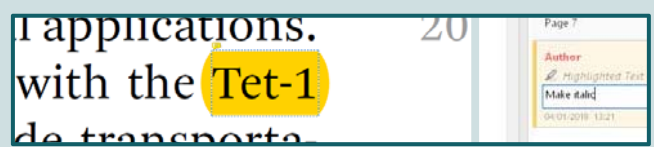
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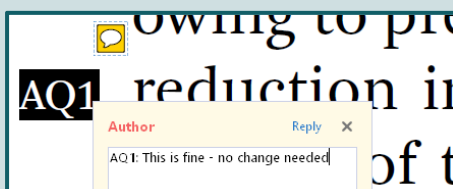
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Abstract

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This chapter describes the effectiveness of microwave irradiation as a new synthetic technique for the conversion of glycerol into valuable chemicals. In particular, microwave irradiation quickly activates the reactants, favouring their interaction with the catalysts and leading to the conversion of glycerol for the formation of several important chemicals.

CHAPTER 15

Microwave-assisted Glycerol Conversion into Valuable Chemicals

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15.1 Introduction

1,2,3-Propanetriol or glycerol is a non-toxic biodegradable compound and a high-value commercial chemical. It is mainly used in the manufacture of various foods and beverages, cosmetics, pharmaceuticals, polyether, polyols, alkyd resins, *etc.*, traditionally being unattractive as a feedstock chemical due to its high price.[1] The hydrolysis reaction of fats and natural oils from animals and plants, in an acid or basic medium, is a traditional means to obtain glycerol, although synthetic routes by transforming raw materials, which in turn are obtained from petroleum, also exist.[2]

In the last fifteen years, the huge production of biodiesel has resulted in a notable increase in the production of so-called "crude glycerol".[3] The high production of biodiesel can be explained by its inherent advantages as a substitute to fossil fuels, such as the low toxicity, as well as its biodegradable,

renewable and biocompatible character and lesser emission attributes. Fur- 1
thermore, biodiesel can be easily integrated into the logistics of the global
transportation system[4] and fits into existing engines with little or no modi-
fications needed.[5] In fact, biodiesel dominated the glycerol market with a
61% share in 2019.[6]   5

Biodiesel is obtained as a mixture of methyl or ethyl esters of fatty acids
(FAME or FAEE) from vegetable oils or animal fats through a transester-
ification reaction with a mono-alcohol, usually methanol or ethanol, in the
presence of an alkali metal homogeneous catalyst, usually sodium hydroxide
(NaOH) (Figure 15.1). The transesterification reaction involves the formation 10
of crude glycerol as a by-product in quantities of around 10% by weight
with respect to the total biodiesel produced, that is, for each ton of biodiesel,
100 kg of glycerol is generated.[7]

The crude glycerol mostly contains impurities such as free fatty acids and
methanol, making it a less preferred product in the market for glycerol.[6] It is 15
necessary to purify this crude glycerol to make it industrially applicable. The
purification procedures are costly and depend on the economics and the
availability of production facilities. Therefore, alternative uses of crude gly-
cerol need to be investigated to make biodiesel production more profitable.
With this in mind, it is easy to understand the efforts carried out by the 20
scientific community in order to obtain value-added products from glycerol,
following the biorefinery concept, Figure 15.2. Thus, recent reviews collected
different approaches to transform glycerol into value-added products.[8-10]

The reactions leading to these products are hydrogenolysis, dehydration,
esterification, etherification, acetalization, *etc.*, shown in Figure 15.3. In 25
general, in those transformations, purified glycerol is employed.

The effects of impurities on the crude glycerol conversion need to be
further investigated.[11] Furthermore, particular attention has been paid to
sustainability; therefore, different reaction parameters and conditions,
e.g., solvent-less procedures, heterogeneous catalysts, reaction temperature, 30
have been changed in order to make the process "greener". In fact,
employing a solid catalyst, instead of a homogeneous one, is indeed very
favourable due to its simple separation and regeneration, as well as the
recycling potential of the material for multiple cycles. This ensures a high

35

40

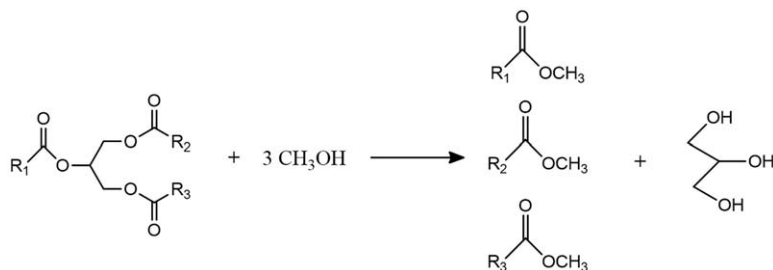**Figure 15.1** Biodiesel production by transesterification of triglycerides with 45
methanol.
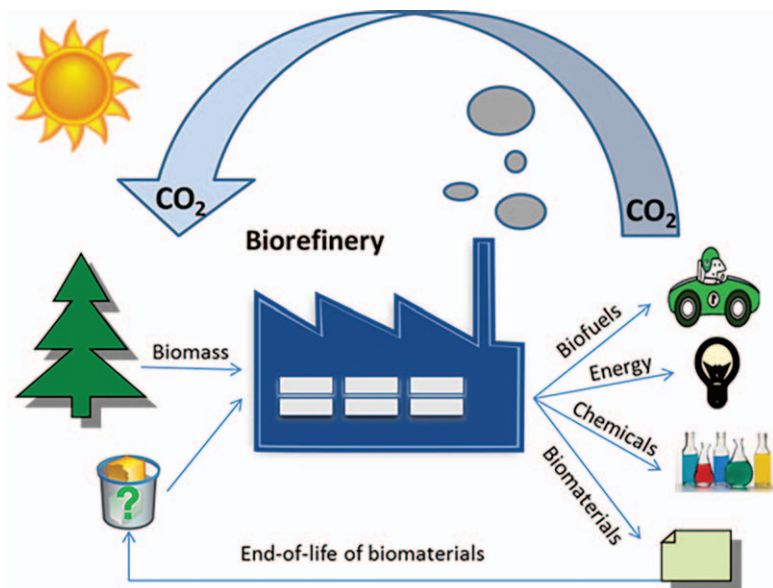
Figure 15.2 Towards a sustainable biorefinery. Adapted from Estevez *et al.*[26] Reproduced from ref. 26, https://doi.org/10.3390/en12122364, under the terms of the CC BY 4.0 license https://creativecommons.org/licenses/by/4.0/.
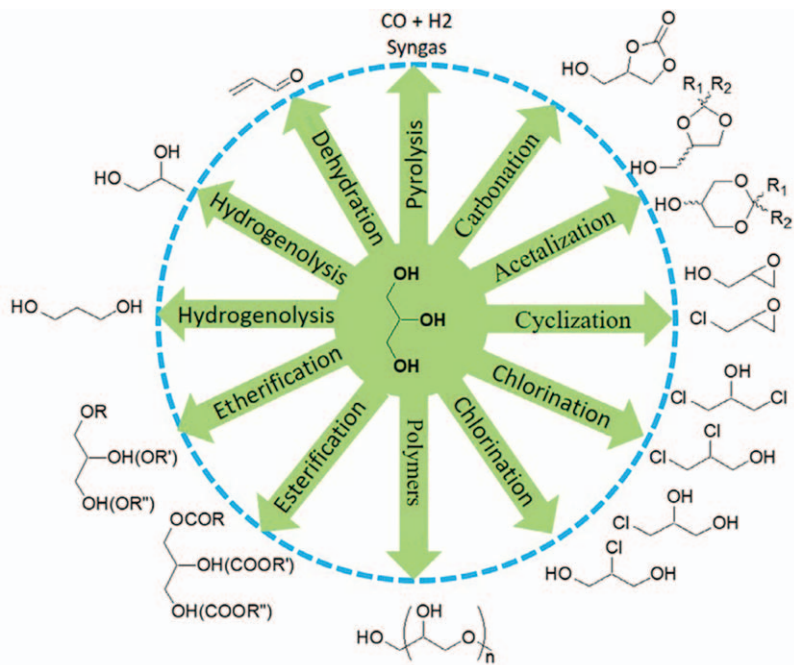

