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Hierarchical Zeolites as Catalysts for Glycerol Upgrading Reactions

Zeólitas Hierárquicas como Catalisadores para Reações de Valorização do Glicerol

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In a context where society has a strong dependence on fossil fuels, research in biofuels is necessary to offer a more sustainable future. In this perspective, biodiesel has attracted much attention due to its high applicability. As a byproduct of biodiesel synthesis, glycerol is one of the main concerns in this field because its demand is lower than the supply, and also due to the accumulation in the industry may transform it into waste. To overcome this issue, several studies have proposed investing in glycerol chemical conversion. These reactions allow many industrial products such as acrolein, solketal, toluene, xylene, alcohols, and many others. Acid groups catalyze most glycerol conversion reactions, and zeolites are quite promising since they have intrinsic acidic properties. However, their microporous structure might offer diffusional limitations, preventing the access of glycerol molecules to acidic sites in the internal surface, causing a decrease in their performances or even deactivation. Studies have reported different methods to produce mesopores in the zeolite structure (hierarchical zeolites) and how they can affect its properties, including glycerol conversion and yields to several products. This paper discusses how hierarchical zeolites can produce value-added compounds from glycerol and resist deactivation.

Keywords: Green chemistry; glycerol upgrading; hierarchical zeolites; heterogeneous catalysis; solid acid catalyst

1. Introduction

Rising concern about climate changes caused by gaseous emissions during fossil fuel burning has encouraged great efforts to develop more sustainable renewable energy sources.[1] In that way, biomass is an essential renewable source to achieve a more sustainable society and less dependent on fossil resources through bio-based fuels.[2] Among these bio-based fuels, biodiesel is one of the most studied worldwide, being produced mainly from oil-enriched biomass. Biodiesel production occurs by transesterification of triglycerides with alcohols, such as methanol (in basic catalyst presence) as shown in Figure 1.[3] USA and Brazil are the most important producers of biodiesel worldwide, reaching around 6.43 billion liters in 2020, and the market predictions reveal an increase in next decade production of this biofuel.[4] In addition to transesterification, esterification of fatty acids[5] and hydroesterification of triglycerides (hydrolysis followed by esterification)[6] are also routes for biodiesel production.

From Figure 1, glycerol is a coproduct of transesterification reaction, and 1 kg of this

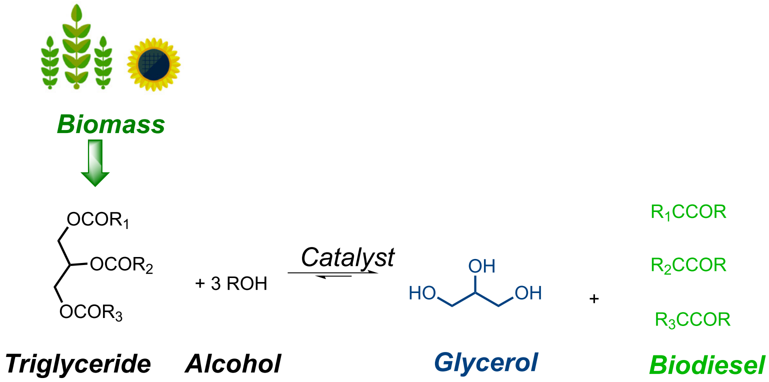

Figure 1. Biodiesel and glycerol obtention by transesterification reaction

compound is obtained for each 9 kg of biodiesel.[7,8] The term glycerol only refers to the pure compound 1,2,3-propanetriol. In contrast, the purified commercial product containing around 95% glycerol is usually known as glycerin, which can present slight changes in its composition and physical properties depending on the source.[9] After acidic treatment, to neutralize the catalyst the "blond glycerin" is obtained, constituted of 80 wt.% of glycerol, water, methanol, and salts.[10–14] In that context, henceforth, we will refer to glycerol as the pure chemical compound 1,2,3-propanetriol, and when necessary other nomenclature will be used to refer to a nonpure compound.

The dynamics of glycerol production have been changing over time since biodiesel consumption and production are guided by several governmental and economic factors. Several industrial sectors utilize glycerol, in cosmetics, food and beverage, resins, lubricants, adhesives, etc.[15] Nevertheless, the large amount of glycerol produced as a coproduct of biodiesel manufacture every year stills overcomes the demand, and it becomes necessary to find new routes to glycerol utilization.[16] If not correctly used, the high accumulation of this compound may transform it into a residue.[8,15] Thus, considering the large production of glycerol and its steady market value decrease, it is imperative to develop new applications for this compound and alternatives to transform it into value-added molecules. In this context, glycerol can generate high value-added chemicals, such as glycerol carbonate, glycerol 1-monoethers, acrolein, glycidol, solketal, organic acids, alcohols and others. The reactions to form these high-valued chemical products from glycerol vary depending on the target compound (Figure 2).[17,18]

Acids catalyze most glycerol upgrading reactions in at least one of their steps, and both homogeneous and

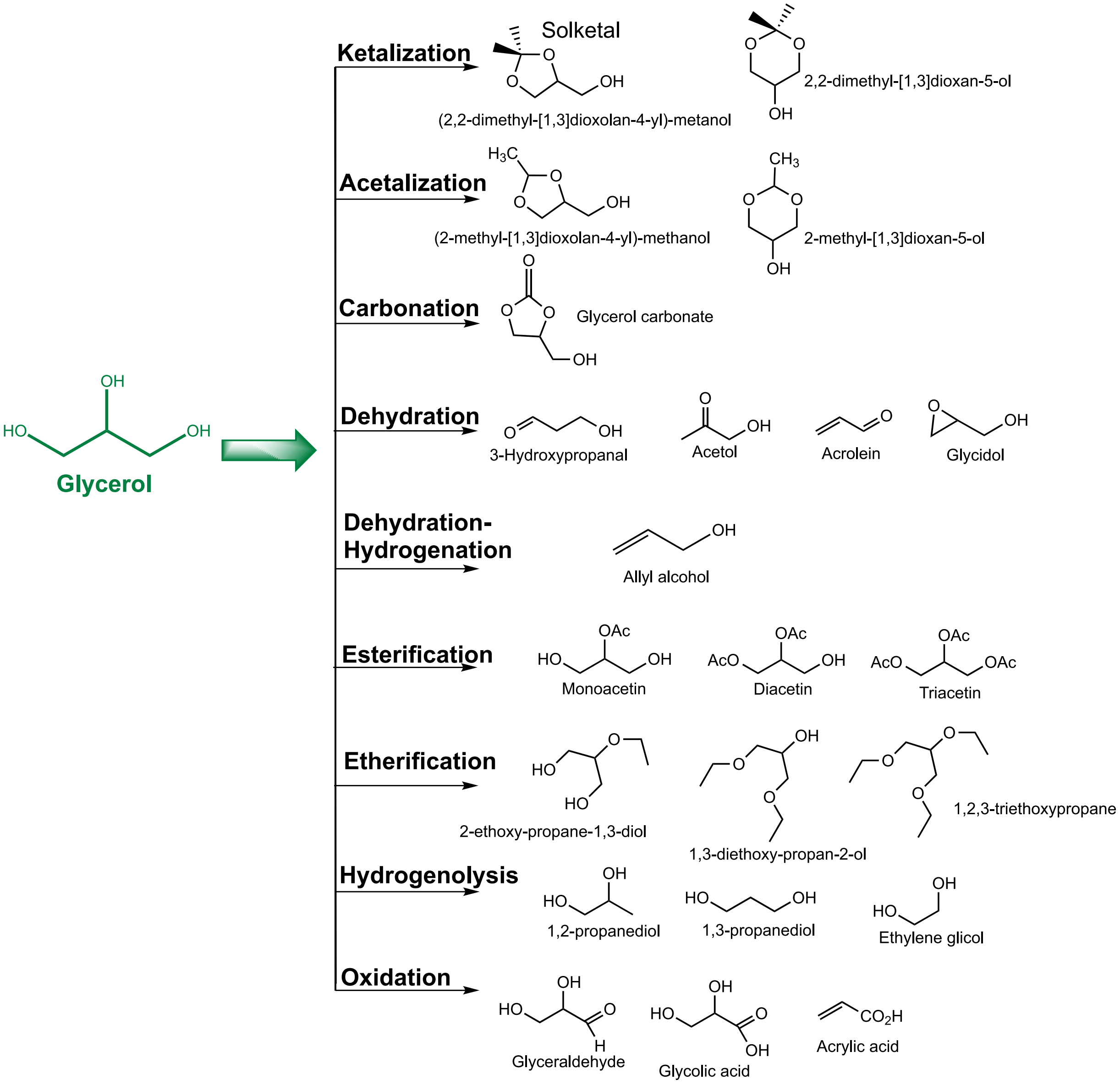

Figure 2. Upgrading reactions of glycerol to high-value chemical compounds

heterogeneous catalysis represents a crucial role in these transformations.[19] Mineral acids, such as HCl, H_2SO_4 and HNO_3, are commonly employed as homogeneous catalysts for those transformations. Despite their high activity, homogeneous catalysis protocols often have separation steps as a drawback, requiring more energy to separate the catalyst from the products.[20] On the other hand, heterogeneous catalysts can be quickly recovered from the reaction medium, and several efforts have been made to achieve highly stable and active materials. Supported metal oxides, clays, functionalized silicas, bifunctional catalysts (acidic and metallic sites), and acidic resins are examples of heterogeneous catalysts for oxidation, dehydration, etherification, and hydrogenolysis reactions of glycerol.[21,22] Among these acid catalysts, zeolites play a pivotal role in most glycerol upgrading reactions due to their tunable and intrinsic acidity, thermal stability, and channels of micropores.[18,23–25]

Several zeolites (MFI, BEA, SAPO-34, USY, and FAU) have been reported as catalysts to reactions of dehydration, etherification, acetalization, and acetylation to convert glycerol into chemical products of higher industrial interest.[19,26,27] However, a comparison between zeolites micropore channels (Table 1) and glycerol kinetic diameter (0.67 nm)[28] reveals that these catalysts' performances might be affected by diffusional limitations.[13,29,30]

Table 1. Comparison between zeolites pore dimensions and kinetic diameter of biomass-derived molecules[17,29,31]

Zeolite Framework type	Pore size (nm)
FER	~0.35 x 0.48 (8 MR); ~0.42 x 0.54 (10 MR*)
MFI	~0.51 x 0.56 (10 MR)
MOR	~0.34 x 0.48 (8MR); 0.65 x 0.7 (12 MR)
BEA	~0.56 x 0.67 (12 MR)
FAU	~0.74 x 0.74 (12 MR)

*MR: member rings

Considering that, to avoid diffusional limitations of large organic molecules into zeolites micropores, new methodologies are essential to improve the catalytic efficiency of these materials.[32,33] Thereupon, one of the most promising pathways is the introduction of mesopores into zeolites structure and generating a hierarchically structured pore system, *i.e.,* hierarchical zeolites.

The generation of these mesopores in zeolite structures often might delay the deactivation of these materials in zeolite-catalyzed reactions, such as glycerol upgrading. Previous studies discuss the deactivation and the diffusion phenomena relationship in coke production. Briefly, the mesoporosity allows a more straightforward diffusion process, which can avoid coke formation inside the pores (particularly micropores), which is one of the causes for deactivation.[18,34] In this sense, some impurities found in glycerol and some byproducts of glycerol upgrading reactions, such as water, methanol, and other compounds, are an issue in the deactivation process since they block the active sites of the catalysts and prevent the reagents' access.[18,35]

In this review, we focused on the advantages of hierarchical zeolites for glycerol upgrading reactions and their acidic properties, and also, we present a comparison with the non-hierarchical systems. In addition, we will also discuss several deactivation processes that are common in these types of upgrading reactions.

2. Microporous Zeolites and Hierarchical Zeolites on Glycerol Upgrading Reactions

Several methods can be applied to zeolites to create mesopores in their structures. In that way, some synthetic strategies are summarized in Table 2.[36–38]

In this sense, many studies towards glycerol upgrading evaluated the effect of these mesopores in the zeolite catalytic performance.[35,39–41] Concerning this subject, these approaches can change the zeolite structure and its acidic properties, which may influence the catalysts' performances since acidic sites control the majority of the glycerol upgrading reactions.[18,42] For this reason, we present an overview of hierarchical zeolites applications for distinct transformations of glycerol, a comparison of the mesopores generation effect in multiple contexts, and how they can influence catalytic parameters (conversion, yield and selectivity). Since it is difficult to generalize the influence of each type of acid site (Brønsted or Lewis) or its strength (strong, moderate, or weak), each glycerol upgrading reaction has its particularities (catalysts and acidic properties). In this way, the following items will bring more details specific to each of these reactions using acid catalysts.

