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Catalytic Dehydration of Glycerine to Acrolein

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Abstract

The biodiesel production yields glycerine as a by-product in quantities around 10 vol% of produced biodiesel. Acrolein can be obtained from glycerine by a dehydration reaction. Catalytic processes in gas phase have been developed to obtain acrolein from a renewable feedstock using heterogeneous catalysts. The main process variables are the reaction temperature, the concentration of glycerol in water, and the space velocity in fixed-bed reactors. A thermodynamic study of the equilibrium has been made to estimate the conversion to equilibrium as a function of temperature. The reactors have been heated usually between 523 and 603 K. Generally, an aqueous glycerol solution is preheated in a preheating zone at a temperature enough to vaporize the feedstock, between 473 and 533 K, depending on the concentration of reactant required in the feed. Some of the most active catalysts in the gas-phase reaction (yield >70%) were $\text{NH}_4\text{-La-}\beta$ zeolite, Pd/LaY zeolite, hierarchical ZSM-5, WO_3/ZrO_2 , WO_3/TiO_2 , $\text{ZrO}_x\text{-NbO}_x$, $\text{WO}_x\text{-NbO}_x$, $\text{WO}_3\text{-SiO}_2/\text{ZrO}_2$, $\text{NbO}_x\text{-WO}_x/\text{Al}_2\text{O}_3$, $\text{H}_3\text{PO}_4\text{-MCM-41}$, SAPO-40, NbPSi, Pd- $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Zr-MCM-41}$, $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Cs-SBA-15}$, $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Nb}_2\text{O}_5$, Cs-doped $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{Al}_2\text{O}_3$, $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2$, and $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$.

Keywords: glycerine dehydration, acrolein, renewable production, acid catalyst

1. Introduction

During the last decades, the growing demand of energy and the depletion of fossil resources have resulted in the research and development of sustainable technologies for the production of valuable chemical compounds and fuels, and biomass conversion through catalytic processes is a potential alternative. One of the most viable choices for the partial replacement of petroleum diesel is the use of biodiesel as fuel in internal combustion engines. The biodiesel production yields glycerine (glycerol or 1,2,3-propanetriol) as by-product in quantities around 10% of the volume of produced biodiesel, and, as a result of the development of biodiesel industry, the global production of glycerine has increased while its market price has consequently declined [1].

From this perspective, intensive research has been carried out in recent years to develop biotechnological and catalytic processes that allow the change of the current status of glycerine as a by-product into a raw material for the production of compounds of industrial and technological interests [1, 2]. The catalytic dehydration of glycerine has become important because it may yield acrolein (2-propenal)

as the main reaction product and represents a route for its renewable production, in contrast with the current process based on the partial oxidation of propylene derived from the petrochemical industry [3].

Acrolein is the simplest unsaturated aldehyde and exhibits high reactivity due to the presence of a C=C double bond conjugated with the carbonyl group. The acrolein has been used as herbicide in irrigation systems and as antimicrobial in liquid fuels, process lines, and in water recirculation systems and is a crucial intermediary in the industrial production of a wide range of compounds such as methionine, acrylic acid, acrylic acid esters, polymers, propanol, propionaldehyde, allyl alcohol, 1,3-propanediol, acrolein acetals, alkoxy-propionaldehydes, and pyridine bases [4].

The glycerol dehydration is mainly carried out in gaseous phase in the presence of an acid catalyst such as protonated or metal-promoted zeolites, mixed metallic oxides, functionalized oxides, or supported heteropolyacids [5], at atmospheric pressure and reaction temperatures between 453 and 773 K [6]. Depending on the reaction conditions and the physicochemical properties of the catalyst, acetol (1-hydroxy-2-propanone) and acetaldehyde (ethanal) may be produced by parallel dehydration routes, while small amounts of aldehydes, carboxylic acids, and/or alcohols in the range of C₁–C₃ are results of subsequent reactions of the dehydration products [7].

This chapter highlights the advances in the gas-phase catalytic dehydration of glycerine to acrolein.

2. Thermodynamics of the glycerol dehydration

The thermodynamic analysis of a chemical system provides valuable information for the design of chemical reactors such as the heat released or absorbed by the reaction, the behavior of simultaneous and consecutive reactions regarding the temperature, and the equilibrium concentration of each compound involved in the system at a determined temperature. In this sense, the glycerol dehydration reaction proceeds through three parallel routes as shown in **Figure 1**, from which acetol and acrolein are the main products (reactions 1 and 2), while acetaldehyde and formaldehyde may be produced in minor proportions (reaction 3) [7, 8].

The reaction enthalpies (ΔH_r°) of the three parallel routes at the gas phase evidence that the production of acetol (reaction 1) is an exothermic process releasing 34 kJ·mol⁻¹ at 298.15 K, while the system becomes endothermic to obtain acrolein (reaction 2) and acetaldehyde (reaction 3), requiring 28.8 and 56.8 kJ·mol⁻¹, respectively (**Table 1**). The theoretical values of the equilibrium constants (K_p) indicate

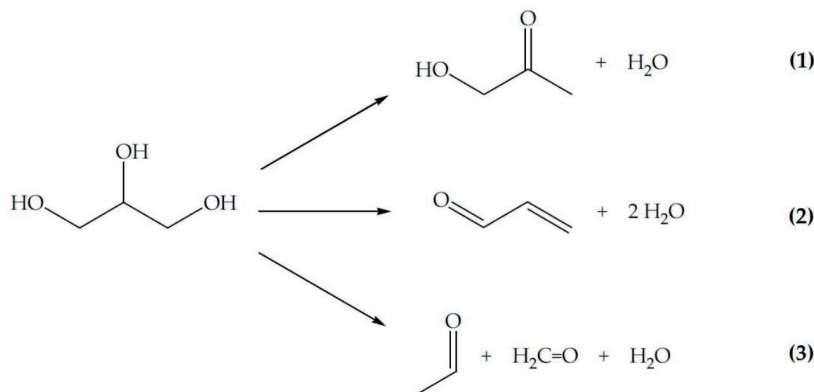


Figure 1.
Parallel reactions involved in the glycerol dehydration.

that the three reactions are thermodynamically feasible from 300 to 900 K [7]. From experimental results, Talebian et al. [9] performed calculations of equilibrium constants for the conversion of glycerol to acrolein (reaction 2) between 553 and 613 K. The trend of the equilibrium constants (from 7.6 to 7.95) is in agreement with the direction of the theoretical estimations; however, the values are smaller than the theoretical ones. The difference may be attributed to the fact that the authors considered the effect of water as solvent besides that the experimental system did not reach the chemical equilibrium, resulting in glycerol conversions smaller than the theoretical and concentrations of reactants and products that lead to different values of the thermodynamic equilibrium constant [7].