Figure 15.3 Added-value products from glycerol obtained by heterogeneous catalytic processes.

level of efficiency of the materials accompanied by a decrease in the pro-
cessing cost. In addition to this, in recent years, the catalytic reactions have
been carried out using microwaves as a way of heating, to make the pro-
cesses even more sustainable from an energy point of view.

Microwave irradiation is an electromagnetic irradiation in the range of
wavelengths from 0.01 to 1 m, corresponding to a frequency range of
0.3–300 GHz. Most microwave reactors for chemical synthesis operate at
2.45 GHz frequency. This technology can be very useful in chemical pro-
cessing because it enables volumetric heating of the products instead of
surface heating *via* convection and conduction. Microwaves cause molecular
motion through the migration of ionic species or rotation of dipolar species
or both to generate heat because of friction among molecules. Materials that
interact with microwaves by absorbing the irradiation are called microwave
dielectrics. Microwave heating (also called as dielectric heating) transforms
electromagnetic energy to thermal energy and can be delivered directly to the
reacting or processing species by using their dielectric properties or by
adding absorbers to materials, which allows more volumetric heating of
materials. The electric and magnetic field components are responsible for
microwave dielectric heating and magnetic loss heating, respectively. These
two components of microwaves interact differently with the material under
different mechanisms. In summary, the use of microwave irradiation allows
a rapid and uniform internal heating, leading to considerable energy and
time savings and to a sustainable process.

The glycerol conversion under microwave irradiation is still an innovative
procedure and for this reason, very few processes are reported in the
literature. The glycerol dehydration to obtain acrolein has been recently
reported by Xie *et al.*[12] According to the authors, the uniform temperature
distribution within the solid particles of the catalyst is very important to
achieve low coke formation, mainly at high temperatures at which the
reaction normally takes place. Furthermore, microwave heating proved to be
more effective than the conventional heating even at lower temperatures,
achieving a total glycerol conversion and a value of selectivity to acrolein of
70%, at 250 °C. Likewise, the production of pharmacological interesting
compounds from glycerol such as aryloxypropanediols, has also been re-
ported through a one pot, facile, fast and solvent free synthesis under
microwave irradiation over K_2CO_3 as a heterogeneous catalyst.[13] The com-
bination of different techniques with MW irradiation resulted in a decrease
in the reaction time and a higher yield with a cleaner profile, thereby in-
creasing efficiencies of the reaction. However, one of the most investigated
processes to valorize glycerin using microwaves as a heating source is the
production of oxygenated fuel additives.[8,14,15] A fuel additive is a chemical
substance that can be blended with fuel (diesel, gasoline, and/or biodiesel)
and it is capable of enhancing the engine performance by improving fuel
properties, cleaning engine parts, reducing the consumption ratio, and/or
decreasing greenhouse gas emissions. The oxygenated fuel additives ob-
tained from glycerol can be classified in three groups depending of the type

of transformation reaction: the acetins obtained through glycerol acetylation, the glycerol ethers obtained by the reaction of glycerol either with isobutene or *tert*-butyl alcohol and the glycerol formal and ketals, obtained by the reaction of glycerol either with formaldehyde or propanone. The microwave assisted glycerol esterification, for the production of tri- and di-acetins, is relatively unexplored. In fact, to the best of our knowledge, only one study reported the use of natural zeolites for the formation of acetins under microwave irradiation.[16] Although the glycerol conversion was more than 95%, the selectivity towards the formation of tri- and di-acetins was very poor (4.5% and 15%, respectively, after 60 min of reaction). It is a process that needs to be still studied in depth. So, in this chapter, the attention will be focused on microwave assisted acid-catalyzed etherification and acetalization reactions.

15.2   MW-assisted Glycerol Etherification

The formation of polyglycerols from glycerol etherification has attracted a lot of attention in recent years. Polyglycerols have an enormous potential various fields such as polymers, cosmetics, food, dispersants, pharmaceutical industries, lubricants, biomedical, or drug delivery systems. The production of these polyglycerols occurs when glycerol undergoes self-combination, generating linear, cyclic or branched di-glycerols or even larger molecules (tri-glycerols, tetra-glycerols, *etc.*).[17] Although this reaction was first studied using basic homogeneous catalysts like hydroxides, carbonates, and oxides[18,19] as well as acidic homogeneous catalysts (such as sulfuric, benzene-sulfonic, and dodecyl benzene-sulfonic acids),[20] the high solubility of glycerol and/or a nonselective oligomerization led to a shift in focus to the use of heterogeneous catalysts. In this regard, several heterogeneous catalysts have been studied, such as alkaline-earth metal oxides (MgO, CaO, SrO, *etc.*),[21] ionic exchange resins, zeolites, clay minerals, or mesoporous silicas (SBA-15 and MCM-41),[22,23] showing activity in the glycerol etherification reaction. Nevertheless, the severe reaction conditions needed caused different problems, such as the low selectivity, the stability of the catalyst due to the leaching of active sites, and other reasons. To overcome these problems, some research studies have explored the use of microwave irradiation as a heating method, in order to mitigate these reaction conditions. Sajid *et al.*[24,25] found that an increase in the selectivity towards target molecules, mainly di- and tri-glycerols, is achieved by using microwave heating instead of conventional one, attaining 80% of glycerol conversion at 260 °C after only two hours of reaction time. Furthermore, longer reaction times promoted the formation of higher levels of undesired oligomers.