2.1. Glycerol dehydration

This reaction can be conducted in liquid or gas glycerol aqueous solution at high temperature conditions (250-500 °C) and pressures from 1 up to 50 atm.[43] To glycerol dehydration reaction can be used H_3PO_4/Clay, H_3PO_4 (5 at 20 wt%)/Al_2O_3, $Al_2(SO_4)_3$, H-BEA, H-MFI, MCM-56;[43] PW/SiO_2, PW/ZrO_2, SiW/AC, MCM-49, MCM-22, MCM-56 and ZSM-11, H-MFI, Nb_2O_5, SAPO-11, SAPO-36, VPO, TiO_2-PO_4, WO_3/ZrO_2, Zn_2SO_4[44] and other acids materials as catalyst. The active sites used for this reaction can be both Brønsted and Lewis acid sites; however, the literature reports that an optimal acidic strength is needed for a high glycerol dehydration rate. In this context, weak acid sites lead to low selectivity, whereas strong acid sites promote catalyst deactivation through polymerization products deposition over its surface.[44,45]

Porous catalyst support greatly influences the selectivity and yield of the products of the glycerol dehydration

Table 2. Strategies for hierarchical zeolites production

Method	Description
	Bottom-up approaches
Hard templating	Introduction of solid materials into zeolite synthesis and the mesopores and macropores are created after calcination or dissolution; Examples of rigid templates: carbon black, carbon nanotubes, carbon nanofibers, ordered mesoporous carbons, colloidal silica, polymer beads, resin beads, calcium carbonate, bacteria, wood, leaves, and sugarcane bagasse. Produces zeolites with broad porosity and second porosity through micropores.[36]
Soft templating	Introduction of non-rigid templates removed by a calcination process. Examples of soft templates: surfactants, polymers, organosilanes. A low amount of micropores is formed, defect-rich structures, expensive, harsh synthesis conditions, and time-consuming.[36]
Assembly of nanosized zeolite	Strategies without templates. These strategies are based on the aggregation of nanocrystals, crystallization of amorphous gels, and self-pillared zeolites.[36]
Zeolitization of solids	Based on the conversion of amorphous mesoporous silica-based materials into zeolites with crystalline walls. This method often leads to structurally unstable zeolites, and only a few zeolites are produced using this strategy.[36]
	Top-down approaches
Dealumination	Involves Al removal through steaming, calcination or acid leaching. Furnishes zeolites with good thermal stability and enhanced mesoporosity; however, it decreases the total acidity of zeolites.[36]
Desilication	Removal of Si from the zeolite structure by alkaline treatment. This treatment can also generate mesopores and enhance Lewis acidity, yet this method decreases the total acidity of the material.[36–38]
Desilication with recrystallization	Partial dissolution of the zeolite under alkaline medium (NaOH or NH_4OH under mild conditions) followed by hydrothermal treatment in the presence of a surfactant. This method leads to low silica loss or damage to crystals of zeolite.[37]
Surfactant templated crystal rearrangement	The commercial zeolite is submitted to a harsh alkaline medium to its amorphization and followed by recrystallization in the presence of a surfactant.[36]

reaction. A microporous material can prevent the reactant molecules from accessing the catalyst's active sites, resulting in low catalytic activity and a lower yield, as only the sites on the surface of the catalyst will be available. This feature affects the glycerol dehydration reactions and the other reactions discussed in this review. Therefore, to facilitate the access of the reactants to the active sites in the structure of the porous catalyst, it is preferable to use mesoporous materials for the glycerol upgrade reactions. Considering that, hierarchical zeolites emerge as highly promising catalysts.[39,45–52]

Kostyniuk and co-workers reported the synthesis of glycidol in a single gas phase step with a fixed bed reactor and Liu and co-workers reported the theoretical study of glycidol production using hierarchical zeolites as catalysts.[53] Glycidol is an essential value-added molecule obtained from glycerol and applied as a solvent, cosmetics, polymers, detergents, disinfectants, and fine chemical industry as starting materials for analgesics and antiviral drugs.[54,55]

A hierarchical ZSM-5 zeolite (Si/Al=750) impregnated with cesium catalyzed the reaction. Cesium nitrate was impregnated at three concentrations – 10, 20, and 40 wt.% – and analysis of temperature-programmed desorption of ammonia (NH_3-TPD) and pyridine Fourier Transformed Infrared (FTIR) showed that with increasing concentration of $CsNO_3$, the amount of acidic sites decreased due to metal ion exchange. Consequently, basic sites were created in samples. In the sample with 10 wt.% of Cs, weak Lewis sites were detected due to AlO_x structures and $CsNO_3$ species deposited on the catalyst surface, respectively. A reduction in the crystallinity of the sample was confirmed by X-ray diffraction (XRD); these changes indicate that dissolution of silicon oxide led to the formation of mesopores, as showed by N_2 physisorption results. The authors' objective was to synthesize glycidol in a single-step reaction by the intramolecular dehydration of glycerol, and the sample with 20 wt.% of $CsNO_3$ exhibited the best glycerol conversion and glycidol selectivity 86.3 and 64.3%, respectively. In addition, Kostyniuk suggested that the catalyst deactivation depends on the amount of $CsNO_3$ active phase (basic sites) and the coke formation.[53]

Acrolein is one of the most important products obtained from glycerol upgrading since it is primarily used to produce acrylic acid and hence acrylates and also might be used as starting material in the fine chemical industry. For example, DL-methionine production, which living organisms do not produce this essential amino acid.[44] Considering that several studies have been devoted in the literature for glycerol conversion to acrolein using hierarchical zeolites, aiming to avoid coke formation and to achieve more stable catalysts.[55]

Martins and co-workers studied the influence of three different ZSM-5 zeolites, with different Si/Al ratios, in the gas-phase dehydration of glycerol to acrolein.[46] The generation of mesopores was performed on an ZSM-5 zeolite (Si/Al = 40) by desilication method, using an alkali treatment in different molar ratios of hydroxyl:silicon, ranging from 0.2 to 1.2. Other zeolites were also evaluated but without any alkaline treatment. N_2-physisorption on both modified and unmodified zeolites showed the presence of mesopores in almost all of the materials. The modified zeolites presented, as expected, a larger mesopore volume and a decrease in micropore volume. After the catalytic tests, the treated zeolite with 0.8 hydroxyl:silicon molar ratio presented the best results, enhancing the selectivity of acrolein, the main dehydration product of glycerol, up to 26.2%. All the other treated zeolites also showed a selectivity rate near 20%. The study also showed the positive impact of the mesopores generation, facilitating the reactants' access to the active acidic sites, which results in a higher conversion rate. In addition, other products such as propanal, allyl alcohol, acetaldehyde, and acetol were observed with a low yield, in which their formation is mainly described by Figure 3.[46]

The essential contribution of Martins' work, after comparing the catalysts, was to demonstrate that in addition to acidity, the glycerol conversion and the catalyst stability are influenced by the solids' structure and by their textural properties.[46]

Zhang and co-workers discussed the influence of textural and chemical characteristics of HZSM-5 zeolites over the dehydration of glycerol to acrolein.[49] The zeolites were prepared by a bottom-up method, starting with an aluminosilicate gel with specific contents of SiO_2, Al_2O_3, Na_2O, tetrapropylammonium bromide (TPABr), and KF. X-ray fluorescence (XRF) was used to determine the Si/Al, which were 99 (commercial, used as reference), 100, 102, 105, and 110. The authors mentioned that it was possible to achieve specific pores topologies by changing the water content on the mixture. Moreover, a crystalline seed with 200 nm of diameter was added to the gel to form the desired pores. Scanning Electron Microscopy (SEM) analysis showed differences on the surfaces of the catalysts: the ones prepared with a lower water content presented a smoother surface, while the ones prepared with more water had more rugous surfaces. The smoother ones also presented more mesopores, according to Transmission Electron Microscopy (TEM) images, while the ones with rugous surfaces originated intercrystalline mesoporosity. The N_2-physisorption analysis also showed this difference since all the samples exhibited type I and IV isotherms, but showed different hysteresis loops assigned to their different mesopores shapes. This diversity was also observed in micropores shapes by Argon adsorption isotherms at -186 °C. The Hg intrusion revealed that smoother zeolites have almost no accessible mesopores larger than 4 nm, while the rugous ones had 70% of mesopores available. A non-aqueous potentiometric titration measurement showed few available acidic sites on the occluded mesopores zeolites, FTIR after pyridine adsorption also showed that all samples possessed both Lewis and Brønsted acidic sites. All the samples presented 100% of glycerol conversion at the beginning, and as expected, the non-hierarchical material was severely deactivated. The sample prepared with the highest water content demonstrated a lower decrease (95% even after 24 h), while a pure HZSM-5 sample without mesopores deactivated quickly after 3 h. These results also

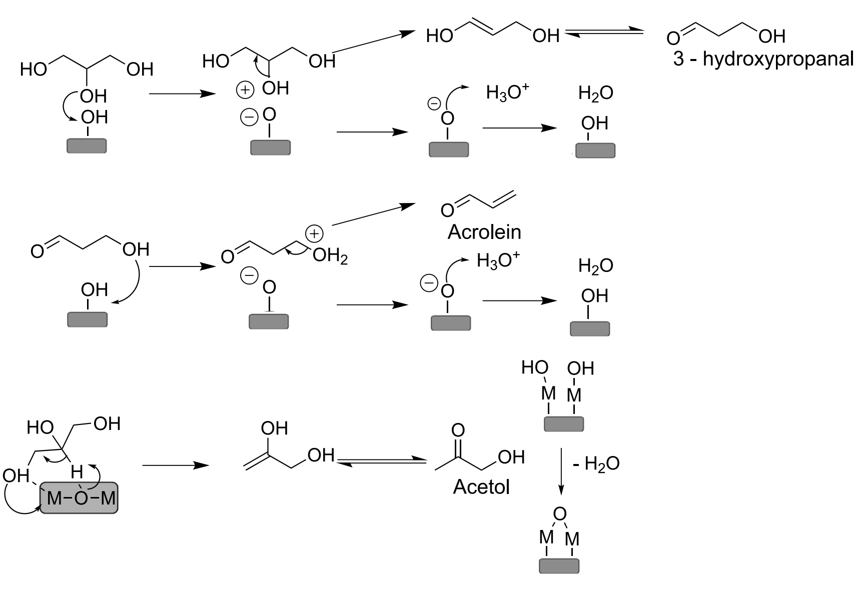

Figure 3. Mechanism proposal for glycerol dehydration reaction using zeolites[46]

showed that the interconnected pore topology of the zeolites with higher water contents presented a beneficial effect on glycerol conversion than the occluded ones (zeolites synthesized using a lower amount of water). In addition, small mesopores also showed not to be so suitable for the dehydration reaction.[56]

Querini and co-workers studied the influence of desilication in the performance of ZSM-5, Beta, and Y zeolites at gas-phase glycerol dehydration reaction.[47,57] Beta and Y zeolites, despite the good results, had slightly inferior performances than ZSM-5. In that way, commercial ZSM-5 zeolites were exposed to an alkali treatment to promote the desilication and the formation of a hierarchical meso/microporous structure. The N_2-physisorption analysis confirmed mesopores formation and presenting a good increase in the values of the mesoporous area (254 to 325 $m^2 g^{-1}$), although an expected decrease in the micropores volume was observed. The desilication method did not damage the zeolites' structure; however, their crystallinity was decreased by 10%. SEM images showed no damage to the structure of the zeolites modified by alkaline treatment, only presenting a slightly rougher surface. A similar ratio of strong to weak Brønsted acidic sites before and after the treatment, revealed by infrared spectra after pyridine adsorption, thus, not affecting the active sites of these catalysts. Gas chromatography detected acrolein, acetaldehyde, propanal, and acetol formation in a typical catalytic run. The catalytic results suggested a slower catalytic deactivation for treated zeolites compared to the non-treated ones. The selectivity for acrolein of both catalysts (non-treated and hierarchical ZSM-5) was similar, standing around 80%. However, the treated zeolites presented a lower coke deposition at the external surface, restraining the micropores' obstruction with oligomerization products.[47]