Presented in **Figure 2**, the equilibrium molar fractions (y_i) of each compound indicate that production of acetol prevails at mild temperatures, mainly from 300 to 480 K, attaining $y_{\text{acetol}} = 0.50\text{--}0.47$ as its highest concentration between 300 and 400 K, while its molar fraction decreases approximately 97% from 400 to 600 K.

Contrary, the acrolein concentration increases along the reaction temperature range reaching its maximum and staying around at $y_{\text{acrolein}} = 0.31$ between 600 and 800 K. For reaction 3, below 500 K, the degree of advancement estimated is neglectable, increasing and remaining between 500 and 800 K, which results in low molar fractions of formaldehyde and acetaldehyde, reaching a maximum value of $y_i = 0.034$ for each product at 900 K.

Reaction	ΔH_r° (kJ·mol ⁻¹)	$\ln(K_p)$							
		298 K	300 K	400 K	500 K	600 K	700 K	800 K	900 K
1	−33.99	29.39	29.30	25.91	23.85	22.43	21.36	20.53	19.86
2	28.84	19.11	19.18	22.15	23.96	25.09	25.82	26.28	26.57
3	56.77	6.93	7.07	12.77	16.11	18.24	19.68	20.71	21.48

Table 1.
Standard enthalpies and equilibrium constants of glycerol dehydration reactions.

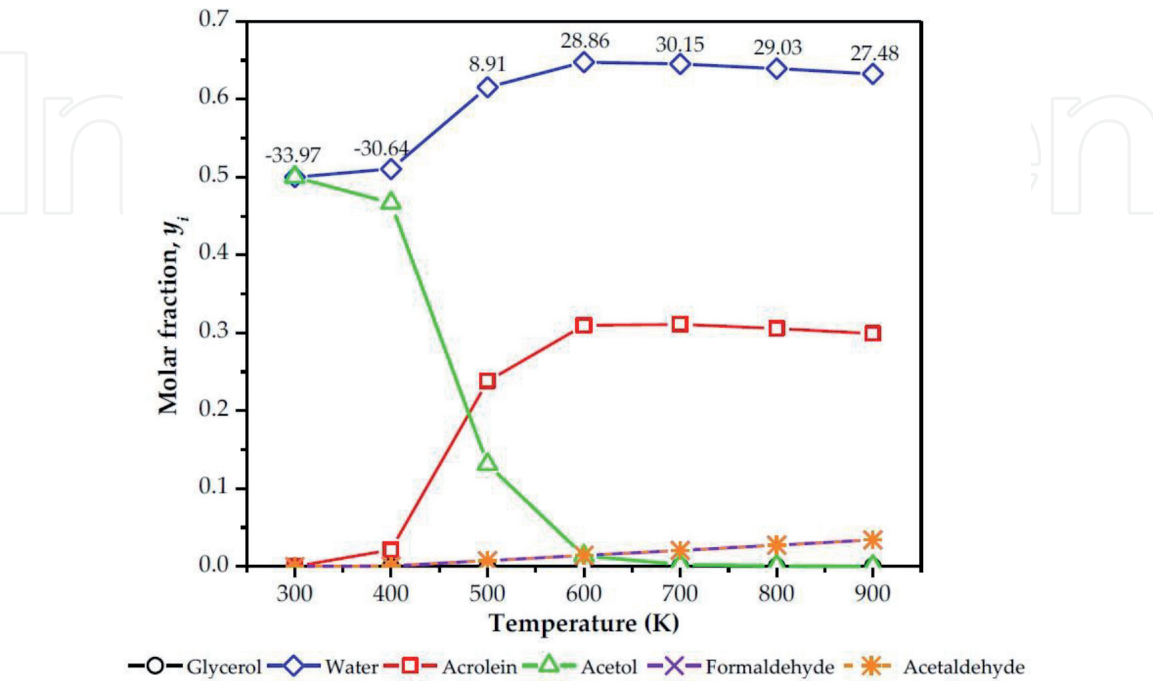


Figure 2.
Equilibrium molar fractions of products as function of temperature of glycerol dehydration [7].

On the other hand, as was expected, the molar fraction of water in the whole system shows a higher value than the rest of the compounds all over the temperature range over $y_{\text{water}} = 0.50$ and increases to 0.64 simultaneously with the formation of acrolein. In this reaction two molecules of water are released per molecule of glycerol. The numerical values over the molar fraction curve of water indicate the heat of reaction (in $\text{kJ}\cdot\text{mol}^{-1}$) of the overall system after an enthalpy balance, pondering the degree of advancement of each independent reaction [7].

3. Reactors for the glycerine dehydration in gaseous phase

Performing of the gas-phase catalytic dehydration of glycerine is usually accomplished in continuous fixed-bed and fluidized-bed reactors. These types of reactors are described in the following.

3.1 Fixed-bed reactors

As shown in **Figure 3(a)**, the fixed-bed reactor consists mainly on a steel alloy tube provided with an inner mesh on which the catalyst particles are deposited occupying the internal volume. A distributor tray is placed below the reactor entrance, to offer a uniform feedstock flow, as well as a layer of a nonporous and inert material such as fused ceramic on top of the catalytic bed [10]. For the catalytic dehydration of glycerine, the reactor is heated usually between 523 and 603 K. Moreover, an aqueous glycerol solution is preheated in a preheating zone at a temperature enough to vaporize the feedstock, between 473 and 533 K depending on the concentration of reactant required in the feed, and is carried by a pure inert gas flow, usually nitrogen (N_2), or in mixture with reactive gases like hydrogen (H_2) or oxygen (O_2) to diminish the catalyst deactivation [7, 11, 12].

The gaseous mixture of glycerine, water, and the carrier gas is continuously fed downward the reactor in nearly plug flow at a known molar or volumetric flow, regarding the reactant or the carrier gas, respectively. The output stream from the reactor may consist of a mixture of the carrier gas, water, unconverted glycerine, acrolein, and condensable and noncondensable by-products. The condensable compounds may be separated and purified by distillation, while the noncondensable products may be treated in absorption units [13].