In addition to the etherification reaction of glycerol to produce polyglycerols, the acid catalyzed etherification of glycerol with either isobutene (IB) or *tert*-butyl alcohol (TBA), to produce oxygenated additives for fuel has become as one of the best options to valorize glycerol from the biodiesel industry. In general, by using IB as a reactant, higher values of conversion and selectivity to h-GTBE than in the etherification with TBA are attained.

However, the use of IB is conditioned by different factors. First, IB is obtained through the catalytic cracking of crude oils, therefore, its price depends directly on the crude oil prices, in addition to being derived from a non-renewable source. Second, the use of additional pressure is required to keep the IB in the liquid phase. In fact, the mass transfer between the two phases is a limiting factor in this reaction, highlighting the importance of using a solvent to achieve a better catalytic performance. Regarding environmental aspects, the solventless reaction must be promoted. Last but not least, an important drawback is the secondary reactions of IB, as the oligomerization, promoted by strong acid sites, giving rise to a decrease in the selectivity to the desired products. These drawbacks can be solved by using *tert*-butyl alcohol, which remains liquid at the reaction temperatures usually employed, allowing the mass transfer between the phases, and acts as both a solvent and a reactant, avoiding the use of solvents capable of dissolving glycerol, along with the technological problems associated with such solvents, as well as typical drawbacks of a complex three-phase system. Likewise, the oligomerization of IB can be diminished, and the use of high pressure to carry out the reaction is not needed. Furthermore, TBA is currently obtained from the polypropylene production. Thus, etherification of glycerol with TBA has emerged as one of the most promising alternatives for glycerol valorization.[26] This reaction, Figure 15.4, is usually catalyzed by acids and it is maintained in equilibrium. In the first path, a fast protonation of TBA on acid sites takes place, giving rise to a tertiary carbocation that reacts with glycerol. Hence, mono-*tert*-butyl glycerol ethers (MTBGs) are obtained, followed by the formation of di-*tert*-butyl-glycerol ethers (DTBGs) and tri-*tert*-butyl glycerol ethers (TTBGs).
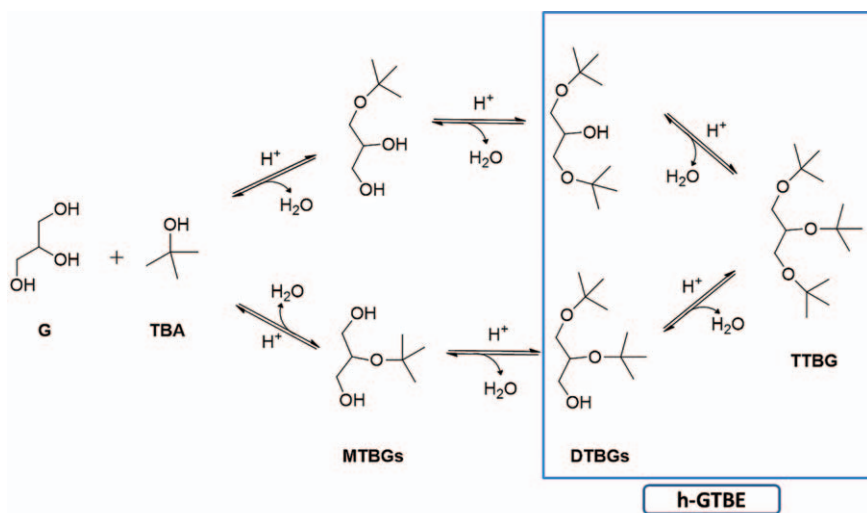

Figure 15.4   Scheme of the reaction pathway for the etherification of glycerol with *tert*-butyl alcohol.

While the MTBGs cannot be blended with fossil fuel, the DTBGs and TTBG, the so-called high ethers (h-GTBE), can be employed as excellent diesel and biodiesel additives,[27,28] improving cold properties and reducing the consumption and gas emissions.[29,30] Moreover, isobutene can be formed from the dehydration of the alcohol in addition to water. Both by-products can compete with TBA and glycerol for the acid sites on the catalytic surface. The maximum yield of the reaction products is limited by the thermodynamic equilibrium. Thus the formation of water in every step can promote the hydrolysis of the ether bonds formed, shifting the equilibrium to the left. In addition, the water molecules can solvate the acid sites, leading to a faster deactivation of the catalysts.

At the beginning, the reaction was studied over homogeneous acid catalysts such as sulfuric acid or *p*-toluenesulfonic acid, although the use of heterogeneous catalysts has been gaining importance. Table 15.1 presents a compilation of acid heterogeneous catalysts employed in the etherification of glycerol with TBA, as well as the reaction conditions employed. In general, the reaction is carried out at temperatures between 60 and 120 °C, with an excess of TBA relative to glycerol, which is logical according to the Le Chatelier principle as it helps to shift the equilibrium toward the formation of the products.

As can be seen in Table 15.1, the acid exchange resins (entries 1–4) with sulfonic groups in their structure have been widely used as catalysts in this reaction.[31] As their name indicates, ion exchange resins are polymers

Table 15.1   Etherification of glycerol with *tert*-butyl alcohol using different catalytic systems and reaction conditions.

Entry	Catalyst	Reaction conditions						Ref.
		T (°C)	Catalyst loading (wt% of G)	TBA/G	Time (h)	X_G (mol%)	$S_{h\text{-GTBE}}$ (mol%)	
1	A-15-dry	60	7.5	4	8	79	19	31
2	A-35-dry	90	7.5	4	8	69	24	32
4	A-15	70	7.5	4	6	94	30	33
3	A-15	60	7.5	4	8	80	20	34 and 35
5	SCC-S	120	5	4	7	81	21	36
6	BC 1:3	120	5	4	6	75	29	37
7	Hierarc-beta zeolite	75	5	4	24	77	35	38
8	FHB	75	5	4	24	75	37	39
10	USY-650-L-2	90	7.6	4	4	75	21	40
11	$S_{50}TS_{50}O$	75	5	4	24	98	29	41
12	C(10)AlPO(1.5)-250	85	5	4	15 min	83	25	42
13	C-AlPO(6)-6	85	5	4	15 min	97	18	43
14	SiO_2 PrSO$_3$H	130	5	4	30 min	93	27	44
15	M-HY	85	5	4	15 min	59	22	45
16	OC(0.5)100Mw	85	5	4	15 min	77	28	46