In addition, the synthesis of acrolein from glycerol was also studied by Huang and co-workers over hierarchical ZSM-5 zeolite at different temperatures (260, 280, 300, and 320 °C).[39] The zeolite was synthesized using an assisted ultrasound method (HP-ZSM-5, Si/Al = 178), and the material had its catalytic activity compared with commercial ZSM-5 zeolite with a similar Si/Al ratio (Si/Al=193). The precursors were mixed in the following molar composition: SiO_2:Al_2O_3:TPABr:H_2O = 400:1:120:12000, and the crystallization occurred at 180 °C for 48 h. XRD patterns, SEM, and TEM images confirmed the formation of ZSM-5 structure, and textural properties demonstrated the formation of intracrystalline mesopores. Analysis of NH_3-TPD and Py-FTIR showed strong and weak; Lewis and Brønsted acidic sites, respectively.[39,45] Compared to the commercial zeolite, HP-ZSM-5 showed a higher conversion and stability against deactivation, with 82% selectivity for acrolein after 50 h of reaction at 320 °C.[39]

Possato and co-workers, in another study, described the conversion of glycerol into acrylic acid in a single-step reaction catalyzed by vanadium oxides supported on ZSM-5 zeolites.[48] The hierarchical materials were prepared using alkaline with NaOH 0.6 mol L^{-1} at 60 °C for 1 h and followed by acid treatment using HCl or oxalic acid. After these treatments, the Si/Al ratio has decreased, and analysis of the textural properties showed that the mesopore volume has increased. Moreover, the treatment with oxalic acid reduced the amount of acidic sites, and when using HCl, a less effective decrease occurred, as shown by NH_3-TPD. The desorption curves of the impregnated samples were slightly different from the others, with a significant increase of the peaks at low temperatures. XRD patterns demonstrated that after impregnation, the crystallinity of pure zeolite was preserved. The acrylic acid synthesis occurred in two steps: dehydration of glycerol into acrolein over the acidic sites and oxidation of this compound over redox sites (Figure 4). The results displayed a high value of glycerol conversion (89%) for the vanadium-based hierarchical zeolite treated only with NaOH with 15% of acrylic acid selectivity. These results corroborate the increase in mesopore volume, which clearly showed the influence of the diffusional process in this reaction.[48]

A high silicon ZSM-5 zeolite (Si/Al = 150) was studied by Zhang and co-workers in the glycerol conversion into acrolein. The commercial zeolite was treated with an aqueous solution of NaOH (0.2 mol L^{-1}) for 6 h at 60 °C, and in parallel, zeolites with phosphates groups and transition metals (Sn, Cr, Mn, Mo) were synthesized.[49,51] The results showed that hierarchical zeolite presented a higher yield (63%) even after 30 h of reaction, thus demonstrating its resistance against coke poisoning. The zeolites treated with phosphates and transition metals showed good selectivity (89%) and yield (with a maximum of 83%) due to the higher concentration of Brønsted acids sites. Therefore, the zeolite with the best performance, considering factors as thermal stability, yield, and selectivity for acrolein, was the material containing phosphate groups and tin.

A new method to generate hierarchical structure in ZSM-5 zeolites by changing the crystal sizes was reported by Beerthuis and co-workers.[50] Its efficiency was tested in the glycerol to acrolein reaction. This preparation method used a ZSM-5 seeding solution, in which zeolite crystals

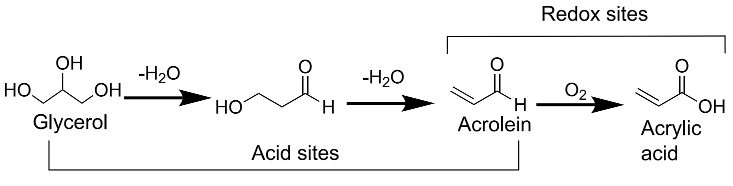

Figure 4. Synthetic route of acrolein from glycerol[48]

could grow on a bottom-up approach, thus avoiding the need for a structure-directing agent (SDA). The produced zeolite proved to be five times more stable than the commercial ones. The grown crystals were prepared in three different sizes and compared to a sample of commercial ZSM-5. The authors highlighted that those solutions with higher concentrations were more susceptible to generating small crystals. Cetyltriammonium bromide (CTAB) was also studied as a template for the formation of mesopores from nanosized zeolites. The experimental procedure and the catalytic tests revealed no need for ion exchange, considerably reducing the catalysts' production time. The obtained mesoporous zeolites generated crystals containing smaller pore volumes and areas than the commercial ones. On the other hand, the yields and selectivity to acrolein of these materials were higher than the commercial zeolites. While the commercial material presented a yield of 41% and a selectivity of 75% to acrolein, the nanosized zeolite presented a yield of 62% and a selectivity of 83%.[50]

Neves and co-workers described the synthesis of ZSM-5 zeolites with Si/Al ratios of 25, 50, and 75 (HZ25, HZ50, and HZ75) and their application in the glycerol dehydration reaction to acrolein. [51] The characterization of the catalysts by (NH_3-TPD) indicated the presence of acid sites in all samples. Textural and morphological analyses revealed that all the catalysts have similar pore sizes and a mixture of micropores and mesopores with volume ratios (micro/meso) of 70, 60, and 38%, for the samples HZ25, HZ50, and HZ75, respectively. The catalysts kept the activity for 4 h, and this activity had a significant decrease after 2 h of reaction. HZ25 and HZ50 provided conversions above 99% and HZ75 of 88%, in which the highest selectivity to acrolein was achieved by the HZ25 (80%) material. In addition, the authors also observed that the zeolites with a higher mesopore/micropore ratio presented the lower formation of coke, thus proving that a mesopore formation is quite beneficial for this reaction. Moreover, the thermogravimetric analysis (TGA) identified a higher coke formation in HZ75, due to a lower mesopores formation and consequently presented limited mass transfer.[54]

Fernandes and co-workers evaluated SAPO-40 zeolites in the gas-phase dehydration of glycerol. The hierarchical SAPO-40 was synthesized from a bottom-up approach, using organosilane as a porogen agent. [52] The textural evaluation indicated an increase in the surface area and mesopore volume. Compared to the microporous SAPO-40, the hierarchical material presented higher conversion (100% against 89%) and higher selectivity for acrolein (81% against 72%). After 120 h of reaction, both micro and mesoporous zeolites show a decrease in the conversion, related to the deactivation due to coke formation. The amount of coke produced in the hierarchical material was higher than microporous SAPO-40; however, the blockage of the pores was less effective in the mesoporous material due to the reduction in the constraints to the circulation of reactants and products.

2.2. Glycerol dehydration-hydrogenation

The glycerol dehydration-hydrogenation reaction can be carried out in aqueous or vapor phase, with conditions that vary from 160-250 °C and 1-80 atm, typically using molecular hydrogen gas and several heterogeneous catalysts, such as Pt/ASA, Pt/TiP, Pt/WOx, Pt/WOx/Al_2O_3, Pt/ZrW, Ru/ZrW, Ag/ZSM-5, Zr-Ni/H-beta Cu/Al_2O_3, Cu/MgO, Cu/ZnO, Cu/ZrO_2, $Cu_2Cr_2O_5$, Cu-Al, Cu-$H_4SiW_{12}O_{40}$/SiO_2, Ni–Cu/Al_2O_3 and Ru–Mo/C nanotube and other metallic materials with acidic sites are employed.[58–67] Glycerol dehydration is carried out on the Brønsted acid or basic sites on the support surface, and an increase in the strength of these sites leads to an enhancement of the catalyst activity. On the other hand, Lewis acid sites are responsible for the hydrogenation of acetol into propanediols,[68,69] in which strong Lewis acid sites increase glycerol conversion and yield in this reaction.[41,68,70] Likewise, Zhou and co-workers pointed out that empty "*d*" orbitals in the metal also enhances de catalytic activity.[71] Bifunctional catalysts presenting both acidic sites (Lewis and Brønsted) and metal sites are commonly used. Here, it is important to mention that hydrogen molecules and glycerol show a competitive reaction pathway for the active sites, which might directly influence the reaction ratio.[63–66]

The catalytic supports not only influences the dehydration step but also directly affect the product yield since it can enhance the adsorption capacity of the catalyst, improving the glycerol conversion.[60] In this way, supports that present tuneable properties, such as acidity and pore size, are desirable since they can be modified to favour the conversion and selectivity.[41,72]

Lari and co-workers studied a bifunctional hierarchical zeolite for the reaction to convert glycerol into allyl alcohol. Allyl alcohol is another crucial compound prepared from glycerol upgrading.[41] This compound is used as a precursor to plasticizers, flame-resistant materials, denaturants for ethanol, herbicide, and fungicide, Figure 5.

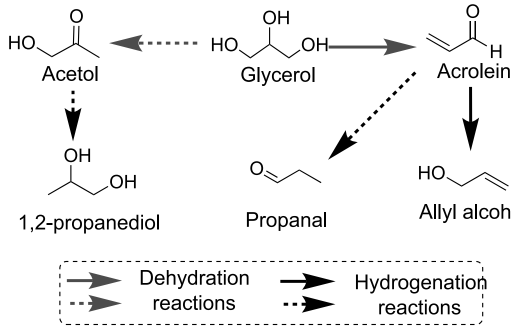

Figure 5. Proposal for the conversion of glycerol through dehydration and hydrogenation reactions

The reaction was divided into two parts: the dehydration and hydrogenation step. The first part is influenced by Brønsted acidity, and the second part, by the presence of metallic sites. To evaluate these effects, commercial ZSM-5 zeolites (Si/Al = 40), which underwent an acidic treatment and then a wet impregnation with several metals (Pt, Pd, Au, Ru, and Ag), were obtained. The zeolite chosen for the impregnation was the one that went for both basic and acidic treatments, respectively – due to its higher conversion into acrolein (62%), a product of the first step of the reaction, in which acetol detection was lower than the other materials (a consequence of lower Lewis acidic sites amount).[41]

Moreover, it is important to highlight those hierarchical zeolites presented a lower deactivation due to coke deposition than the commercial zeolites or even pure alumina. The zeolite impregnated with silver showed the best conversion and the highest selectivity (53.5 and 13.1%, respectively) among the samples. After optimization, the zeolite impregnated with 5% of silver reached a glycerol conversion of 80% and allyl alcohol selectivity of 20%.[41]

2.3. Glycerol ketalization, acetalization, and acetylation reactions

The glycerol ketalization (with ketones) and acetalization (with aldehydes) reactions occur by acid catalysis, generally at temperatures between 25-120 °C and under atmospheric pressure. A high glycerol conversion is achieved using catalysts with strong acidity (relatively more acid sites per unit mass). This reaction employs homogeneous acid catalysts with Brønsted acid sites and heterogeneous with Lewis acid sites catalysts. Typically, homogeneous acid catalysts are sulfuric acid, hydrochloric acid, phosphorus pentoxide, and p-toluene sulfonic acid.[28] Although these catalysts are traditionally applied, they have some disadvantages, such as the corrosion of reactors and the difficulty of recovering and reusing. The examples of heterogeneous acid catalysts are zeolites (H-BEA, ZSM-5), clays (K-10 Montmorillonite), and resins (Amberlyst-15, Amberlyst-36, Nafion–H NR 50).[28,73–85] However, heterogeneous catalysts present some difficulties, such as maintaining surface stability and avoiding coke formation.[28]

The ketalization of glycerol allows achieving an essential oxygenated fuel additive – solketal. Solketal might be added to gasoline and thus decreasing the pollution through particulate matter emission and increasing the octane number. Moreover, solketal acts as liquid properties modulator for low-temperature transportation fuels, "green solvent", plasticizer, surfactant, disinfectant, and flavoring. In this sense, Rossa and co-workers studied a catalytic route to produce solketal from glycerol via ketalization reaction with acetone (Figure 6).[28] Although the authors used a commercial Beta zeolite (SAR = 19), the N_2-physisorption measurements demonstrated an intergranular mesoporosity on these materials. The authors reported an extensive study of the kinetic parameters of ketalization reaction, and all tests showed good selectivity for solketal, with at least 94% of selectivity. Nevertheless, reusability tests showed a considerable decrease in conversion rate, dropping exponentially after the first use. The deactivation of the acidic sites by hydration was the probable reason for the destabilization of the zeolite structure, and the intrinsic mesoporosity of the Beta zeolite was not adequate to avoid it.