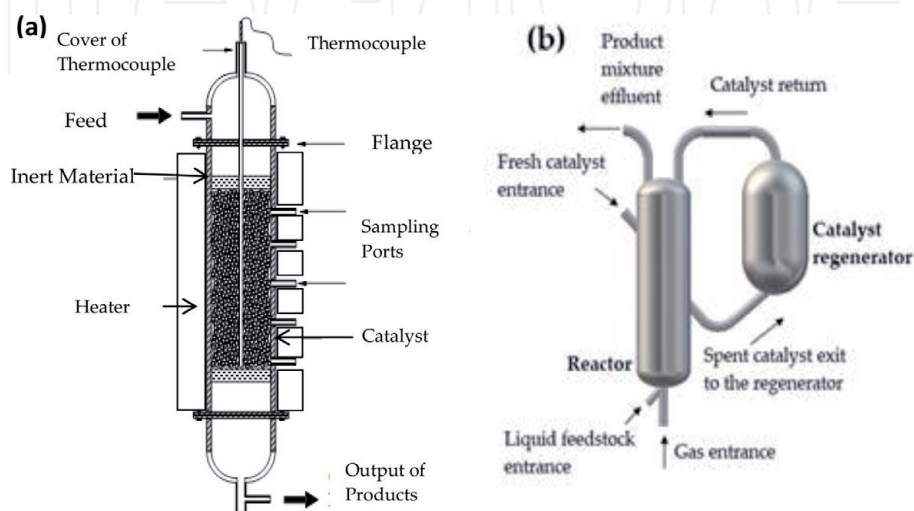


Figure 3. Schematic diagrams of reactors used in the gas-phase catalytic dehydration of glycerol to acrolein: (a) fixed-bed reactor and (b) fluidized-bed reactor.

One of the first processes to convert glycerol into acrolein in gaseous phase using a fixed-bed reactor was patented by Schwenk et al. [14]. The authors reported the use of tubes to contain and heat bulk of supported phosphates through which pure or water-diluted glycerol vapors were passed at temperatures between 573 and 873 K. Glycerine was converted to acrolein with yields between 75 and 80% depending on the reactant concentration in the feedstock. Similarly, the patent of Neher et al. [15] reported the use of α - Al_2O_3 spheres impregnated with phosphoric acid deposited in a 15-mm diameter steel tube to convert vaporized aqueous glycerol solutions to acrolein at 573 K, resulting in acrolein yields between 75 and 65% depending on the glycerol concentration in the feedstock. It is noteworthy that the catalytic activity was maintained after 60 h of operation.

3.2 Fluidized-bed reactors

The fluidized-bed reaction systems consist of two coupled units: the reactor itself and the catalyst regenerator as presented in **Figure 3(b)**. In the reactor, a bed of solid catalyst (with particle sizes between 75 and 130 μm) is initially deposited on a screen. Subsequently, a fluid (a mixture of the feedstock and a carrier gas) is fed at the bottom of the vessel passing through the catalyst at a velocity high enough to suspend and distribute the solid particles along the reactor, causing the catalyst to behave as a fluid. This process is known as fluidization. When the steady state has been reached, the catalyst is continuously fed at the top of the reactor and moved downward against the fluid stream to be removed from the fluidized bed subsequently. Once discharged from the reactor, the spent catalyst is sent directly to the regenerator where the coke is burned off with air at temperatures between 823 and 925 K. The regenerated catalyst is promptly sent back to the reactor providing the necessary heat for performing the reaction. The rate of circulation of the solids is dictated by the heat balance and the catalyst activity [16, 17].

Corma et al. [18] carried out the catalytic dehydration of glycerol in a fluidized-bed reactor in the presence of a ZSM-5-based catalyst, finding that the best operation conditions were 623 K, a catalyst/feed ratio of 11.5, residence time equal to 0.9 s, weigh hourly space velocity (WHSV) of 335 h^{-1} , and a concentration of 20 wt % of glycerol in the aqueous feedstock, reaching 100% of conversion and 62.1% of acrolein yield. The authors also compared the performance of this system against a fixed-bed reactor at the operating conditions. While the glycerol conversions and the product distributions were quite similar, the main difference between both processes was the higher amount of coke deposited on the catalyst used in the fixed-bed reactor (1%) than that deposited during the fluidized-bed operation (0.2%).

In other studies [19], the catalytic dehydration of a 28 wt % aqueous glycerol solution was performed at 553 K using phosphotungstic acid supported on titania ($\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$) as catalyst in a fluidized-bed reactor of 52 mm in height and 8 mm in internal diameter. The authors used a mixture of argon and oxygen to fluidize 1.5 g of catalyst and determined that the minimum velocity of fluidization was $1.4 \text{ cm}\cdot\text{s}^{-1}$; however, the catalytic tests were carried out at a velocity three times higher than this value. Under these conditions, the glycerol conversion was complete, and the acrolein yield reached 48.3%. It was found that as much as 85% of the glycerol was converted to coke in the first hour and less than 20% to acrolein. However, the acrolein selectivity increased and the coke selectivity decreased with time-on-stream (TOS).

3.3 Process variables

There are three process variables reported in the literature to be the most important for the catalytic dehydration of glycerine: the composition of the aqueous

glycerol solution, the reaction temperature, and the space velocity. In the next sections, the effects of these variables on the catalytic dehydration of glycerol are presented.

3.3.1 Composition of the aqueous glycerol solution

Since pure glycerol is highly viscous (1.5 Pa·s at 293 K) and presents a very low vapor pressure (0.05 MPa at 533.6 K) [20, 21], the use of aqueous solutions has been a strategy to overcome these drawbacks allowing the vaporization of glycerol and its use as feedstock in catalytic processes. However, the composition of the glycerine solution affects the performance of the reaction. **Figure 4** presents the results of glycerol conversion and product yields regarding the concentration of glycerol in the feedstock when using phosphotungstic acid supported on niobium pentoxide ($\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Nb}_2\text{O}_5$) as catalyst [22]. The conversion of glycerol declined from 99.8 to 94%, while the acrolein yield decreased from 91.8 to 67.7% with the increment in glycerol concentration from 10 to 40%. Similar results were observed for acetol, while for acetaldehyde there was not a clear trend. It is important to notice the enhancement in the yield of by-products (allyl alcohol, acetic acid, and unknown compounds) with the increase of glycerol in the feedstock, indicating the occurrence of side reactions. The use of other catalysts such as H-ZSM-5, H- β , H-ferrierite, silica-alumina mixtures, and supported heteropolyacids gave similar behaviors of the glycerol conversion and acrolein yield with the increase of glycerol concentration [23–26].