fabricated from an organic substrate, with the most commercialized ones
being made from polystyrene sulfonate. Among these resins, A-15, a styrene–
divinylbenzene copolymer exhibiting a high concentration of strong acid
sites, has been most commonly used in the etherification reaction.[32,33]
achieving high rates of glycerol conversion (80–95%) and of selectivity
to h-GTBE (between 20 and 30%).[32,34,35] However, these types of resins ex-
hibit some limitations, such as lack of thermal stability, susceptibility to
swelling and shrinking in organic media, and their hydrophobic character,
since the sulfonic acid groups are the only hydrophilic part of the structure. As
mentioned above, the water generated in each step of the reaction can solvate
the sulfonic groups, leading to a faster deactivation of these catalysts due to
their predominant hydrophobic character.[33] To overcome these problems,
other catalytic systems have been studied in recent years. Thus, catalytic sys-
tems based on carbon, mainly prepared from biomass and sulfonated through
different strategies, have gained significant importance. Gonçalves et al.[36]
evaluated the behaviour of sulfonated carbons prepared from agroindustrial
wastes, showing a high catalytic performance (a glycerol conversion value of
80.9% and a selectivity to h-GTBE of 21.3%) after 4 h of reaction, at 120 °C and
using a 5 wt% catalyst loading (entry 5). The acidity of the catalysts was decisive
in determining their catalytic performance, although the hydrophilic character
of the carbons also played an important role by enabling the absorption of the
water generated during the reaction and palliating the negative influence that
this water usually has in the catalytic activity and selectivity to h-GTBE.
Likewise, Gonçalves et al.[37] also studied the preparation of carbons through
hydrothermal treatment of glycerol, which was obtained from biodiesel pro-
duction, along with sulfuric acid, achieving high ether yields of around 20%
and also exhibiting good reusability as up to 8 subsequent reactions were
performed without an appreciable loss of activity.

In addition to acidity, the textural properties of the catalysts also exhibit
an important role in this reaction, due to the large size of the h-GTBE
molecules. In this sense, silica-based materials with different structures and
textural properties have been tested in the etherification reaction. Thus,
González et al.[38] studied the effect of hierarchical porosity in a β-zeolite, and
found that it exhibited a better catalytic behaviour compared to conventional
zeolites, which was attributed to the enhanced accessibility of reactants to
the active sites. Furthermore, the hierarchical zeolite after a fluorinated
treatment improved the selectivity to h-GTBE, due to the increase in the
number of strong acid sites that it exhibited. The decisive role of the
Bronsted acidity and porosity was corroborated by the authors,[39] studying
several types of zeolites, such as mordenite, beta and ZSM-5 zeolites modi-
fied by protonation, dealumination, desilication-protonation, lanthanum
exchange and fluorination. Thus, the best catalytic behaviour ($X_G = 75\%$ and
$S_{h\text{-GTBE}} = 37\%$) was associated with the highest acidity and the larger pore
size of the zeolite.

Veiga et al.[40] evaluated the catalytic performance of zeolites that
were subjected to a steaming treatment and acid leaching to eliminate

extra-framework aluminum, and reported that the hydrophobicity/hydro-philicity relationship of the catalysts had a great influence on the catalytic activity, in addition to their acid and textural properties. In a related study, Estevez *et al.*[41] reported that the presence of silanol groups on a sulfonated hybrid silica catalyst prevented the negative effect of water on active sites of the catalyst. This fact, together with the high density of acid sites that the solid exhibited, resulted in an improvement in the catalytic performance showed by the A-15 at long reaction times of 24 h.

Upon reaching the point where the properties that a catalyst must have to appropriately perform the etherification of glycerol with *tert*-butyl alcohol, appeared to be understood, Estevez *et al.* proposed, for the first time, the use of microwave irradiation as an alternative way of heating for this reaction.[42] Catalytic tests were carried out under both microwave irradiation and conventional heating, over novel organosilica–aluminum phosphates with sulfonic groups in their structure, which was synthesized by a simple and cheap sol–gel method. As can be seen in Figure 15.5, similar results in terms of glycerol conversion and selectivity to h-GTBE were achieved over the same catalyst, 90% and 25%, respectively, although under microwave irradiation, less temperature and reaction times were needed. The higher energy generated by microwave heating, in comparison to conventional heating, leading to the breaking of hydrogen bonds formed between the free hydroxyl groups (Al–OH; P–OH and Si–OH) and the sulfonic acid sites, even at lower temperatures, can explain these results.

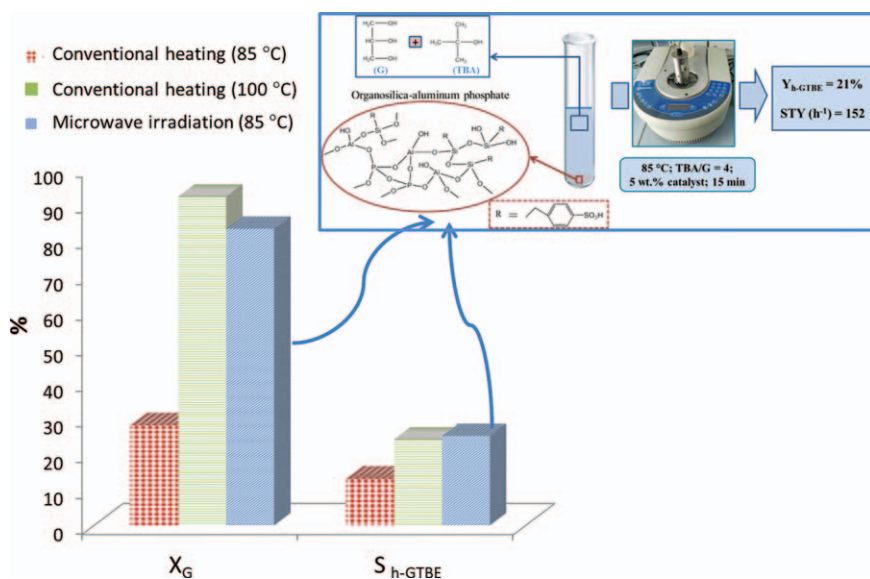**Figure 15.5** Glycerol conversion (X_G) and selectivity to h-GTBE ($S_{h\text{-}GTBE}$) under microwave irradiation and conventional heating. Reaction conditions: 5.0 wt% of catalyst referred to the starting amount of glycerol, TBA/G molar ratio = 4.