Kowalska-Kus and co-workers transformed different untreated zeolites: Beta (BEA-P, Si/Al=12), mordenite (MOR-P Si/Al=17), and ZSM-5 (MFI-1-P, Si/Al=12, and MFI-2-P, Si/Al=27) in hierarchical zeolites for the conversion of glycerol in solketal. The zeolites were submitted to an alkaline treatment with a sodium hydroxide solution (0.2 mol L^{-1}) at 80 °C for 2 h. In addition, some zeolites were treated in acidic solutions after alkaline treatment, firstly in a 0.5 mol L^{-1} aqueous solution of nitric acid and then in a 0.5 mol L^{-1} citric acid solution.[86] The results of the XRD analysis proved that zeolites kept their crystallinity; however, the percentage of zeolites treated in alkaline solutions tended to be reduced. In contrast, zeolites treated in an acidic medium did not suffer such crystallinity decrease. The N_2-physisorption measurements showed that zeolites developed mesopores since changes in the mesoporous area data were observed, in which Beta zeolite went from 32 to 50%, mordenite from 19 to 34%, and ZSM-5 from approximately 10 to 50%. Also, their surface areas enhanced up to 20-25% (ZSM-5), 10% (Beta) and 3% (mordenite). Furthermore, a conversion of 80% was reached for the hierarchical materials and the zeolites treated in basic solutions presented the highest values of selectivity (~100%) and yield (80%) of solketal (Figure 6), which were significantly higher than the parent (non-hierarchical) zeolites.

Talebian-Kiakalaieh and Tarighi reported a Y mesoporous zeolite by a top-down dealumination method using citric acid and applied to solketal production from crude glycerol.[35] Further, to ensure its acid strength and active sites, the material was functionalized with phosphotungstic acid (HPW). Inductively coupled plasma analysis (ICP-OES) confirmed dealumination process through an increase in the Si/Al ratio, from 3.15 to 6.20. N_2-physisorption measurements showed an increase in the total surface

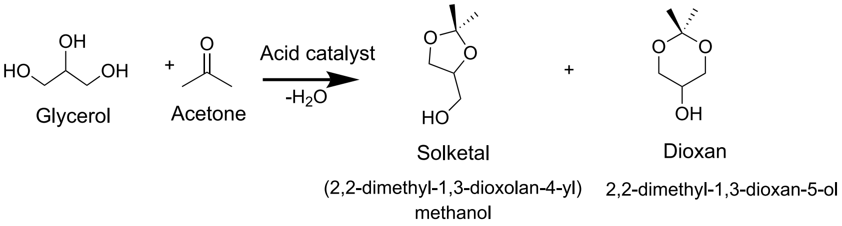

Figure 6. Solketal synthesis *via* glycerol ketalization with acetone

area, and acidity assessment by NH_3-TPD analysis showed high concentrations of strong acid sites on the untreated zeolites. In contrast, the treated ones showed mostly weak acidic sites. The non-treated zeolites showed low catalytic activities, while the hierarchical materials presented almost seven times higher solketal yields. By varying acidity and mesoporosity evaluating their efficiency, the authors confirmed that those are the most crucial parameters on the activity of the desired catalysts (97.85 % solketal yield and 100% glycerol conversion).

Kowalska-Kuś and co-workers compared the performance of hierarchical zeolites with 3 different topologies – ZSM-5, Beta, and mordenite – in the acetone with glycerol acetylation reaction under a continuous flow reactor.[17] The mesopores were generated by alkaline treatment (0.2 mol L^{-1} at 80 °C for 2 h) followed by acid treatment with citric acid (0.5 mol L^{-1} at 80 °C for 3 h). The zeolites suffered morphological and textural changes, but they all produced mesopores after the treatments. However, in Beta and mordenite zeolites, the mesopores were characterized as intercrystalline mesopores, according to the N_2-physisorption isotherms. The total acidity and the strength of acidic sites also changed, in which for ZSM-5, the total acidity increased for both weak and strong acidic sites. Mordenite showed no change in the total acidity, but there was a reduction in the strong sites amount and, for the Beta zeolite, a reduction in strong acidic sites and the total acidity of the solid was observed. These zeolites were tested in their original and hierarchical forms, in which hierarchical Beta and ZSM-5 presented a higher activity in glycerol ketalization as a consequence of the larger pore size formed, eliminating a restriction in the diffusion (with high glycerol conversion and solketal selectivity, 90%). On the other hand, hierarchical mordenite does not present any improvement – assigned to a marked decrease in the crystallinity of this material.

Hierarchical MCM-22 zeolites using the bottom-up approach with organosilanes (with 8 and 12 carbon atoms and named MWW-8 and MWW-12, respectively) were reported by Rodrigues and co-workers, and the materials were applied to the glycerol ketalization reaction.[40] The zeolites were characterized by ICP-OES, nuclear magnetic resonance (NMR), XRD, SEM, nitrogen physisorption, NH_3-TPD, and Pyridine adsorption FTIR techniques. These procedures proved the treatment efficiency with organosilanes, even though the physical-chemical and textural properties of zeolites remained unchanged. The MWW-12 zeolite showed a glycerol conversion of 83% (which is 33% higher than MWW-8 and 64% higher than untreated MWW zeolite) and high selectivity for solketal (~95%). Furthermore, due to the modification of the Si/Al ratio, the MWW zeolites reduced their densities of Brønsted and Lewis acidic sites. However, this change in the acidic properties and the modification of the reaction mechanisms – a consequence of larger mesopores – favored the overall reaction.

Another significant reaction of glycerol upgrading is its reaction with formaldehyde and thus producing a mixture of oxygenated rings with 5 and 6 members called glycerol formal (GF), as shown in Figure 7. GF molecules (5-hydroxy-1,3-dioxane and 4-hydroxymethyl-1,3- dioxolane) might be used as binders, water-based-inks, solvents with low toxicity, and also as co-monomers for polymers.[87]

In this context, Sonar and co-workers reported the production of GF compounds using hierarchical Beta zeolites.[87] Firstly, a Beta zeolite (Si/Al=14) was synthesized and then submitted to a top-down approach to introduce mesopores *via* alkaline treatment with different amounts of NaOH 0.1 mol L^{-1} solution (5, 10, 30, 150, and 300 mL). XRD patterns showed a collapse in the zeolites' crystalline structure as the volume of alkaline solution was increased. The efficiency of Si removal was observed from the NMR technique, revealing Si/Al ratios of 13, 11, 10, 9, and 7 as the alkaline solution had its volume increased. In addition, N_2-physisorption measurements and NH_3-TPD revealed, respectively, a progressive increase in the mesopores volume and a decrease in the total acidity as Si/OH ratio decreased. The synthesized Beta zeolite presented low glycerol conversion (25%) but high selectivity for dioxane (70%). All the hierarchical materials showed low conversions, except for the one treated with the lowest amount of base. After optimizing parameters, this material had a conversion of 78% of glycerol with a selectivity of 15% for dioxane and 85% for dioxolane compounds. In that sense, a significant deleterious effect was observed for the other samples of hierarchical Beta zeolites assigned to the partial destruction of their crystalline structure.

In glycerol acetylation reactions, mineral acid catalysts have been widely used for this reaction, usually at 25-180°C, under atmospheric pressure. One of the advantages of this type of catalyst is good catalytic activity, but mineral acids are toxic, corrosive, and difficult to separate from the reaction mixture. Different types of solid acid catalysts are applied, such as resins (Amberlyst-15), niobic acid, zeolites (HUSY and HZSM-5), functionalized mesoporous silica (niobium-containing SBA-15), sulfated zirconia, supported heteropolyacids, and clays (K-10 Montmorillonite and modified Montmorillonite).[74,75,78,79,85]

The selectivity and conversion of these reactions are influenced by the supports used. Studies have shown that

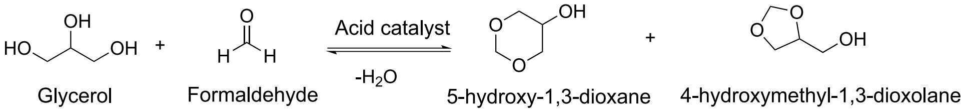

Figure 7. Glycerol formal synthesis from glycerol and formaldehyde

catalysts based on zeolites, resins, and heteropolyacids guarantee conversions and selectivities above 90%. However, the specific area of the catalytic support can be reduced when functionalized to furnish a highly acid material due to the blockage of the catalyst pore channel, thus decreasing catalytic activity. Still, these acids sites might be leached and act as homogeneous catalysts and thus causing a conversion and selectivity decrease for the heterogeneous material.[75,77]

The glycerol acetylation with acetic acid is another strategy to produce value-added compounds such as monoacetin (MA, monoacetylated products), diacetin (DA, diacetylated products), and triacetin (TA, triacetylated product), as illustrated by Figure 8. These products find applications such as biodiesel quality improvement as additives (especially DA and TA), thus regulating cold properties and viscosity. Moreover, these products also can be used as a gasoline additive to adjust its anti-knocking properties.[88]

In that sense, Popova and co-workers described the esterification reaction of glycerol with acetic acid catalyzed by hierarchical mordenite zeolite (Figure 8).[27] The non-hierarchical zeolite was previously synthesized using a seed approach, and then the mesopores were inserted by top-down acidic treatment using hydrofluoric acid and ammonium fluoride. Further, the hierarchical material was impregnated with 15 wt.% zirconium. The procedure did not lead to any significant change in the crystallinity compared to its parent material, and the Zr atoms were well dispersed – since no diffraction peaks related to ZrO_2 were found. N_2-physisorption measurements demonstrated that hierarchical zeolite presented virtually the same specific surface area and higher pore volume and pore size than the non-hierarchical one. In addition, NH_3-TPD acidity characterization revealed a slight increase in the acidic sites amount of the hierarchical material compared to the non-hierarchical one. The Zr-post modification in the hierarchical zeolite caused a marked increase in the total amount of acidic sites. FTIR characterization with pyridine adsorption showed a higher Brønsted acidic site increase in the pure hierarchical mordenite, and its post-modification with Zr caused a notable increase in the Lewis acidic sites. SEM technique displayed that hierarchical material presented grains with a large amount of debris compared to its parent zeolite, thus revealing a superficial effect on the zeolite due to the top-down method applied. The catalytic tests showed a significantly higher glycerol conversion for the hierarchical mordenite (89%) and Zr-hierarchical mordenite (94%) compared to its parent zeolites (68 and 74%, respectively). Concerning ester selectivities, the hierarchical material with Zr presented higher selectivity (64%) to the triacetylated product (triacetin) – a bulkier molecule formed due to the facilitated diffusion of reactants and products. Interestingly, this material also presented a high activity (3% decrease of glycerol conversion) and selectivity to TAG even after three reaction cycles.

Following this path, Tonutti and co-workers used a hierarchical ZSM-5 zeolite produced by a top-down approach. They studied the acetylation of glycerol with acetic acid and in the isobutane alkylation. [57] The authors used three different aqueous solutions of sodium hydroxide (NaOH), with concentrations of 0.2, 0.3 and 0.4 mol L^{-1} for 30 min. at 65 °C. Also, a sulfonated SBA-15 was synthesized and had its catalytic activity compared to the zeolitic materials. As a result, the alkaline treatment affected the crystallinity of the zeolites, changing the crystallinity from 100 to 75.6% (ZSM-5(0.2)), 84.0% (ZSM-5(0.3)), and 77.3% (ZSM-5(0.4)). Interestingly, the hierarchical zeolites presented higher acidity than the microporous ZSM-5. The ZSM-5(0.3) material showed the most increased activity, which the authors assigned to the combination of mesoporosity and strong acidic sites. Moreover, there was a higher diffusion of the voluminous product molecules (mainly DA and TA) in the hierarchical zeolites. The least active zeolite (ZSM-5(0.4) presented the highest resistance against deactivation – a process arising from the deposition of bulky molecules. As expected, the sulfonic-functionalized SBA-15 showed the most increased activity and selectivity to DA and TA products (DA + TA = 70%) as a consequence of larger mesopores and no restriction in the diffusion of large molecules.