These results suggest that at low glycerol concentrations (large amounts of water), the water molecules may modulate side reactions of glycerol and acrolein such as etherification, oxidation, hydrogenolysis, condensation, and polymerization, thus enhancing the acrolein selectivity [23, 27]. On the contrary, with high glycerol concentrations, the diminishment in conversion and acrolein yield is attributed to the decline of the dehydration activity caused by the decrease of available active sites on the catalyst surface by glycerol condensation, promoting side

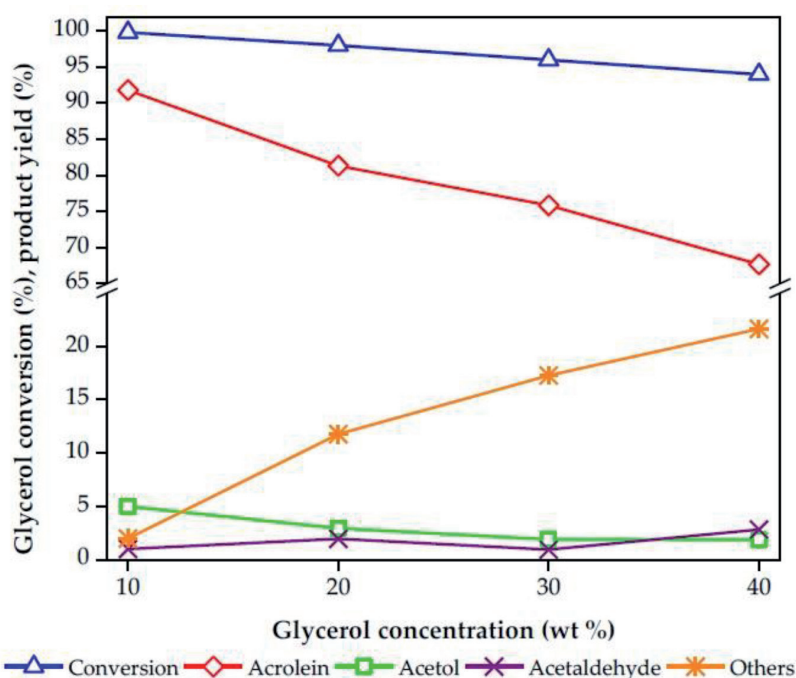


Figure 4. Effect of the glycerol concentration in the feedstock on the glycerol conversion and product yield. Data from [22].

reactions and carbon deposition [27]. Consequently, the catalyst stability with the time-on-stream (TOS) is adversely affected when increasing glycerol content in the feed. **Table 2** summarizes this behavior, considering the effect of the water content (from 15.7 to 91.7 mol %) on the glycerol dehydration over H-ZSM-5 (150) with time-on-stream [23].

3.3.2 Reaction temperature

The reactor temperature determines the products present in the glycerine dehydration reaction mixture, and according to thermodynamics, the acrolein production would be predominant from 480 K reaching its maximum at 600 K [7]. Experimentally, the increase in reaction temperature increases the glycerine conversion and therefore the acrolein yield.

Figure 5 presents the influence of temperature on the glycerol conversion and acrolein yield for the gas-phase reaction over catalysts of 20 wt % of phosphomolybdic acid ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$, HPMo), phosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$, HPW), and silicotungstic acid ($\text{H}_4\text{SiW}_{12}\text{O}_{40}$, HSiW) supported on commercial alumina (Al_2O_3 , A5) in a fixed-bed reactor [28]. Above 548 K, the acrolein yield declined because the decomposition reaction toward acetaldehyde and formaldehyde is favored at high temperatures; however, the temperature at which this reaction begins to be prominent also depends on the acidity of the catalyst employed, varying from 548 to 598 K.

Table 3 shows the effect of reaction temperature, between 553 and 593 K, and TOS on the glycerine dehydration in the presence of MCM-22 (molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$) as catalyst [29]. As previously stated, at initial stages of the process, the glycerol conversion enhances with the temperature increase. However, severe catalyst deactivation with TOS occurs at higher temperatures. An improvement of the acrolein selectivity was also observed with the rise of temperature at initial activities, maintaining the trends along the TOS and resulting in a higher acrolein yield at 593 K even after 10 h. Similar behavior has been reported for the glycerol dehydration performed over several catalysts such as H-ZSM-5 (150), H- β (25) and H-ferrierite (55), La- NH_4 -modified H- β (13) zeolite, and aluminosilicophosphate nanospheres (ASPN-40) [23, 24, 30, 31]. The influence of the reaction temperature on the catalyst deactivation is related to coking of the catalyst as a result of subsequent reactions between acrolein, acetol, acetaldehyde, and glycerol. At low temperature, the compounds involved in coking are glycerol and acrolein oligomers and aldol condensation products, while the increment in temperature may promote more secondary reactions of the dehydration products resulting in the formation of unsaturated, heterocyclic, and aromatic compounds of high molecular weight [27].

Water content (mol %)	Glycerol conversion (%)			Acrolein yield (%)		
	2 h	6 h	12 h	2 h	6 h	12 h
15.7	68	27	19	10	6	3
51.9	66	27	18	24	11	8
76.3	75	38	28	49	22	12
91.7	71	41	29	53	35	26

Table 2.
Effect of the water content in the feedstock on the glycerol conversion and the acrolein yield with time-on-stream. Data from [24].