Further insights into the synthesis of these organosilica–aluminumphos- 1
phates were obtained by using three different silica precursors, 2-(4-chloro-
sulfonylphenyl)ethyltrimethoxysilane (C), 3-(mercaptopropyl)trimethoxysilane
and bis(3-(triethoxysilyl)propyl)tetrasulfide, with Al/P molar ratios varying from
3 to 10 and pH of the final gel varying from 3 to 9, maintaining the Al/Si = 3 5
molar ratio. The catalysts synthesized were tested in the microwave-assisted
etherification of glycerol, and among them the catalysts with the highest acidity
and predominantlya mesoporous character exhibited the highest catalytic ac-
tivity, a glycerol conversion value of 97% and a selectivity to h-GTBE of 18%.[43]

In addition, other catalytic systems have been tested in this reaction under 10
microwave irradiation, such as different zeolites modified with sulfonic acid
groups as catalysts.[44] Concretely, zeolites HY and HZSM-5 were dealuminated
by acid treatment and subsequently functionalized with two different orga-
nosilica precursors, 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane, and
(3-mercaptopropyl)trimethoxysilane. The highest values of site time yield 15
(STY), defined as mmol of produced h-GTBE per mmol of active sites and per
hour, reported to date were achieved over the HY zeolite functionalized with
2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane, with a value of 174 h^{-1}.
Likewise, different sulfonic acid silica- or titania-based catalysts have also
been tested in the microwave assisted etherification of glycerol with *tert*-butyl 20
alcohol.[45] Results demonstrated that the activity was related mainly with the
acidity and the textural properties of the solids, achieving almost total
glycerol conversion and a 25% yield to h-GTBE in 30 min of reaction time.
Particular attention was paid to the sustainability of the process by using the
second raw material (glycerol), recycling the catalysts and implementing an 25
energy saving procedure (microwaves).

Cost-effective catalysts have also been investigated. Hence, Estevez *et al.*
synthesized a carbon material from one of the most abundant biomass
wastes in Andalusia, the olive stone. Furthermore, in that study, the
microwave irradiation was employed not only for the catalytic reaction but 30
also during the synthesis of the catalysts, since the incorporation of the
sulfonic group into the carbon structure was performed under microwave
irradiation, making the global process more sustainable, Figure 15.6.[46]
Regardless of sulfonation conditions, all the solids exhibited similar par-
ticle size, with sulfur being spread out homogeneously on the carbon surface. 35
In addition, the positive effect of using microwave irradiation in the prep-
aration of the sulfonated carbons was proved by observing that the sulfon-
ation time needed to attain an identical sulfur incorporation percentage was
considerably reduced under microwave irradiation in comparison to con-
ventional heating (30 min *vs.* 2 h). In addition, these findings corroborate the 40
results previously obtained by their research group, which achieved glycerol
conversion values over 80% at 15 min under microwave irradiation. Likewise,
they demonstrated that the catalysts exhibited a good reusability, ruling out
the leaching of sulfonic groups from the catalyst surface.

Very recently, Zhou *et al.*[47] studied the synthesis of glycerol *tert*-butyl 45
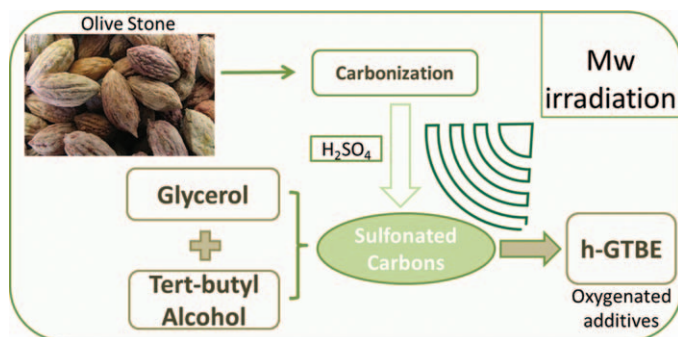ethers under different energy supplies, such as microwave, ultrasound,

Figure 15.6 From olive stone to sulfonated catalysts and its application in the etherification of glycerol with *tert*-butyl alcohol under microwave irradiation.[46] Reproduced from ref. 46 with permission from Elsevier, Copyright 2020.

ultraviolet energy, conventional heating and ball milling. The best results were obtained under microwave irradiation and a deep kinetic analysis disclosed that microwave irradiation is able to decrease the activation energy of the reaction in approximately a 20%, in comparison with conventional heating.

Moreover, the use of acid heterogeneous catalysts enables the employment of waste oil for the biofuel production. In fact, waste oils, as fried oils, are often subjected to thermic treatments that cause breaking of the chemical bonds leading to accumulation of free fatty acids (FFA). FFAs represent an important cause of catalyst poisoning, especially in the case of basic catalysts. On the other hand, the employment of sulfonic heterogeneous catalysts allows simultaneous transesterification of triglycerides and esterification of FFAs, with an optimization of the biofuel production. According to these considerations, the described sulfonic amorphous silica[48] was successfully applied in the microwave-assisted transformation of waste oil for the production of ready-made biofuel. In particular, a mixture of substrate/*tert*-butyl-methyl ether in 1:10 ratio was subjected to reaction with the 1% catalyst at 20 W in 3 h. Following this procedure, a mixture of biodiesel and its additives was produced in only one-step, avoiding the expensive and demanding purification process, Figure 15.7. The produced biofuel was, then, ready to use, making biodiesel production more profitable. Moreover, the use of acid heterogeneous catalysts allows the employment of waste oil for biofuel production. The excellent results obtained allowed the patenting of the technology, which was subsequently licensed to companies in the biorefinery industry.[49]

15.3   MW-assisted Glycerol Acetalization

Acetalization is an organic reaction that occurs through the nucleophilic addition of an alcohol to a ketone or an aldehyde leading to the formation of a ketal or acetal. The reaction usually proceeds under acidic conditions, and
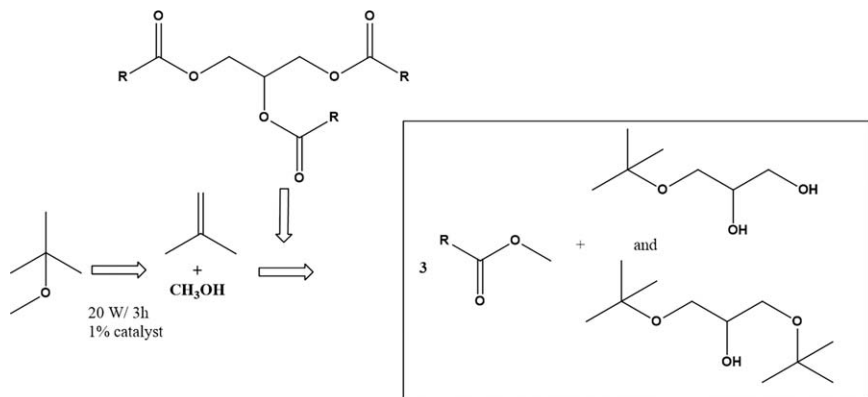
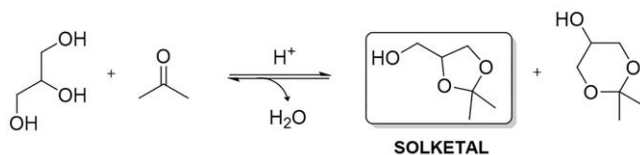**Figure 15.7**   One-step production of biodiesel and its additives.