2.4. Glycerol etherification

Etherification of glycerol is an essential pathway to produce oxygenated diesel additives and possesses a pivotal role in the emissions reduction of volatile organic compounds. In addition, etherification products also can be used to tune diesel properties such as viscosity and cloud point and improve the octane number in the gasoline blend.[89]

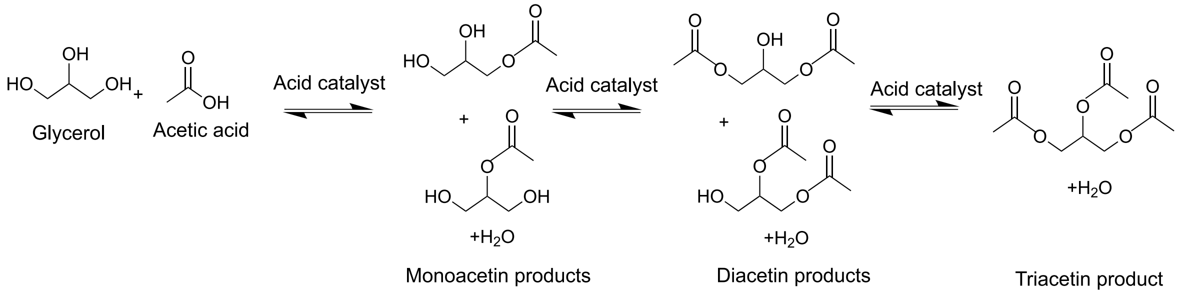

Figure 8. Glycerol acetylation reactions with acetic acid

This reaction is commonly operated in a liquid phase at low temperatures (100-230 °C) and pressures up to 21 atm. Regarding the catalysts, Silica/Hyflon, MFI zeolite, $CsHCO_3$, various metal oxides, and acidic resins are commonly used. For this reaction, both acidic and basic sites can be used, depending on the desired product.[90–94]

As for the catalytic supports, they present essential features. Among the main points are the textural, acid, and polarity characteristics. Porous materials with high surface areas furnish a high acid strength and ease the access of the glycerol molecules, while the polarity would be associated with the adsorption strength of glycerol.[90–94]

González and co-workers used a bottom-up method to develop mesopores in a Beta zeolite (H-Beta) using organosilane as a template and a post-modification with fluorine (H-Beta-F).[95] In addition, the authors prepared a non-hierarchical Beta zeolite (Si/Al=27) without the crystallization step and without the addition of organosilane (Beta zeolite). The materials were applied in the etherification reaction of glycerol with *tert*-butanol and isobutene, as shown in Figure 9 and 10, respectively. The characterizations showed that the structures of fluorinated hierarchical zeolites (H-Beta-F) were not damaged. However, a decrease in microporous and an increase in mesoporous volumes were observed. NH_3-TPD measurements revealed only a slight reduction in the acidic sites of these materials when compared to the microporous Beta zeolite and Py-FTIR characterization showed an increase of the Brønsted acidic sites. The catalytic evaluation with *tert*-butanol revealed that glycerol conversion over the hierarchical Beta zeolite (77%) and its fluorinated version (65%) was markedly higher than the non-hierarchical material (27%) and non-hierarchical without fluorine treatment (62%). Besides the reaction with *tert*-butanol, the catalysts also were evaluated in the reaction of glycerol with isobutene. In this case, the same trend was observed, in which a glycerol conversion over the hierarchical Beta zeolite (97%) and its fluorinated version (96%) was markedly higher than the non-hierarchical material (50%) and non-hierarchical without fluorine treatment material (48%). In addition, the authors observed a higher selectivity to bulkier glycerol triether for the hierarchical materials (8%) as a consequence of the generated mesopores, allowing a better diffusion of the reactant and access to Brønsted acidic sites.

A top-down approach for the preparation of hierarchical Beta zeolites from a commercial one (Si/Al= 12.5) was described by Saxena and co-workers and applied in the glycerol etherification with *tert*-butanol (Figure 9).[96] A desilication process was performed using NaOH 0.5 mol L^{-1} under reflux conditions. In addition, a nanocrystalline Beta zeolite (Si/Al=12.8) was also synthesized for comparison with the other mentioned materials. Energy-dispersive X-ray analysis (EDX) showed that the desilicated hierarchical sample presented a Si/Al ratio of 6.1 and thus confirming the successful alkaline desilication top-down approach. Despite that high Si removal from the commercial material, its crystalline structure was kept as observed in the XRD characterization. N_2-physisorption measurements displayed the highest mesopore volume and pore diameter for the desilicated sample compared to the nano and bulk ones. The conversion of glycerol reached 98%, and the desilicated zeolite presented the best selectivity to the triether of glycerol (~75%) – bulkier product formed as a consequence of larger mesopores and availability of acidic sites. Furthermore, this hierarchical Beta zeolite was able to keep its activity and selectivity to the trietherification product even after four reaction cycles.

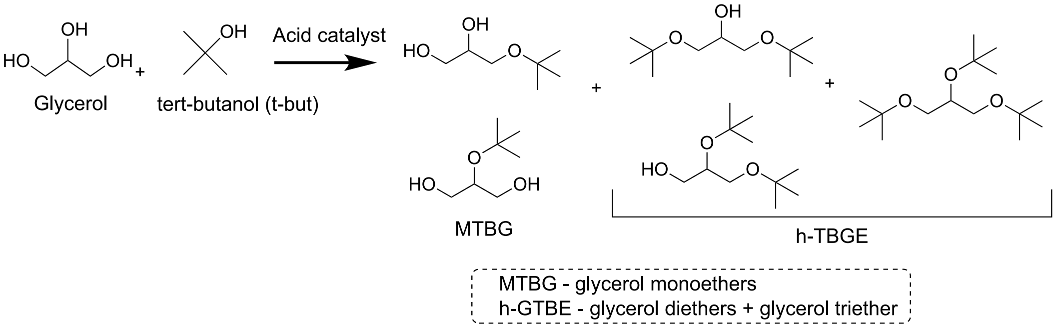

Figure 9. Etherification reaction of glycerol with *tert*-butanol

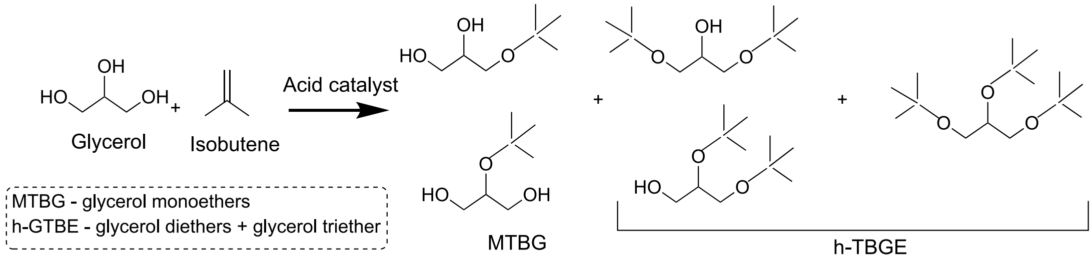

Figure 10. Etherification reaction of glywcerol with isobutene

Simone and co-workers used a bottom-up approach to synthesize hierarchical ZSM-5 zeolites (Si/Al = 50 and 100), and the materials were applied in the glycerol etherification with *tert*-butanol (Figure 9).[97] For that, the authors synthesized a $C_{22}H_{45}$ $-N^{+}(CH_3)_2-$ C_6H_{12} $-N^{+}(CH_3)_2-C_6H_{13}$ structure-directing agent and two ZSM-5 zeolites with different morphologies were prepared (unilamellar and nanosponge materials). N_2-physisorption characterizations demonstrated the formation of mesopores on both materials, in which the unilamellar ZSM-5 presented higher mesopore volume and diameter than ZSM-5 nanosponge. In addition, a bulk ZSM-5 zeolite (non-hierarchical material) was characterized and used to compare with hierarchical zeolites synthesized. NH_3-TPD results revealed that hierarchical materials have lower acidic sites, and the zeolites with lower Si/Al presented higher acidity. In addition, unilamellar ZSM-5 was slightly more acidic than nanosponge. The catalytic evaluation showed markedly higher glycerol conversion for the hierarchical zeolites - unilamellar (79-82%) and nanosponge (78-83%) – compared to bulk ZSM-5 (4-6%). A higher selectivity to tri-*tert*-butylglycerol (TTBG) was also observed for the hierarchical ZMS-5 zeolites (76-81%) compared to the non-hierarchical one (51-61%), and the trietherification product presented a high selectivity in the mesopore-containing materials (10%). In contrast, the bulk ZSM-5 showed only traces of that product. In this sense, the authors assigned this observation to the efficient mesopores creation on both morphologies of ZSM-5 and more accessible acidic sites.

Gonzalez-Arellano and co-workers reported the etherification of glycerol with benzyl alcohol (Figure 11) using hierarchical ZSM-5 zeolites prepared by top-down approach from commercial zeolites with different Si/Al ratios (40 and 15).[98] The commercial zeolite was submitted to a desilication treatment using a 0.8 mol L^{-1} NaOH solution at 65 °C for 30 min, followed by acid washing (HCl 0.1 mol L^{-1}). The hierarchical ZSM-5 zeolite presented a higher surface area than the commercial zeolites. As expected, a higher mesopore volume and acidity (evaluated with NH_3-TPD) were slightly higher than its parent material. The catalytic activity in glycerol etherification with benzyl alcohol had similar conversion values for the samples tested (~70%). However, the mesoporous ZSM-5 favored a higher selectivity for DBG due to the facilitated accessibility of glycerol and products diffusion. In addition, the non-hierarchical ZSM-5 zeolite with Si/Al=15 ratio was quite selective to the MBG product and thus corroborating that mesopore presence is essential to produce bulkier molecules such as DBG.

2.5. Glycerol aromatization reactions

Aromatic compounds such as benzene, toluene, and xylene (BTX) are extensively used in several industry segments, such as fine-chemical, chemical, agriculture, dies. Some of these compounds are also used as a gasoline formulation. Despite the great importance of these compounds, our society still depends on oil for their production through pyrolysis or catalytic reforming reactions. In that way, BTX production from glycerol represents an encouraging pathway to produce these chemicals using renewable sources. A reaction summary is presented in Figure 12.[99]the induction period of GTA process became longer. The GTA reaction route was almost unaffected over HNO3 treated HZSM-5 catalyst. However, the liquid route of GTA procedure was enhanced while the gas route was restrained over steaming dealuminated HZSM-5 catalyst. The mild HNO3 treatment could preferentially remove the non-shape selective acid sites from HZSM-5 extra-framework, promoting BTX aromatics formation. In contrast, dealumination by harsh steaming transformed HZSM-5 framework tetrahedral Al species (FAL

This reaction is usually carried out in a gas or liquid phase, with moderate temperatures (400 °C) and a maximum pressure of 20 atm. It is important to mention that most of the studies use atmospheric pressure. Many groups perform glycerol dilution to decrease its high viscosity, although it is not essential in some cases.[100–103] Several studies focus on using H-ZSM5 zeolites, with or without acid/base treatment, and, in some instances, metal-exchanged materials are employed. Both Lewis and Brønsted acid sites efficiently form these aromatic compounds (Figure 12). However, Brønsted acid sites are essential for the cyclization reactions and subsequent processes. Furthermore, the strength of the acid sites is critical since highly acid materials can cause the formation of heavy aromatic compounds and thus leading to the deactivation of the catalyst.[100–103]

The zeolites used for this reaction offer both Lewis and Brønsted acid sites. However, as they are located inside