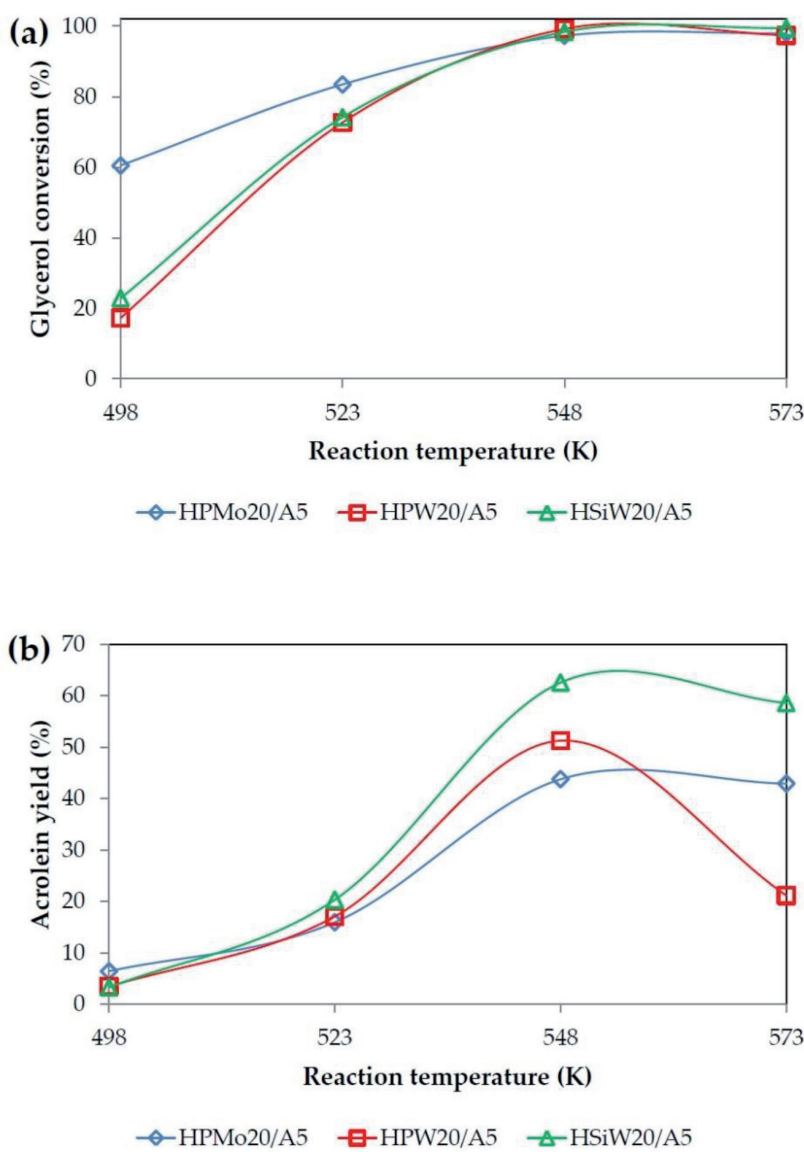


Figure 5. Effect of the reaction temperature on (a) the glycerol conversion and (b) the acrolein yield. Data from [28].

Temperature (K)	Glycerol conversion (%)			Acrolein selectivity (%)		
	1 h	5 h	10 h	1 h	5 h	10 h
553	80	44	33	22	15	8
573	85	46	9	49	28	30
593	100	48	22	54	42	22

Table 3. Effect of the reaction temperature on the glycerol conversion and acrolein selectivity with time-on-stream. Data from [29].

3.3.3 Space velocity

When working with continuous reactors, the space velocity is useful to relate the feed rate to the amount of catalyst. The feed rate may be expressed as the volumetric flow rate of liquid (Q_l), the total gas volumetric flow (Q_g , involving reactive and inert species), or the mass flow rate of reactant (\dot{m}_r), while the catalyst amount may be the volume (V_{cat}) or the weight of catalyst (W_{cat}) loaded into the reactor. The

resulting terms are known as liquid hourly space velocity (LHSV), gas hourly space velocity (GHSV), and weight hourly space velocity (WHSV) which have units of reciprocal time and are defined in Eqs. 4–6. Care should be taken concerning the choice of the reference conditions, since the three ways of expressing space velocity find extensive use.

$$LHSV = \frac{Q_l}{V_{cat}} \tag{4}$$

$$GHSV = \frac{Q_g}{V_{cat}} \tag{5}$$

$$WHSV = \frac{\dot{m}_r}{W_{cat}} \tag{6}$$

Figure 6 shows the effect of the WHSV on the glycerol conversion and yield of products of the glycerine dehydration over a Pd-HPW/Zr-MCM-41 catalyst [26]. It was evidenced that the WHSV has significant influence on the catalytic activity. The glycerol conversion increased from 90–94% with increasing WHSV from 0.17 to 0.35 h⁻¹. However, a further increase in WHSV led to a decrease in glycerol conversion up to 73% at 1.04 h⁻¹. According to the authors, this behavior was explained by the fact that increasing space velocity implies shortening the residence time for glycerol. Regarding the acrolein yield, it also presents a maximum value of 80% at 0.35 h⁻¹ and decreased with the increase of WHSV because the formed acrolein may further react with unconverted glycerol. This was supported by the opposite trend shown for the yield of other products (including acetic acid, allyl alcohol, and unknown products) reaching together a maximum yield of 13.9% at 1.05 h⁻¹. Similar results have been reported for the reaction in the presence of NH₄-La-modified H-β zeolite, hierarchical mesoporous H-ZSM-5 zeolites, and phosphotungstic acid supported on Cs-modified SBA-15 [30, 32–34]. Regarding the effect of space velocity on the glycerol dehydration with TOS, no marked trend was found during 20 h periods resulting in neglectable change in the glycerol conversion and acrolein yield [34].

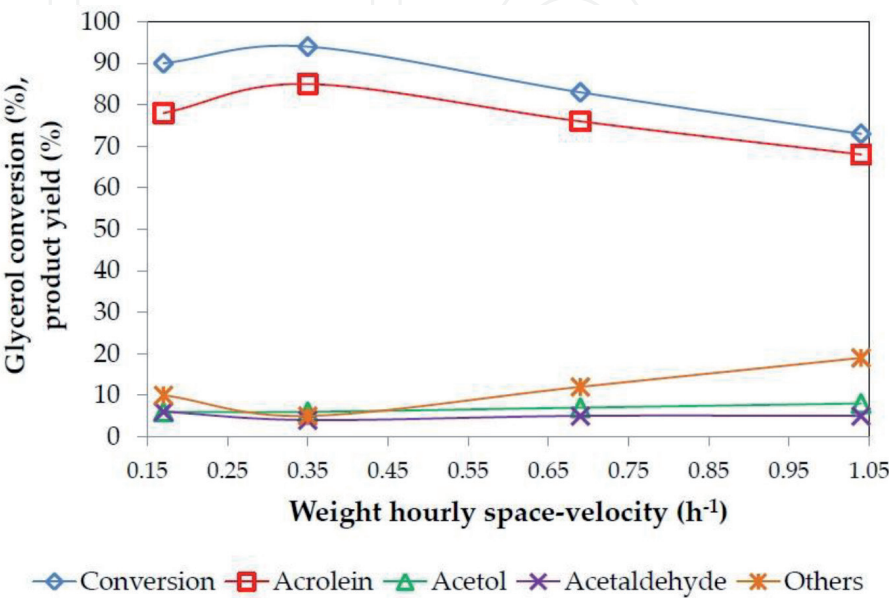


Figure 6.
Effect of the weight hourly space velocity on the glycerol conversion and product selectivity. Data from [26].

4. Catalysts used for the glycerine dehydration

As briefly pointed out in Section 3.1, the first attempts to perform the catalytic dehydration of glycerine were using supported mineral acids. However, the use of these catalysts involved some disadvantages, mainly the corrosive effect in pipes and vessels as well as healthy risks during their handling and rapid catalyst deactivation. On the other hand, the development of new heterogeneous catalysts during the last decades has led to an improvement of chemical processes, either in the technical, environmental, and health aspects. In this sense, during the last years, several heterogeneous acid catalysts such as protonated, metal-promoted, and hierarchical zeolites, mixed metallic oxides, functionalized oxides, and supported heteropolyacids have been evaluated to perform the catalytic dehydration to acrolein in gaseous phase. **Table 4** summarizes some relevant catalysts used in the gas-phase conversion of glycerine to acrolein, as well as the reaction conditions and their catalytic performance.