Figure 15.8   Scheme of the reaction pathway for the acetalization of glycerol with acetone.

it is reversible, easily reaching the equilibrium between the reactants and products. Glycerol acetalization has been, in the last few decades, one of the most studied reactions to convert glycerol into acetals or ketals, extensively used in biorefineries, pharmaceutics and different type of industries. Among the variety of acetals and ketals produced, the formation of solketal (2,2-dimethyl-4-hydroxymethyl-1,3-dioxolane) has been particularly studied since it represents a versatile molecule in several large-scale applications. Solketal is colourless and odourless liquid, highly soluble in water and with eco-compatible characteristics towards both humans and the environment. Due to these characteristics, solketal is, in fact, principally used as a green solvent in pharmaceutics (as additives in injectables or in ointments, as a building block for synthesis), polymers, cleaning products, ink formulations, and pesticides.[50,51] Its principal utilization remains the field of biofuels, in which solketal is considered an important fuel additive and anti-knocking agent since it leads to a significant decrease in hydrocarbon emission and, at the same time, improves the oxidation stability of liquid fuels and enhances the octane number and density when added to gasoline.[29,52–54]

As can be seen in Figure 15.8, the acid-catalyzed reaction between glycerol and acetone allows the formation of the 5-membered ring (1,3-dioxolane or solketal) that is thermodynamically favoured with respect to the corresponding 6-membered ring (1,3-dioxane).[55]

As already evidenced in the introduction, the use of heterogeneous acid catalysts is, really, advisable from several points of view including the efficiency of the process and the environmental and economic sustainability. Moreover, the variation of the reaction parameters (such as reagent ratios, thermal sources and solvent-free methodologies) can also improve the catalytic performance of these materials.

During the last few years, several acid materials including zeolites, acid exchange resins, metal-based materials, heteropolyacids, acid modified montmorillonite and acid functionalized silica[56–58] have been used to catalyse the glycerol acetylation.

Table 15.2 presents a representative selection of acid heterogeneous catalysts applied in the solketal synthesis. Analysing the reported studies, it is possible to observe the evolution, over several years, of the used reaction conditions gradually towards more and more eco-sustainable conditions. The chloride or aromatic solvents used (entry 1)[59] were replaced with the more sustainable ethanol (entry 2),[52] eventually carrying out the acetalization reaction under solvent-free conditions by using an excess of acetone (entries 3–12).[60–69] In fact, the use of a high amount of acetone with respect to glycerol allows to shift the equilibrium towards the formation of solketal, which leads to higher selectivity and yields of the desired product. As for the thermal source, the reactions are usually carried out under conventional heating at a temperature ranging from 45–90 °C. Recently, the conventional heating is being substituted with the microwave irradiation, whose huge benefits, both in terms of efficiency and sustainability of the chemical process, are described in the introduction of this chapter. To the best of our knowledge, very few studies have been published recently involving the use of microwave assisted synthesis of solketal starting from glycerol, (entries 8–12), and among them, only three mentioned studies investigated the use of heterogeneous catalysts (entries 9, 10 and 12).

Silica based materials present the advantages of a high surface area, structural stability under different reaction conditions and, above all, the formation of a covalent link between the acidic active site and the –OH of the silica support. With respect to an impregnation method, usually used in metal-based materials (entries 4, 5, 7 and 9) or in sulphate or phosphate catalysts, (entries 10 and 11) in fact, the use of a grafting procedure, allows to avoid (or strongly reduce) the leaching of the linked acidic functions. Sulfonic functionalized mesoporous silicas were, for the first time, tested in the solketal production by Vicente *et al.* (entry 6). After the optimization of experimental parameters, the reaction was carried out in two step batches of 30 min each, leading to good results both in terms of glycerol conversion (80–90%) and solketal selectivity (81%).

The studied MW-assisted procedures (entries 8–12) showed the use of homogeneous (entry 11) or metal-based catalysts (entry 9), low solketal selectivity with the formation of isomers (entry 8), high temperature (entries 8 and 9), high watt power (entry 9) and/or long time (entry 10), so, in order to improve the efficacy of the process, the catalytic performance of propyl

Table 15.2 Solketal synthesis by the glycerol acetalization under different reaction conditions.

Entry	Catalyst	Reaction conditions	Obtained results	Ref.
1	Amberlyst-36	Organic solvents (CH_2Cl_2, toluene, $CHCl_3$); refluxing temperature; $t = 1.5$ h	A mixture of a 5- and 6-member rings (76% yield)	59
2	Amberlyst-35	Ethanol, gly : acetone 1 : 2.5, $T = 25$–45 °C	Solketal yield (74%)	52
3	Zeolite H-beta	Solvent-free; gly : acetone 1 : 2, $T = 70$ °C, $t = 1$ h	Glycerol conversion (90%)	60
4	Ni-activated carbon	Solvent-free; gly : acetone 1 : 8, $T = 45$ °C, $t = 3$ h	Glycerol conversion (98%); selectivity of 5- and 6-member rings (86 : 10)	61
5	$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	Solvent-free; $T = 25$ °C, gly : acetone 1 : 6, $t = 15$ min	Glycerol conversion (95%); solketal selectivity (98%)	62
6	SO_3HPh-SBA-15 or SO_3HPr-SBA-15	Solvent-free; 2 steps; gly : acetone 1 : 6, $T = 70$ °C, $t = 30$ min × 2	Glycerol conversion (80–90%); solketal selectivity (81%)	63
7	ZrMo-KIT6	Solvent-free; gly : acetone 1 : 8 $T = 50$ °C, $t = 4$ h	Glycerol conversion (86%); solketal selectivity (98%)	64
8	Catalyst-free	MW; solvent-free; $T = 140$ °C; 600 W, $t = 15$ min	Glycerol conversion (90%); selectivity of 5- and 6-member rings (60 : 40)	65
9	(Fe, Co, Ni, Cu, Zn)-Mordenites	MW; solvent-free; $T = 100$ °C; 500 W, $t = 15$ min; gly : acetone 1 : 3	Glycerol conversion (95%); solketal selectivity (98%)	66
10	Fe-AlPOs	MW; solvent-free; $T = 60$ °C; $t = 30$ min;	Glycerol conversion (94%); solketal selectivity (96%)	67
11	Homogeneous H_2SO_4; pTSA; $FeCl_3$	MW; solvent-free; $T = 65$ °C; 600 W, $t = 15$ min; gly : acetone 1 : 6	Glycerol conversion (99%); solketal selectivity (98%)	68
12	SO_3HPr-Am or SO_3HPr-KIT-6 or SO_3HPr-SBA-15	MW solvent-free; $T = 40$ °C; <20 W, $t = 2$ min; gly : acetone 1 : 12	Glycerol conversion (91%); solketal selectivity (98%)	69