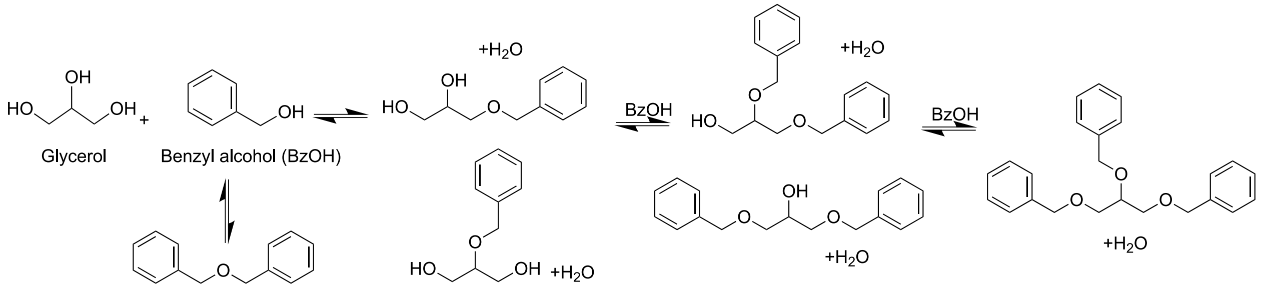

Figure 11. Etherification reaction of glycerol with benzyl alcohol

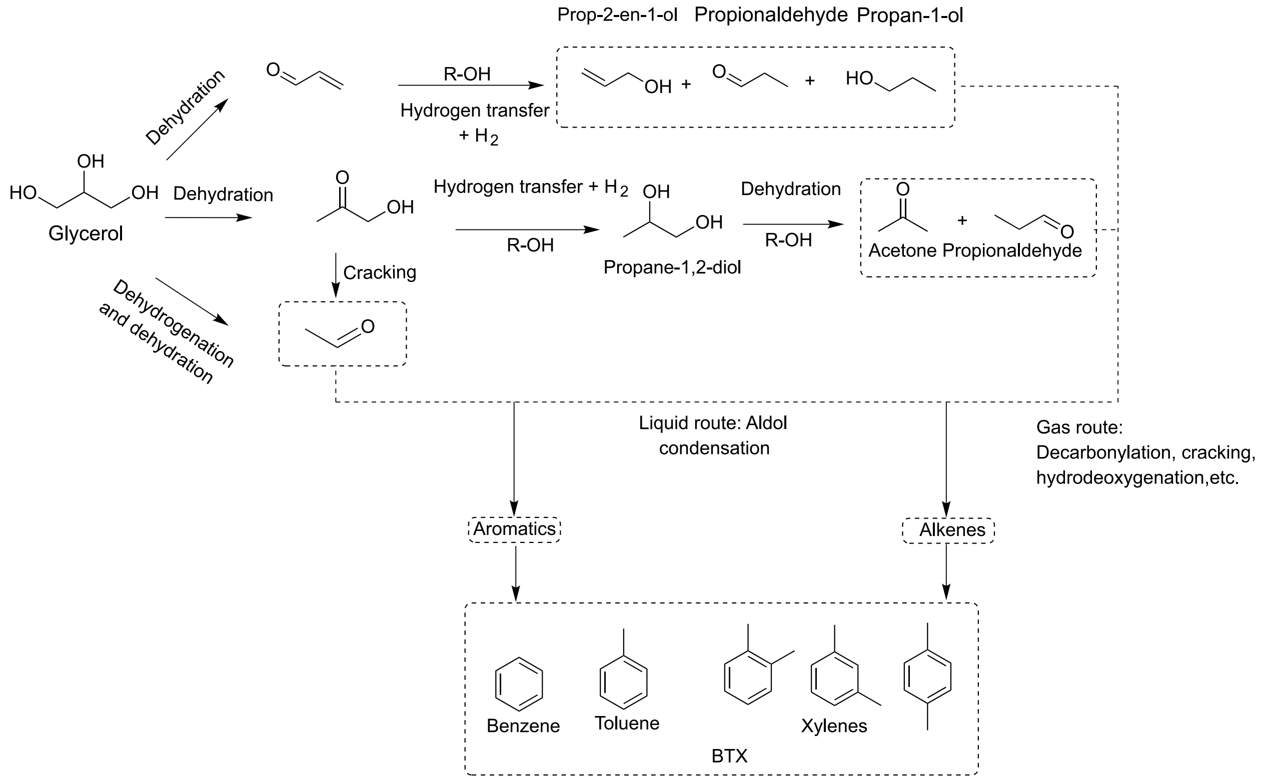

Figure 12. Aromatization of glycerol to BTX compounds

the material's pores which might represent diffusional issues and also the formation of undesirable products, at the same time that the large pores cause the deactivation of the catalyst. In addition, metal loading may be a good factor concerning balancing the availability of acid sites. However, there are still few studies on which metal would be more efficient for this function.[100–103]

Xiao and co-workers employed a commercial ZSM-5 zeolite (Si/Al=25) and a hierarchical material derived from this commercial zeolite as catalysts to convert glycerol (in methanol medium) into aromatic compounds using gas-phase reaction. [104] Using a top-down approach, the commercial zeolite was grouped according to the concentration of the sodium hydroxide solution used to desilicate this material (200 mL of NaOH 0.1; 0.2; 0.3; 0.4; 0.5 or 0.7 mol L^{-1}) at 75 °C for 2 h. The materials were named as AT-nM (where n = 0.1; 0.2; 0.3; 0.4; 0.5 or 0.7). The XRD results show that the crystalline structures of zeolites treated with sodium hydroxide solution up to 0.4 mol L^{-1} were not affected. However, the zeolites treated with the 0.5 and 0.7 mol L^{-1} solutions had a significant degree of amorphization of their structures. Furthermore, through the nitrogen adsorption analyses, the mesopore volume was progressively increased as the NaOH concentration increased; however, a decrease in the total surface area was observed, suggesting an amorphization process. In parallel, higher concentrations of alkaline solution caused an increase in the Lewis acid and a decrease in the Brønsted sites amount. The catalytic evaluation of ZSM-5 zeolites revealed that glycerol conversion over hierarchical zeolites depended on the alkaline treatment. The materials treated at higher NaOH concentrations presented lower conversion and BTX yield. The best BTX yield, of 26%, was observed for the hierarchical ZSM-5 zeolite treated with 0.3 mol L^{-1}, whereas the parent zeolite presented a yield of 18%. In addition, the glycerol conversion for these materials was 40% and 14%, respectively. The reuse reactions revealed that AT-0.3M zeolite presented a low deactivation while the commercial zeolite presented a severe degree of deactivation due to carbon deposition.

Wang and co-workers described the production of BTX from glycerol/methanol solution (Figure 12) employing a ZSM-5 hierarchical zeolite –obtained from basic treatments with NaOH, CH_3ONa, NH_4OH, $NaHCO_3$, tetrapropylammonium hydroxide (TPAOH) or tetramethyl guanidine (TMG), using concentrations of 0.3 and 0.9 mol L^{-1} at 80 °C for 2 h in a commercial ZSM-5 (Si/Al=25). Si/Al measurements by ICP revealed that the lowest ratio was achieved by the ZSM-5 treated with NaOH or sodium methoxide 0.9 mol L^{-1}.[103] All the other materials presented Si/Al ratios close to their parent zeolite. The relative crystallinity values revealed the severity of these mentioned treatments, in which the crystallinity of these samples was close to 55%. Textural characterization also displayed a significant decrease in the specific surface area for both of these samples (ZSM-5 treated with 0.9 mol L^{-1} of sodium hydroxide or sodium methoxide) and the highest mesopore volumes. In addition, macropores formation was also observed, which demonstrates, according to the authors, the collapse of the micropore structure. Analysis of pyridine

FTIR shows that for bases at a concentration of 0.3 mol L^{-1}, the amount of Brønsted acidic sites increased, and the increase in concentration to 0.9 mol L^{-1} led to lower acidity for NaOH and CH_3ONa. The BTX reaction over both the original ZSM-5 and hierarchical zeolites showed glycerol conversions of approximately 99%, and the selectivities of the products were divided into gaseous fragments, aromatic compounds, water, and oxygenated liquid compounds. The highest aromatics production (~40%) was observed by the hierarchical zeolites treated with sodium hydroxide and sodium methoxide 0.3 mol L^{-1}. Furthermore, the zeolite with larger mesopores led to a significant coke deposition and consequently to the deactivation of the catalysts.

Later, Wang and co-workers employed a hierarchical ZSM-5 zeolite prepared *via* top-down method starting from a commercial ZSM-5 (Si/Al=25).[99] The material was submitted to the dealumination process using nitric acid 6 mol L^{-1} at 80 °C for 8 h. Another two samples were prepared by steaming the commercial zeolite for 3 h at 500 °C, and a portion of the hierarchical sample also underwent the same procedure. Textural characterization showed that acid-treated zeolite presented a slight increase in the total specific surface area and a modest increase in the mesopore pore volume compared to the non-treated zeolite. The steamed samples showed lower surface areas, and the mesopore volume was virtually equal to the hierarchical material.

Furthermore, the acid-treated ZSM-5 zeolite presented a marked decrease in the total acid amount compared to the commercial ZSM-5 material. The steamed samples showed a significant reduction in the total acid amount, almost three times lower than the non-treated ZSM-5. The catalytic evaluation revealed that acid-treated ZSM-5 did not improve the BTX production and presented the exact value of mass fraction displayed by the commercial zeolite (~23%). The authors suggested that HNO_3 treatment selectively removed the non-shape selective sites from the surface of the catalysts, which avoided further alkylation to produce polyalkylbenzenes and then BTX. Moreover, the steamed and acid-treated ZSM-5 presented the best production of BTX (34%) as a consequence of intramesopores created after both post-synthetic treatments.[99]

2.6. Glycerol hydrogenolysis and other reactions

Glycerol hydrogenolysis is a promising pathway to produce mostly 1,2 or 1,3-propanediols (1,2-PDO and 1,3-PDO, respectively). In addition, lower yields of 1-propanol, methanol, ethanol, and others are observed.[105] 1,2-PDO and 1,3-PDO are extensively used in several industry sectors and have their cost increased over the years. Such diols are used in the fine chemical industry, polymers synthesis, plasticizers, transportation fuels, cosmetics, green solvents, antifreeze agents, oxidation to propylene, resins, inks, and propylene terephthalate.[106] This reaction occurs between 70-250 °C and is catalyzed by metals (*eg*.: Ni, Cu, W, and Pt), which can be supported on metal oxides and zeolites. The Brønsted acid sites are used to convert glycerol, and the hydrogen activation occurs in a metallic site.[105,106]

Niu and co-workers studied the glycerol conversion to 1,2-PDO over a Cu-supported (with different Cu loadings) on a hierarchical USY (Ultra stable Y zeolite) prepared by a top-down approach using dealumination through hydrothermal treatment, Figure 13.[107] N_2-physisorption measurements indicated the formation of mesopores in the structure of the hierarchical sample (DUSY) and copper-loaded DUSY (Cu-DUSY). The Cu-based catalysts presented an expected decrease in the specific surface due to Cu particles deposition inside the porous structure. In addition, the mesoporous structure was further confirmed by TEM analyses, in which more rugous and hollows were observed, in contrast with the pure USY zeolite that presented dense grains. The XRD diffractograms of the USY and DUSY confirmed that the dealumination procedure did not influence the typical crystalline structure of the zeolite. NH_3-TPD profiles of the USY and DUSY presented a decrease in the strong acidic sites after the dealumination procedure, whereas the medium acidic sites became more evident after this procedure. The catalytic evaluation displayed that 15 wt.% of Cu loaded on USY zeolite (15CuUSY) presented a lower glycerol conversion and 1,2-PDO selectivity (41 and 69%, respectively). In contrast, the same loading of Cu over the DUSY (15CuDUSY) led to higher conversion and selectivity (79 and 99%, respectively). Furthermore, the secondary products such as 1,3-PDO, glycol, and others were suppressed by the dealumination procedure, which caused a decrease in the amount of strong acidic sites.