Protonated zeolites were studied by Kim et al. [23, 24] as catalysts for the glycerine dehydration in a fixed-bed reactor, taking into account several parameters such as the composition of the catalyst ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio), the reaction temperature, and the amount of water in the feed. Among the tested zeolites, H-ZSM-5 (150), H- β (25), and H-ferrierite (55) showed high catalytic activities with conversions of 93.7, 95.2, and 70.9%, respectively, and acrolein yields around 53.8, 44.7 and 54.6% in the same order, at 614 K.

In other studies, Corma et al. [18] evaluated the activity of a ZSM-5-based catalyst on the conversion of glycerol/water mixtures to acrolein in a fluidized-bed reactor. The highest yield of acrolein (55–61% molar carbon yield) was obtained at 623 K with complete glycerol conversion, while the use of high temperatures (>773 K) resulted in the decrease of acrolein selectivity and the increment of several other compounds, mainly acetaldehyde, $\text{C}_1\text{--C}_4$ alkanes, ethylene, propylene, butenes, acetone, and organic acids.

Zeolites modified by ion-exchange have also been tested in the glycerol dehydration. Dalla et al. [30] studied the dehydration activity of the protonic (H- β) and the ammonium-lanthanum-modified beta zeolites ($\text{NH}_4\text{-La-}\beta$). Both zeolites reached similar initial glycerol conversions (98% and 95%, respectively, at TOS = 0.5 h) at 548 K. However, the $\text{NH}_4\text{-La-}\beta$ zeolite was more selective toward acrolein than the protonic form, reaching 82.9% and 76.4% of acrolein yields. Additionally, the modified catalyst showed lower deactivation at 7 h of TOS than the H- β zeolite.

The activity of the Y zeolite in its protonic form (HY), with La (LaY) and Pd with La (Pd/LaY), was evaluated by Pala et al. [7] at temperatures between 473 and 573 K. The three catalysts were active in the conversion of glycerine in the temperature range. The highest conversions were 61.6, 84.1, and 93% in the order HY, LaY, and Pd/LaY at 573 K. For the three catalysts, the acrolein selectivities increased with the increase in temperature and also followed the trend $\text{LaY} > \text{HY} > \text{Pd/LaY}$, regarding the composition. However, the highest acrolein yields were 57.3, 75.2, and 87.6% at 573 K, for the HY, LaY, and Pd/LaY, respectively, as a result of the increase of the glycerol conversion.

The production of acrolein from glycerine in the presence of hierarchical H-ZSM-5 zeolites has proven to be feasible. Decolatti et al. [32] reported the use of the parent ($\text{Si/Al} = 15$) and desilicated H-ZSM-5 zeolite attaining a glycerol conversion of 62.1% and acrolein yield of 30.6% for the former at 548 K and 1 h of TOS, while the modified zeolite reached 89.6% of glycerol conversion and 72.1% of acrolein yield. Additionally, the untreated zeolite showed high deactivation resulting in 4.5% of acrolein yield after 5 h of TOS, against 58.6% reached by the desilicated zeolite. Further work of Lago et al. [33] showed that desilicated samples of

Catalyst	Reaction conditions ^a	Performance ^b	Reactor type	Reference
H-ZSM-5	8.3 mol% glycerol, 91.7 mol% H ₂ O in He, $F_g = 23.4 \text{ mmol}\cdot\text{h}^{-1}$, T = 613 K, $W_{\text{cat}} = 0.30 \text{ g}$	$X_g = 93.7$ $Y_{\text{acro}} = 53.8$	Fixed bed	[23]
H-Ferrierite	8.3 mol% glycerol, 91.7 mol% H ₂ O in He, $F_g = 23.4 \text{ mmol}\cdot\text{h}^{-1}$, T = 613 K, $W_{\text{cat}} = 0.30 \text{ g}$	$X_g = 70.9$ $Y_{\text{acro}} = 54.6$	Fixed bed	[24]
ZSM-5 mixed with clay binder	20 wt % glycerol aqueous solution, T = 623 K, WHSV = 335 h^{-1} , catalyst to feed ratio = 11.5	$X_g = 100$ $Y_{\text{acro}} = 62.1$	Fluidized bed	[18]
NH ₄ -La- β zeolite	20 wt % glycerol aqueous solution, T = 548 K, WHSV = 0.75 h^{-1} , $W_{\text{cat}} = 0.40 \text{ g}$	$X_g = 95.0$ $Y_{\text{acro}} = 82.9$	Fixed bed	[30]
Pd/LaY zeolite	10 wt % glycerol aqueous solution, T = 573 K, GHSV = 5933 h^{-1} , $W_{\text{cat}} = 0.30 \text{ g}$	$X_g = 93.0$ $Y_{\text{acro}} = 87.6$	Fixed bed	[7]
Modified H-ZSM-5 by alkaline treatment	20 wt % glycerol aqueous solution, T = 548 K, WHSV = 0.75 h^{-1} , $W_{\text{cat}} = 0.40 \text{ g}$	$X_g = 100$ $Y_{\text{acro}} = 74$	Fixed bed	[33]
WO ₃ /ZrO ₂	30 wt % glycerol aqueous solution, T = 553 K, $V_{\text{cat}} = 4.5 \text{ ml}$, GHSV = 4400 h^{-1}	$X_g = 100$ $Y_{\text{acro}} = 72$	Fixed bed	[35]
WO ₃ /TiO ₂	28 wt % glycerol aqueous solution, $Q_l = 0.5 \text{ ml}\cdot\text{min}^{-1}$ plus a $200 \text{ ml}\cdot\text{min}^{-1}$ Ar flow, T = 553 K, $W_{\text{cat}} = 100 \text{ g}$	$X_g = 100$ $Y_{\text{acro}} = 73$	Fluidized bed	[36]
ZrOx-NbOx	20 wt % glycerol aqueous solution, T = 573 K, GHSV = 1930 h^{-1} , $W_{\text{cat}} = 7.5 \text{ g}$	$X_g = 99$ $Y_{\text{acro}} = 71.3$	Fixed bed	[37]
WOx-NbOx	Glycerol-water 1:5 (mol/mol) solution, T = 558 K, $W_{\text{cat}} = 0.20 \text{ g}$	$X_g = 98.9$ $Y_{\text{acro}} = 74.4$	Fixed bed	[38]
WO ₃ -SiO ₂ /ZrO ₂	20 wt % glycerol aqueous solution, T = 573 K, GHSV = 2900 h^{-1}	$X_g = 100$ $Y_{\text{acro}} = 80$	Fixed bed	[39]
H ₃ PO ₄ -MCM-41	20 wt % glycerol aqueous solution, T = 593 K, $W_{\text{cat}} = 0.30 \text{ g}$	$X_g = 97$ $Y_{\text{acro}} = 81.5$	Fixed bed	[40]
SAPO-40	10 wt % glycerol aqueous solution, T = 593 K, WHSV = 0.85 h^{-1} , $W_{\text{cat}} = 0.30 \text{ g}$	$X_g = 100$ $Y_{\text{acro}} = 80.6$	Fixed bed	[41]
H ₃ PW ₁₂ O ₄₀ /TiO ₂	28 wt % glycerol aqueous solution, $Q_l = 0.5 \text{ ml}\cdot\text{min}^{-1}$ plus an additional Ar flow, T = 553 K, $W_{\text{cat}} = 1.5 \text{ g}$	$X_g = 100$ $Y_{\text{acro}} = 48.3$	Fluidized bed	[19]
H ₃ PW ₁₂ O ₄₀ /Nb ₂ O ₅	10 wt % glycerol aqueous solution, T = 598 K, GHSV = 420 h^{-1} , $W_{\text{cat}} = 0.30 \text{ g}$	$X_g = 99.8$ $Y_{\text{acro}} = 91.8$	Fixed bed	[22]