sulfonic amorphous, SBA-15 and KIT-6 silica-based catalysts was recently evaluated in solketal synthesis.[69] The obtained results showed very sustainable reaction conditions. In detail, amorphous and mesoporous silica-based catalysts modified with propyl sulfonic acid groups have been synthesized using different grafting procedures (mild, thermal and hydrothermal grafting). Conventional heating and microwave irradiation were compared as sources of energy for glycerol acetalization, varying one parameter at a time, while keeping the other reaction parameters such as time (2–60 min) and temperature (25–80 °C) constant. By using the same parameters (catalyst, reagent ratio and temperature), when conventional heating is used the equilibrium of the reaction is reached at 40 °C and 7 min. Under microwave irradiation (<20 W), the equilibrium, conversion and selectivity were reached in only 2 min. This fact could be related to the speed and uniformity with which the reaction temperature is reached under microwave irradiation, implying the achievement of the same results in a lesser time. Likewise, the microwave energy would promote a faster activation of the reactant molecules and therefore, the time to reach the reaction equilibrium decreases. To reach the reaction temperature, the microwave apparatus induces the needed power. Once the reaction temperature is reached, the power is alternated between ON and OFF in order to keep the temperature stable. Due to the very low temperature used for glycerol acetylation (40 °C), it is reached in around 20 seconds. The temperature is controlled using an IR probe. A typical profile of variation of T, power and pressure is included in Figure 15.9, which corresponds to the SBA-PrSO$_3$H catalyst. In addition, it can be observed that no pressure is generated during the reaction (blue line is at zero).

After a deep study of the obtained results, the catalytic performance of the materials was found to be higher under microwave irradiation compared to
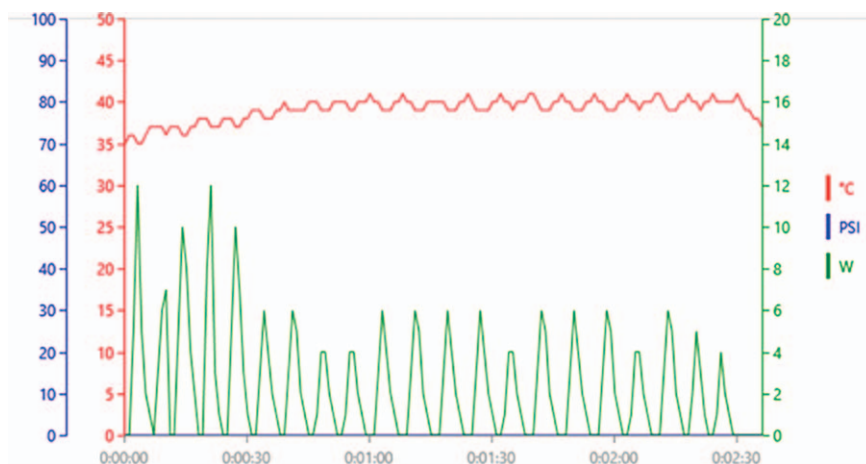

Figure 15.9 Typical MW-profile of variation of T, power and pressure with reaction time in the acetalization of glycerol with propanone.

conventional heating. Moreover, under the optimized reaction conditions   1
(entry 12), the materials prepared through the hydrothermal procedure led
to a superior performance of the catalysts with respect to the materials
AQ:9 produced with the other grafting procedures. In fact, the hydrothermal
grafting not only resulted in the incorporation of higher amounts of acidic   5
functions but, also, facilitated the formation of very stable covalent bonds
with a very effective reuse of the materials in which leaching of acidic groups
and loss of activity were evidenced. The fresh and spent catalysts were well
characterised using several techniques (including N_2 adsorption isotherms,
thermogravimetric analysis, X-ray photoelectron spectroscopy, and X-ray   10
fluorescence spectroscopy).[69] So, in order to be aware of the characteristics
and the activities of the materials covered in this section, in Table 15.3
below, some related data of the sulfonic propyl silica synthetized using the
hydrothermal procedure, are reported. As an example, here the recycling of
propylsulfonic amorphous silica, prepared by hydrothermal grafting, is also   15
reported with the corresponding XPS spectra of fresh and spent catalysts
(see Figure 15.10) from which it is evident that, under the studied reaction
conditions, no leaching of sulfonic groups occurred. During the study, it was
found that the total acidity as well as the textural properties of the materials
were the key factors which helped in explaining the catalytic behaviour of the 20
sulfonic catalysts.

  According to these considerations, a plausible reaction pathway for gly-
cerol acetalization catalyzed by sulfonic silica-based material is described in
Figure 15.11. The sulfonic groups can activate the carbonyl of acetone,
making it prone to the nucleophilic –OH attack by glycerol. The reaction   25
occurs through an acyl nucleophilic addition, followed by a S_N1 nucleophilic
substitution that leads to the formation of a cyclic ketal. The first step is the
protonation of carbonyl oxygen by –SO_3H groups of the catalyst, followed by
the nucleophilic attack of the primary hydroxyl group of glycerol on the
electrophilic carbon of acetone that allows to obtain the corresponding   30
protonated hemiketal. The displacement of a proton allows the formation of
the intermediate hemiketal and the restoration of the catalyst. A further
protonation step, by the catalyst, of the tertiary hydroxyl group and con-
sequent elimination of a water molecule leads to the formation of the cor-
responding carbocation. The latter can undergo ketalization by nucleophilic   35
attack of either the primary or secondary hydroxyl group of glycerol, giving

AQ:10 **Table 15.3**   Structural properties and activities of sulfonic silica prepared by
              hydrothermal grafting.