Following a similar path, Jin and co-workers studied Ru-supported on dealuminated and desilicated Y zeolite and applied in glycerol conversion to 1,2-PDO (Figure 13).[108] Two different strategies prepared the hierarchical materials: a previously steaming commercial Y zeolite (Si/Al =7) was submitted to (i) acid treatment with HCl in different concentrations (0.5–1.5 mol L^{-1}) at 70 °C for 1 h; and (ii) NaOH treatment with 0.5 mol L^{-1} at 70 °C for 1 h. The crystalline structure of the acid-treated zeolites – observed by the XRD results – presented a decrease in their peaks intensities. The one treated with 0.5 mol L^{-1} of sodium hydroxide displayed severe destruction of its structure (showing a halo in its diffractogram – characteristic

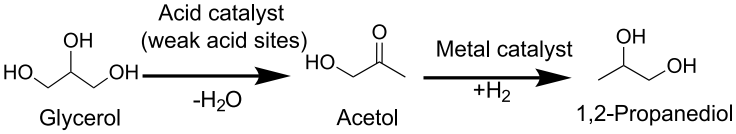

Figure 13. Glycerol conversion to 1,2-propanediol

of amorphous material). The specific surface areas of these acid-treated zeolites suffered a marked increase (along with pore diameter) as the HCl concentration increased. On the other hand, the NaOH treated material had a severe decrease in its specific surface areas due to amorphous materials formation. Moreover, the Si/Al ratio of the dealuminated zeolites was significantly increased (7.9 to 12.5) as the HCl concentration increased, and for the desilicated one, a marked decrease was observed (3.8). Acidity characterizations using NH_3-TPD showed that weak acidic sites were preserved with the HCl treatment. The amount of strong acidic sites increased due to the interaction of OH from the framework and extra-framework Al. On the other hand, the amount of strong acidic sites decreased with the NaOH treatment, and total acidity was virtually the same as the commercial zeolite. The best glycerol conversion and selectivity to 1,2-PDO (81 and 60%, respectively) was observed by the Ru-Y zeolite treated with 1.0 mol L^{-1} of HCl, whereas the material treated with NaOH presented lower glycerol conversion (6.5%) and higher selectivity to 1,2-PDO (82%).

Li and Wu studied the same reaction over a cobalt-doped micro-mesoporous SAPO-11 zeolite (MSAPO-11).[109] The bottom-up method was used, in which di-n-propylamine and N,N-dimethyl-N-octadecyl-N-(3-triethoxysilylpropyl) ammonium bromide were used, respectively, to generate micro and mesoporous structures in the SAPO-11 zeolite. The MSAPO-11 zeolite presented the same crystalline structure as the SAPO-11 one and without any detectable crystallinity decrease. In addition, the comparison of textural properties of these two zeolites showed that MSAPO-11 had a considerably higher specific surface area and mesopore volume, and their acidity also displayed the same trend. The catalytic evaluation of the Co-doped MSAPO-11 (5 wt.% of Co) revealed that mesoporous structure was beneficial to convert a reaction intermediary (acetol, Figure 13) in 1,2-PDO and thus presenting a higher glycerol conversion (94%) and 1,2-PDO selectivity (91%) compared to the other catalysts prepared from non-hierarchical SAPO-11 or with higher Co amount.

The use of zeolites with tuned acidic sites shows a lot of promise for aqueous-phase hydrogenolysis (APH) of glycerol and catalytic transfer of hydrogen (CTH). The use of IrOx/HZSM-5 presented 75% yield towards 1,3-PDO, with TOF of 4.5 h^{-1}, with good stability for reuse.[110] A recent study further explores the well-known effect of Re as a promoter of Ir catalysts, revealing Re/Ir ratios should be optimized for impregnation on HZSM-5.[111] Varying hydrogenolysis approaches have also been proposed for APH. For instance, two catalysts were combined with working in tandem in a fixed bed reactor with two sequential sections. Glycerol flowed first through a H-Beta layer and then through a Ni/Al_2O_3 layer, producing 69% selectivity of 1-propanol at 100% conversion.[105] CTH of glycerol using isopropanol as the hydrogen donor and solvent has been performed on Pd, Pt and Ru supported on hydrothermally-synthesized mordenite to obtain the hydroxylated ether 2-isopropoxy-propan-1-ol, in the absence of externally fed H_2.[112]

The reactions above show that glycerol is a versatile compound in several upgrading reactions. In this way, it can also synthesize essential organic compounds such as quinoline and quinoline derivatives – heteroaromatic compounds. These compounds are necessary starting materials in the pharmaceutical industry and act as corrosion inhibitors, fungicides, and antimalarial drugs. However, their production in the liquid phase is cumbersome due to the need for toxic organic solvents and expensive and toxic feedstocks. In that way, the reaction of glycerol with aniline – producing quinoline and quinoline derivatives – is a promising pathway to be performed *via* gas-phase (called as Skraup route), as shown in Figure 14.[113]

In this sense, Li and co-workers reported a green route for the aromatic quinolone synthesis using hierarchical zeolites-supported catalysts.[113] As precursors, glycerol and aniline were employed in a gas-phase reaction. Since Beta

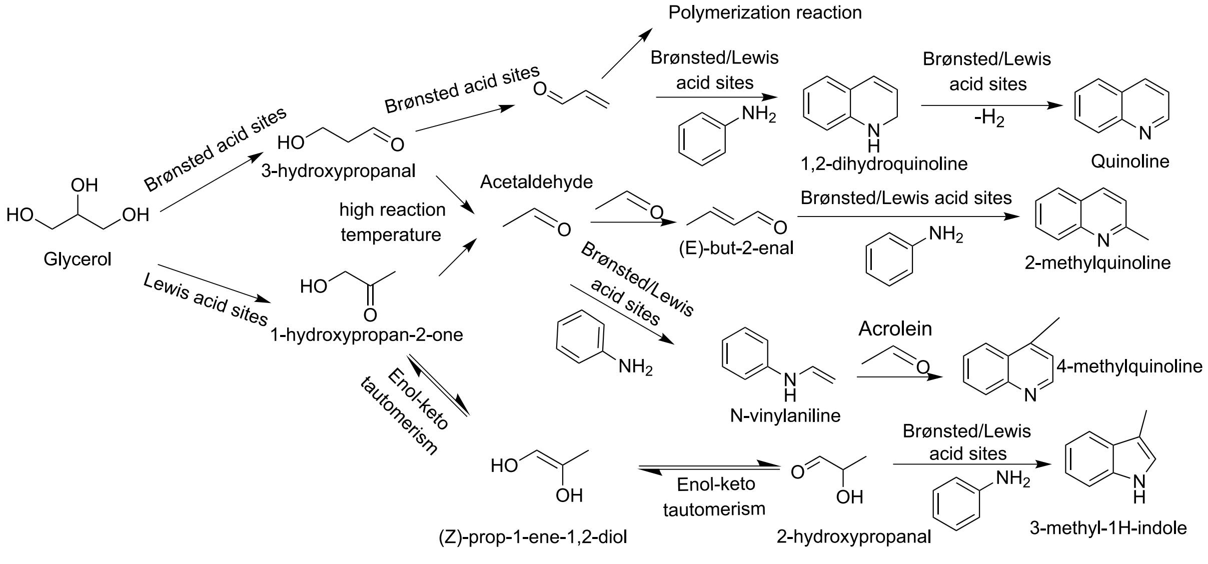

Figure 14. Synthesis of quinoline and quinoline derivatives from glycerol and aniline

zeolites are considered high-efficient catalysts for glycerol conversion to acrolein, the authors used hierarchical Beta zeolite as support for Ni species and clusters. The commercial zeolites were submitted to a top-down treatment with NaOH (0.2 mol L^{-1}) at 65 ^{o}C for 30 min to promote the desilication of the material. The commercial zeolite and hierarchical Beta zeolite were also submitted to ion exchange with several metals: Ni, Mn, La, Cu, Zn, and Fe. XRD measurements revealed that alkali treatment caused a slight decrease in the diffraction peaks assigned to the Beta structure, and Ni-Beta zeolites (commercial or hierarchical) did not show any NiO diffraction peaks. It is essential to mention that most of the characterizations presented in their study were related to the Ni-modified Beta zeolites due to the higher activity in the quinoline synthesis. N_2-physisorption showed a decrease in the specific surface area of the hierarchical materials (pure and Ni-modified) compared to the commercial one, and the mesopore volume and diameter were significantly higher. Acidity assessment through NH_3-TPD revealed that hierarchical Beta zeolite presented virtually the same acid amount of the commercial sample and Ni-modified one was markedly more acid. The authors assigned, by Py-FTIR analysis, to new Brønsted acidic sites created by the metal presence. The catalytic evaluation displayed that all the zeolites presented high conversion of aniline (>93%); however, the highest quinoline yield was observed for the Ni-modified hierarchical Beta zeolite (71.3%). The mesoporous structure of the hierarchical zeolites influenced the transport of bulky products from to the external surface of the catalyst, restraining the deposition of coke and generating a stable catalyst, which shows promising results even after three reaction-regeneration cycles.

2.7. A brief discussion on mesopore influence over glycerol conversion and zeolite deactivation

As previous sections show, mesopore generation in zeolites can significantly improve these catalysts' performance and offer stability against deactivation processes. The data clearly shows that these mesopore creation methods impact the reaction conversion, yields, and selectivities, mainly because they facilitated the diffusion processes and tuned some properties of those zeolites, such as the total acid amount and the type of acidic sites.[30,48,57,86,104] Table 3 shows the hierarchical zeolites type and its conversion values.

However, there is a limitation for these treatments: the damage they may cause to the structure – especially for those involving top-down approaches. Regarding this issue, especially in alkaline treatment, high concentrations of the alkaline solution may damage the surface. Another exciting topic about these methods is the effect on these zeolites' acidity and hydrophobicity. Employing top-down approaches (dealumination or desilication), it is possible to tune the Brønsted and Lewis acidity of these materials, which is vital to enhance the selectivity for some products. However, they often reduce the total acidity of the material. Mainly, the desilication process is applied to promote an increase in Lewis acidity, which in many cases can provide a synergic effect for the desired reaction (e. g. dehydration and aromatization of glycerol). Besides, these processes may interfere with the hydrophobicity of zeolite. The removal of silicon from the structure enhances the hydrophobicity of the zeolite and upgrades the catalysts' performances, avoiding the formation of byproducts in the reaction.[40,104]

Since one of the goals of heterogeneous catalysis is to recover and reuse the catalysts, it is crucial to understand the deactivation processes and their impact on the glycerol transformations.[34,46] For zeolites, some chemical, textural and structural properties may interfere in deactivation and how fast this process can occur. Changes in crystalline structure,[114] sintering process,[115] poisoning, selective adsorption,[18] coke formation[116] are some examples of pathways to deactivation in zeolites.

In glycerol upgrading reactions, some studies reported the deactivation of these materials. Possato and co-workers

Table 3. Hierarchical zeolites type and its conversions values

Hierarchical Zeolite Type	Glycerol Reaction	Conversion (%)	Ref.
SAPO-40	dehydration	99	52
ZSM-5	dehydration-hydrogenation	53	41
ZSM-5	ketalization	80	86
H-MOR	ketalization	80	86
H-BEA	ketalization	80	86
Y	ketalization	99	35
MCM-22	ketalization	83	40
H-BEA	acetalization	78	87
H-MOR	acetylation	89	27
ZSM-5	acetylation	80	57
H-BEA	etherification	97	95
ZSM-5	etherification	83	97

reported microporous and mesoporous ZSM-5 zeolites' deactivation in glycerol conversion to acrolein through coke formation. After 8 h of reaction, micropore volume reaches zero, and the structural parameters change due to coke formation on the surface.[48] In addition, Rodrigues and co-workers disclosed an MCM-22 zeolite deactivation for glycerol conversion to solketal. In this case, water formation as a byproduct can interact with active Lewis acidic sites, thus decreasing the conversion.[40] These two pathways of deactivation (coke formation and poisoning) are the most reported for those reactions and the focus of this review.