Catalyst	Reaction conditions ^a	Performance ^b	Reactor type	Reference
H ₃ PW ₁₂ O ₄₀ /Cs-SBA-15	20 wt % glycerol aqueous solution, T = 573 K, WHSV = 0.72 h ⁻¹ , W _{cat} = 0.50 g	X _g = 100 Y _{acro} = 86	Fixed bed	[34]
H ₄ SiW ₁₂ O ₄₀ /SiO ₂	10 wt % glycerol aqueous solution, T = 548 K, Q _l = 0.028 ml·min ⁻¹ , F _g = 1.8 mmol·h ⁻¹ , W _{cat} = 0.30 g	X _g = 98.3 Y _{acro} = 86.2	Fixed bed	[42]
Cs_doped H ₄ SiW ₁₂ O ₄₀ /Al ₂ O ₃	20 wt % glycerol aqueous solution, T = 573 K, GHSV = 6000 h ⁻¹	X _g = 100 Y _{acro} = 88	Fixed bed	[43]

^aT = reaction temperature, WHSV = weight hourly space velocity, GHSV = gas hourly space velocity, W_{cat} = weight of catalyst, Q_l = liquid flow rate, V_{cat} = volume of catalyst, F_g = glycerol molar feed rate.
^bX_g = glycerol conversion (%), Y_{acro} = acrolein yield (%).

Table 4.
Catalysts, reaction conditions, and performance of the catalytic dehydration of glycerol in gaseous phase.

H-ZSM-5 zeolite resulted in an improvement of the glycerol conversion (100%) and the acrolein yield (66–74%) regarding the parent zeolite (Si/Al = 40) which reached 95% of conversion and an acrolein yield of 53% at 548 K. The desilicated zeolites maintained the glycerol conversion around 70% up to 7 h of TOS, while the acrolein yield decreased to 20% at the same time.

Catalysts of tungsten, zirconium, and niobium oxides have also shown activity in the glycerol dehydration reaction. Dalil et al. [36] investigated a catalyst of tungsten oxide supported on titania (WO₃/TiO₂) in a fluidized-bed reactor. Complete glycerol conversion and acrolein selectivity of 73% were reached after 6 h of TOS at 553 K. Besides the high activity of the catalyst, the authors find that the acrolein selectivity increased from 55 to 73% with the increase in TOS from 1 to 6 h, related to the increase of coke formation over the catalyst.

Lauriol-Garbay et al. [37] produced acrolein from glycerine using mixed oxides of zirconium and niobium (ZrNbO). The catalysts exhibit a selectivity to acrolein of approximately 72%, at nearly total glycerol conversion at 573 K. ZrNbO catalysts still exhibited 82% conversion efficiency after 177 h on stream, while its acrolein selectivity remains unimpaired. The catalyst calcined at 673 K achieved 98.9% of glycerol conversion and an acrolein yield of 74.4% at 558 K. The acrolein yield and the deactivation were found to be higher and slower, respectively, than those of WO₃/ZrO₂ and H-ZSM-5 which are typical acid catalysts [38]. In another study, Znaiguia et al. [39] got 80% of acrolein yield with complete conversion of glycerol at 573 K using a catalyst of tungstated zirconia promoted with silica (WSi/Zr). The authors confirmed that the incorporation of silicon improved the dehydration activity and the catalyst stability.

The catalytic dehydration of glycerol may also occur on oxides promoted with phosphate. Ma et al. [40] evaluated phosphorus-containing MCM-41 mesoporous molecular sieves (H₃PO₄-MCM-41). The catalyst with 25 mass % of supported H₃PO₄ resulted in 84% of acrolein selectivity with glycerol conversion of 97% at 593 K. The conversion of glycerol and selectivity to acrolein greatly depended on the calcination temperature, reaction temperature, and glycerol concentrations. Tests of the catalyst activity with TOS indicated that the HP-MCM-41 exhibited stable activity with high acrolein selectivity up to 12 h. Recently, Fernandes et al. [41] reported the use of hierarchical silicoaluminophosphate 40 (SAPO-40). When

compared with the conventional SAPO-40, this catalyst showed higher acrolein selectivity (80%) at complete conversion and a catalytic lifetime up to 120 h, reaching acrolein yields between 80% and 68% during this period.

Supported heteropolyacids, mainly phosphotungstic ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) and silicotungstic acid ($\text{H}_4\text{SiW}_{12}\text{O}_{40}$), and their alkali-substituted salts present high activity to convert glycerine into acrolein. Viswanadham et al. [22] studied the activity of phosphotungstic acid supported on niobium pentoxide ($\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Nb}_2\text{O}_5$) which was highly active and selective toward acrolein (glycerol conversion 98.8% and acrolein selectivity 92% at 598 K). The catalytic activity depended on the amount of heteropolyacid supported, the calcination temperature, and the reaction temperature. Tests of catalyst lifetime indicated that the solid was stable with high acrolein selectivity up to 10 h on TOS.