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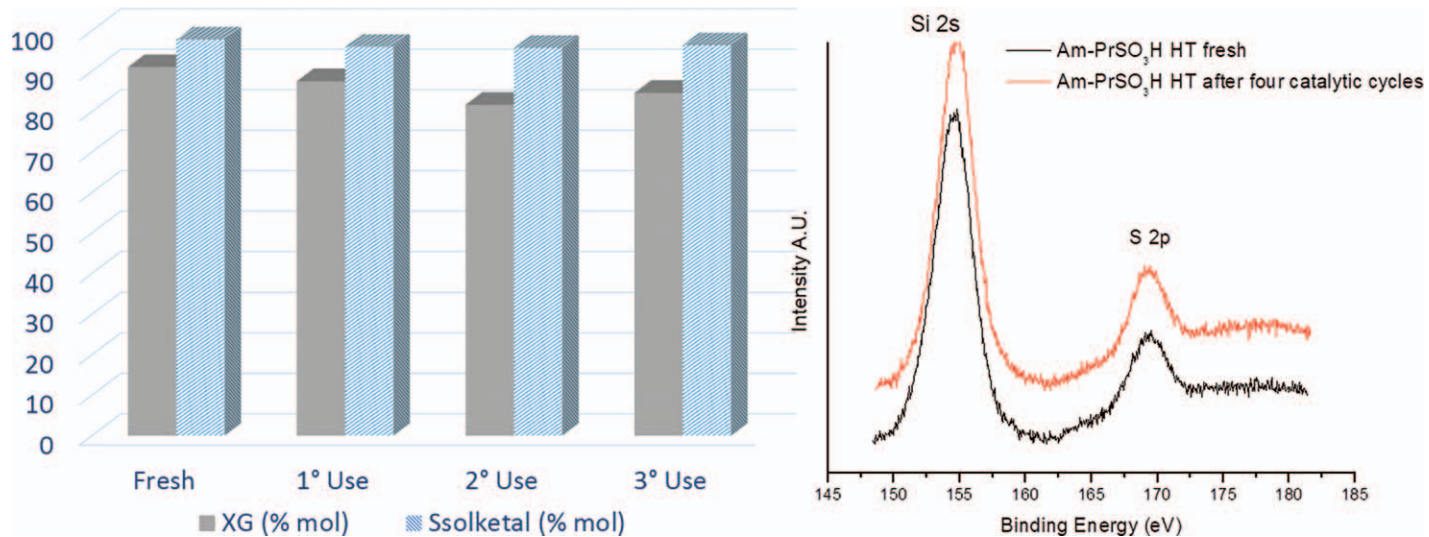| Catalyst	TGA (mmol $SO_3H\,g^{-1}$)	S_{BET} ($m^2\,g^{-1}$)	Acidity[a] (mmol $S\,g^{-1}$)	Density of acid sites	Activity Glycerol conversion	Solketal selectivity
SO_3HPr-Am	1.0	131	$0.8(0.8)^b$	64	$89(82)^a$	$96(93)^a$
SO_3HPr-KIT-6	0.9	458	$0.8(0.7)^b$	19	$91(90)^a$	$98(92)^a$
SO_3HPr-SBA-15	0.9	526	$0.8(0.6)^b$	15	$90(85)^a$	$98(96)^a$

45

Figure 15.10   Performance and stability of amorphous propyl silica in solketal synthesis during several cycles.
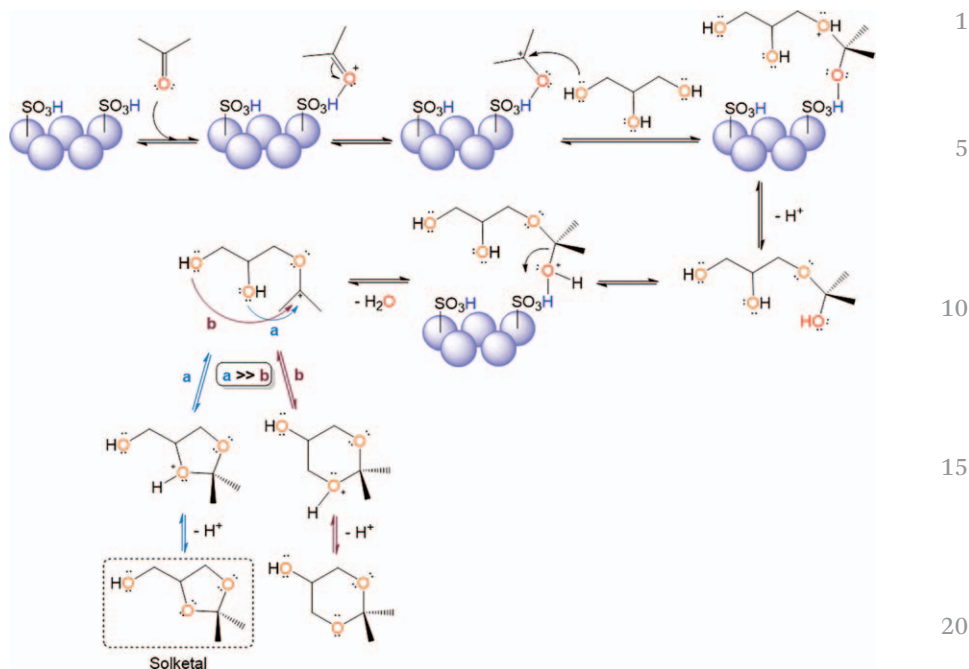
Figure 15.11   Plausible reaction pathway for glycerol acetalization catalyzed by sulfonic silica-based material.

rise a six-membered ring (1,3-dioxane) and five-membered ring (1,3-dioxolane), respectively, after proton displacement with catalyst restoration. This process shows regioselectivity towards the formation of the five-membered ring (solketal) which is the kinetically favoured product due to the proximity of the secondary hydroxyl group to the tertiary carbocation to afford cyclization. Nevertheless, when the reaction is carried out under thermodynamic control (higher temperature and longer reaction time), solketal is still the main product irrespective of whether the reaction is carried out by using thermal or microwave heating. This finding can be explained taking into consideration the geometry of six- and five-membered ring ketal. In the six-membered ring, the presence of axial methyl groups results in a repulsive interaction with two axial hydrogen atoms, whereas in the five-membered ring, the interaction with an axial hydrogen atom farther from the ethyl group makes this repulsive interaction less important, improving the thermodynamic stability of this product.[70]

15.4   Conclusions

The studies reported in this chapter prove the effectiveness of microwave irradiation as a new synthetic technique for the conversion of glycerol into valuable chemicals. In fact, the microwave irradiation rapidly activates the

reactants favouring the interaction with the catalysts and leading, easily, to glycerol conversion resulting in the formation of several important chemicals. With the use of appropriate catalytic materials, the described research studies enable the accomplishment of very fast and efficient reactions. These features make the processes sustainable in terms of energy, time and economy savings. Moreover, the use of waste as secondary raw material not only makes the process sustainable but also leads to the reduction of environmental pollutants. In particular, glycerol as a significant by-product of biodiesel production can be effectively used for the sustainable synthesis of added value products. Finally, the use of microwaves should therefore be encouraged in all those processes contemplated in sustainable biorefineries.

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