Coke is a carbonaceous compound formed on the catalyst surface or inside the pores of the grains and is not desired reaction product. According to Menon and co-workers, catalytic reactions with coke formation can be classified as sensitive to coke (catalytic cracking and hydrogenolysis) or insensitive to coke (Fischer-Tropsch synthesis, catalytic reforming, and methanol synthesis).[117] In coke-sensitive reactions, inactive coke is deposited over the active sites, decreasing the catalytic activity. In the second category, the precursor molecules of coke might be reactive. Menon's classification considers that coke's structure and location affect catalytic activity, and the coke formation mechanisms vary with the type of catalyst.[34,116]

In the case of supported metal catalysts, for example, coke can strongly be chemisorbed or physisorbed, blocking the access to surface active sites - surrounding the metallic particle and deactivating it. Moreover, it also can be occluding micro and mesopores, blocking the entry of reactants inside these pores.[118] Considering the coke formation mechanisms, different coke categories are formed, which vary depending on reactivity and morphology (Figure 15). In this sense, coke can be created in the gas phase and on both catalytic and non-catalytic surfaces. The loss of chemical activity is related to the strong adsorption of coke molecules with acidic sites. In addition, strong acidic sites generate coke precursors, which coat the catalytic surfaces when condensing.[34,119] Besides being adsorbed over acidic sites, the coke molecules present in pore channels can increase the resistance to mass transfer in the catalyst. Besides, they can decrease the reactant concentration in the liquid phase and reduce the reaction rate.[120]

Deactivation occurs faster in those zeolites containing small pores or unidimensional structures. Like porous catalysts, deactivation in zeolites can happen in two ways: local or active site coverage *via* coke adsorption and pore blocking. Zeolites have pores whose sizes are close to those of organic molecules. Therefore, deactivation will likely be by blocking. The bulky aromatic compounds formed in microporous zeolites cannot exit and obstruct the entrance of the pores, condensing efficiently. Thus, cokes are included, and the zeolite is quickly deactivated. In the case of mesoporous zeolites, coke production is hampered in the case of bulky molecules. It is noteworthy that the deactivation by a coke can also be bidirectional, that is, by blocking the pores and covering the active sites.[120,121] Bulky aromatic compounds formed in microporous zeolites are unable to leave, so they obstruct the entrance of the pores, condensing easily.[34,122]

Some studies show that the pore structure, the type of acidity, and its strength can strongly influence factors such as diffusion, conversion, selectivity, and coke

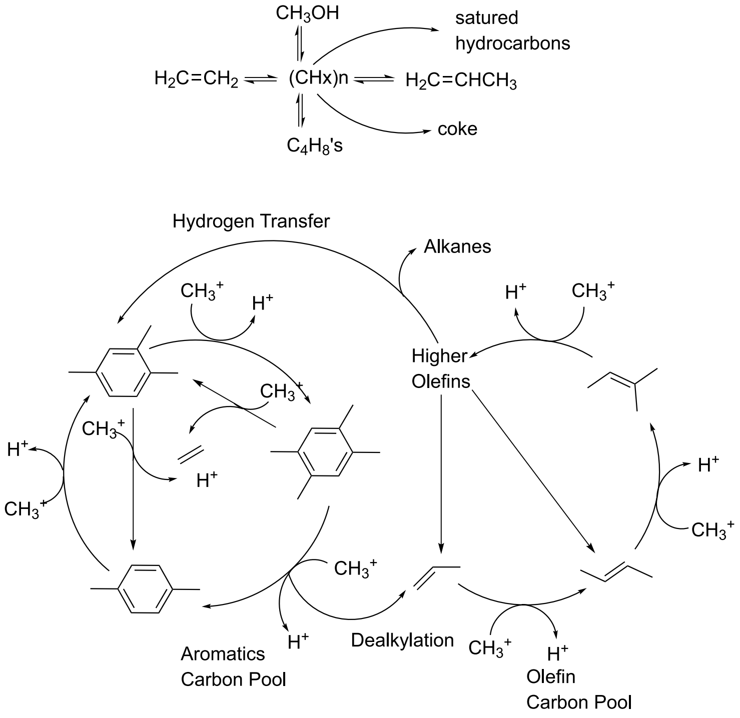

Figure 15. Some illustrative reactions pathways for coke formation over zeolites.[120]

formation.[39,52,123,124] Possato and co-workers described the catalytic properties of monomodal microporous and bimodal hierarchical zeolites in gas-phase glycerol dehydration reactions. The desilication method allowed mesoporous zeolites with fewer diffusion limitations and higher glycerol conversion due to the hierarchical system of secondary pores. The influence of reaction time on the catalytic behavior of the studied zeolites was also analyzed, and thus it was confirmed that the decrease in selectivity with time is due to coke formation. However, the selectivity of acrolein increases during the dehydration reaction because this product formation requires strong acidic Brønsted sites. In contrast, the other products obtained are formed in Lewis sites that were selectively deactivated by coke deposition.[46] This deposition occurs through the blockage of the pores and thus obstructs the access of glycerol molecules. For hierarchical zeolites, coke is not deposited in narrow micropores, but it is found in intracrystalline pockets.[46,48]

Zhang and co-workers developed four ZSM-5 hierarchical zeolites with different mesopores architectures, using an approach known as the "salt-aided seed-induced route".[56] A comparative analysis of the hierarchical samples was carried out to verify the coke tolerance. It was possible to confirm that the existence of mesopores was beneficial for its tolerance, more specifically, the open mesopores. The initial coking rates were measured for a better understanding of the influence of mesopores on this tolerance.

Similar results were described by Lari and co-workers with silver nanoparticles supported on ZSM-5 hierarchical zeolites as a bifunctional catalyst for the continuous dehydration-hydrogenation reaction of glycerol to allyl alcohol in the gas phase. Through thermogravimetric analysis, the formation of two byproducts, acetol, and coke, was observed. Zeolite samples with lower Lewis acidity provided a higher generation of acetol. However, if the zeolite had more Brønsted acidic sites, the coke condensation reactions were favored. Another important aspect, which can be confirmed by the presence of 1.8 wt.% of coke in the catalyst after the reaction, is that the hydrogenation of the catalyst increases stability and resistance to coke formation, as there is a reduction in coke precursor molecules produced by dehydration.[41]

Shan and co-workers synthesized a hierarchical nanosheet of ZSM-5 zeolites (NMZ) with different Si/Al ratios. TGA and differential thermal analysis (DTA) of NMZ zeolite showed coke oxidation processes, and two exothermic peaks at 360 and 510 °C referred to the removal of different types of carbon deposits. Hydrogen-rich carbonaceous residues originated at the most intense peak at 360 °C. Coke becomes more deficient in hydrogen because of hydrogen transfer reactions with a longer reaction time. In the DTA curve of the commercial ZSM-5 zeolite, the same signal intensity was observed at temperatures above 360 °C. The results indicated a higher amount of hydrogen-rich cokes, which may also be responsible for the quick deactivation being located in the micropores. The easier diffusion in the NMZ material suppressed collateral reactions of the products that form coke precursors and decreased its formation rate. In the commercial and non-hierarchical sample, it was found that coke formed blocked the zeolite channels, covering the acidic sites and deactivating them. The commercial zeolite presented only 16.0% of the original micropore surface area, as observed by N_2 physisorption measurements.[125]

There are two main research approaches in kinetic studies of catalyst deactivation processes: one uses the coke content on the catalyst content as an essential parameter, and the other uses reaction time. The kinetic deactivation model considering the coverage of active sites with no diffusion is based on surface homogeneity and heterogeneity. These models help us determine the catalyst's operating time before replacement or regeneration. In the case of zeolites, they indicate that the strength of active sites interferes with the primary reaction and the deactivation process. The development of a mathematical model for coke deactivation in zeolites, however, is complex due to the lack of models that adequately describe: (i) reactional and diffusional phenomena in zeolites; (ii) change in diffusivity related to zeolite pores size and the kinetic diameter of molecules; (iii) the morphological changes originated after deactivation; (iv) the nature and location of the sites where coke is formed.[126,127]

In summary, coke formation is mainly influenced by the strength of acidic sites and pore structure. Hierarchical zeolites with a high mesopore volume allow higher reactant access to the Brønsted acidic sites, limiting coke deposition, facilitating glycerol transport, and increasing coke tolerance capacity. Consequently, the catalyst will be more stable and have better catalytic activity, selectivity, and conversion.

Several molecules, impurities, and byproducts can interfere in the catalyst performance regarding poisoning since these molecules can interact with the catalyst's active sites, blocking the access site of the reactant molecules. In this sense, zeolites have acidic sites that can interact with less acidic molecules, such as water, methanol, and many other impurities in the reaction medium.[28,45,121,128–131]

In this context, in acetalization of glycerol, for example, Talebian-Kiakalaieh and co-workers reported Y hierarchical zeolites for crude glycerol conversion. In this case, the presence of methanol (1-10 wt.%), water, and NaCl (10-15 wt.%) reduced the solketal yield from 97.7 to 86.8%.[35] Kowalska-Kús and co-workers studied hierarchical ZSM-5, and non-hierarchical Beta and Y for crude glycerol acetalization. The authors reported that hierarchical ZSM-5 and non-hierarchical Beta zeolites, despite larger micro or presence of mesopores, suffered a partial deactivation of the strong acidic sites due to glycerol impurities. This change in acidity parameters affects the selectivity of solketal, enhancing the production of other undesired isomers.[123]

In many cases of glycerol conversion, the chemisorption of water has a crucial role in deactivation.[28] Rodrigues and co-workers evaluated the effect of the hydrophobicity of the hierarchical zeolite MCM-22 in glycerol condensation with acetone. The results displayed those zeolites with more hydrophobic character presented a lower decrease in the solketal selectivity. The interaction of zeolite with water is closely related to Si/Al ratio, since as this value increases, the zeolite become more hydrophobic, which make it easier to avoid the chemisorption of water (which occurs mainly in strong Brønsted sites).[40]

3. Conclusions

Considering the advantages of producing hierarchical systems into the zeolites, affirming that these treatments can improve catalytic performance and extend the catalyst lifetime is safe. Besides, it becomes clear that each reaction needs special attention in synthesizing these materials, aiming to obtain a suitable set of physical-chemical properties to favor the compound of interest.

In most cases, the generation of mesopores in zeolites – using either bottom-up or top-down approaches – enabled increases in glycerol conversion and selectivity of the desired product. This is assigned to the higher accessibility of glycerol molecules to acidic sites. Furthermore, regarding the deactivation process, we have highlighted that the pore structure and the strength of Lewis and Brønsted acidic sites can strongly influence coke deposition. The generation of mesopores (especially by top-down methods) affects the availability of these acidic sites. Thus, it is beneficial for increasing coke tolerance and catalyst lifetime. Likewise, these processes (especially desilication) led to changes in hydrophobicity, which is a vital parameter for deactivation by water poisoning. As shown, water molecules play a critical role in this phenomenon, and alterations in Si/Al ratio may interfere in the interaction of zeolites with those molecules. However, the modeling of deactivation processes still needs further investigation. Finding the balance between generating hierarchical zeolites without damage to their surface is also an essential point to concern. Regarding coke formation, there is still a need to evaluate how some well-known regeneration processes of zeolites can help in glycerol upgrading reactions. Even though mesopore creation can reduce coke formation, recovery methods may help understand how to make the catalyst performance even better.

The relevance of zeolites for industrial chemical processes plus the urgency to find new alternatives for glycerol utilization turned the reviewed investigations into significant advancements towards biofuel and green chemistry science. The hierarchical zeolites rise as promising catalysts for several chemical conversions of glycerol, proving its efficiency and versatility. Still, some aspects and phenomena need a better investigation, especially towards the deactivation of these catalysts, to maximize the production of desired compounds using a sustainable pathway.

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Author Contributions

The authors confirm contribution to this review paper as follows: Conceptualization: Vinicius G. Madriaga, Vinicius Rossa, Luanne E. Monteiro, Thiago M. Lima. Investigation: Vinicius G. Madriaga, Vinicius Rossa, Luanne E. Monteiro, Gabriela S. Abreu, João P. R. Mattos. Data Curation: Rodrigo C. Silva, Vinicius G. Madriaga, Vinicius Rossa, Gabriela S. Abreu. Writing – Original Draft Preparation: Vinicius G. Madriaga, Vinicius Rossa, Luanne E. Monteiro, João P. R. Mattos, Gabriela S. Abreu, Sancler C. Vasconcelos. Vizualization: Thiago M. Lima, Vinicius G. Madriaga, Luanne E. Monteiro, Vinicius Rossa, Sancler C. Vasconcelos. Writing – Review & Editing: Thiago M. Lima, Fabio Passos, Sancler C. Vasconcelos, Vinicius G. Madriaga e Vinicius Rossa. Supervision: Thiago M. Lima and Fabio B. Passos. Funding acquisition and Project administration: Thiago M. Lima and Fabio B. Passos.

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