Liu et al. [34] used a mesoporous molecular sieve modified (SBA-15) with cesium as support for $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and used the resulting solid ($\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Cs-SBA-15}$) as catalyst for the glycerol dehydration. The catalyst with 50 wt % of supported heteropolyacid reached the maximum acrolein yield (86%) and complete glycerol conversion at 573 K. Compared with the catalyst prepared with the conventional support (pure SiO_2), the modification of SBA-15 with Cs improved the stability of the catalyst up to 170 h of reaction, and the acrolein yield was the same as before regeneration at 773 K in air.

According to Tsukuda et al. [42], heteropolyacids supported on silica also present high activity in this reaction. The authors found that the catalytic activity depended on the type of heteropolyacid as well as the size of mesopores in the silica support. The highest activity was performed by silicotungstic acid supported on silica with mesopores of 10 nm, reaching 98.3% of glycerol conversion and 86.2% of acrolein yield at 548 K. The activity of silicotungstic acid, doped with rubidium and cesium, supported on a mixture of δ and θ Al_2O_3 , was reported by Haider et al. [43]. The Cs-doped catalyst reached a maximum acrolein selectivity of 91% at 100% glycerol conversion for 90 h of TOS at 573 K, with a 10 wt % glycerol solution. When the glycerol concentration in the feed was increased to 20 wt %, the acrolein yield slightly decreased, and the catalyst was stable during a shorter TOS regarding the reaction with 10 wt % of glycerol in the feedstock.

The main features of these catalysts that affect the acrolein selectivity are the strength and type of the surface acid sites, which are known to promote the dehydration reactions of alcohols [44–46]. Regarding the strength of the acid sites measured in terms of the Hammett acidity (HA), the catalysts have been classified into four groups. The first group is comprised by basic catalysts with HA higher than +7 and shows no selectivity toward acrolein. Catalysts, such as zirconium oxide, with HA between –3 and +7, belong to the second group. These solids show acrolein selectivities not greater than 30% but remain stable for 10 h on stream. Group 3 includes catalysts such as alumina impregnated with phosphoric acid, heteropolyacids supported on alumina, niobium oxide calcined at 773 K, HZSM zeolite, and pure alumina. Their HA values are between –8 and –3 and result in acrolein selectivities up to 70%; however, these catalysts show low stability and rapid deactivation. The fourth group comprehends solids with HA less than –8, such as H β zeolite, niobium oxide calcined at 623 K, alumina silicate, and sulfonated zirconium oxide. These catalysts are less selective to acrolein but more stable with TOS than those of group 3 [47].

Additionally, the type of acid sites present at the catalyst surface has an effect on the products' distribution. It is generally accepted that the Brønsted acidity promotes the glycerol dehydration reaction to proceed through the acrolein route (reaction 2). Some experimental studies have demonstrated the positive influence of the concentration of Brønsted acid sites on the acrolein yield, as well as the relationship of Lewis sites on the production of acetol.

In the study of Pala et al. [7], the distribution of acid sites of HY zeolite was modified by ion-exchange with La and with La and Pd. An increase in the total amount of acid sites was observed after the exchange with La cations, increasing around 1.5 and 2.1 times the concentration of Lewis and Brønsted sites in the LaY catalyst regarding the HY zeolite, at 573 K. A subsequent raise of the total acidity occurred after the impregnation of the LaY solid with Pd, leading to concentrations 2.5 and 3.5 times higher than the acidity of HY zeolite. At any temperature, the introduction of La into the HY zeolite improved the glycerol conversion, attributed to the increase of total acidity. At 573 K and GHSV = 5933 h⁻¹, the acrolein yield raised from 57.3% to 75.2% with the increase in the concentration of Brønsted acid sites after the modification with La. Besides, the incorporation of Pd to the LaY catalyst resulted in an acrolein yield of 87.6% at the same temperature. Since the concentration of Lewis acid sites was also increased after the ion-exchange procedures, the acetol yield followed the order Pd/LaY > HY > LaY with values of 0.07, 0.5, and 2.5%, respectively.

Kim et al. [25] reported the correlation between the acrolein and acetol yields with the concentration of Brønsted and Lewis acid sites, respectively, of a series of silica-alumina and alumina (η -Al₂O₃) catalysts. The acrolein yield enhanced from 3.6% to 17.2% with the increase in the concentration of Brønsted acid sites from 0 to 188 $\mu\text{mol g}^{-1}$, while the acetol raised from 2.2 to 5% with the change of Lewis acid sites from 28 to 192 $\mu\text{mol g}^{-1}$ at 588 K, WHSV = 62 h⁻¹, and 2 h of TOS.

Similarly, Massa et al. [48] performed the glycerol dehydration reaction over catalysts of Nb and W oxides supported on Al₂O₃, SiO₂, and TiO₂ at 578 K, WHSV = 0.94 h⁻¹, and collection of products between 1 and 3 h of TOS. The acrolein selectivity increased from 0 to 70%, presenting a sigmoidal trend regarding the increase in the concentration of Brønsted acid sites from 0 to 1 $\mu\text{mol m}^{-2}$. The promoting effect of Lewis acidity on the acetol production was also evidenced since the change from 0.41 to 2.95 $\mu\text{mol m}^{-2}$ resulted in the enhancement of the acetol selectivity from 5 to 18%, independent of the dispersed phase and the catalytic support.

5. Conclusions

Acrolein can be obtained from glycerine by a dehydration reaction. The main process variables in the gas phase are the reaction temperature, the concentration of glycerol in water, and the space velocity in fixed-bed reactors. A thermodynamic study of the equilibrium has been made to estimate the conversion to equilibrium as a function of temperature. The reactors are usually heated between 523 and 603 K. Some of the most active catalysts in the gas-phase reaction (yield >70%) were NH₄-La- β zeolite, Pd/LaY zeolite, hierarchical ZSM-5, WO₃/ZrO₂, WO₃/TiO₂, ZrO_x-NbO_x, WO_x-NbO_x, WO₃-SiO₂/ZrO₂, NbO_x-WO_x/Al₂O₃, H₃PO₄-MCM-41, SAPO-40, NbPSi, Pd-H₃PW₁₂O₄₀/Zr-MCM-41, H₃PW₁₂O₄₀/Cs-SBA-15, H₃PW₁₂O₄₀/Nb₂O₅, Cs-doped H₄SiW₁₂O₄₀/Al₂O₃, H₄SiW₁₂O₄₀/TiO₂, and H₄SiW₁₂O₄₀/SiO₂. In general, total conversion has been achieved at temperatures from 573 to 598 K. The catalytic process in the gas phase seems more appropriate than the liquid-phase process due to high acrolein yields and direct separation of the product effluent from the catalyst.

Conflict of interest

The authors declare no conflict of interest.

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