

Recent Developments in the Field of Catalytic Dehydration of Glycerol to Acrolein

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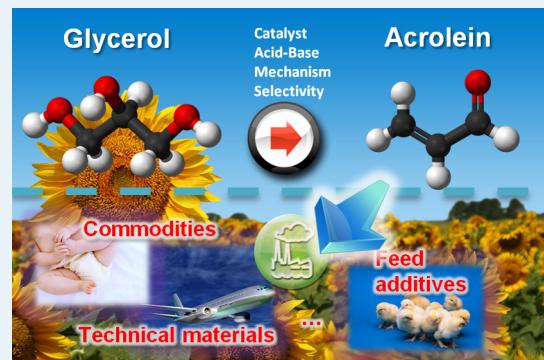
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ABSTRACT: Catalytic dehydration is one of the possible reactions to valorize the large amounts of glycerol yielding from the transesterification process. Thus, since the biodiesel boom in 2004–2005, many publications proposing various catalytic systems can be found. In this review, the current state of the art based on the most recent publications is presented and discussed in detail with respect to the observed catalytic performance as well as long-term stability. Next to the applied development of new catalysts, a main focus is the influence of the most critical parameter: the acidity of the catalyst and its correlation to the catalytic performance (selectivity and conversion). In addition, recent results on the thermodynamic calculation are presented, thus giving an insight into the most probably involved intermediates.



KEYWORDS: glycerol, dehydration, acid catalyst, heterogeneous catalyst, biomass valorization

1. INTRODUCTION

The use of glycerol as a starting material for yielding commodity chemicals is commanding much attention. Indeed, glycerol is widely available because of its formation as a byproduct in the biodiesel production process. In fact, since western governments—especially, the EU-27 group—have decided to blend petro-based diesel fuels with fatty acid methyl esters (FAMEs) issued from renewable resources, large amounts of money have been invested in the biodiesel business, namely, into refineries, but also into subsidiaries for the cultivation of oil plants (colza, canola, sunflower, oil palm, castor-oil plant). Of course, one can discuss the ecological as well as the ethical sense of such decisions, especially knowing that the oil palm plantations are destroying more and more of the rain forest in the Asian region or that the cultivation of colza and sunflower is often in competition with the food industry. Nevertheless, those are socioeconomic issues, which will not be addressed within the frame of the present paper oriented on the technological/scientific aspects.

As a matter of fact, the production of biodiesel is still increasing and is even forecasted to nearly double from 22.7 million metric tons in 2012 to 36.9 million metric tons in 2020 (Figure 1).¹

Thus, hand-in-hand, the amount of glycerol pushed into the market will also increase, as roughly 10 wt % of glycerol is byproduced with biodiesel during the reaction of transesterification of triglycerides with methanol. Of course, since the biodiesel boom in 2004–2005, the markets addressed by the traditional consumers of glycerol (cosmetics, tobacco, etc.)

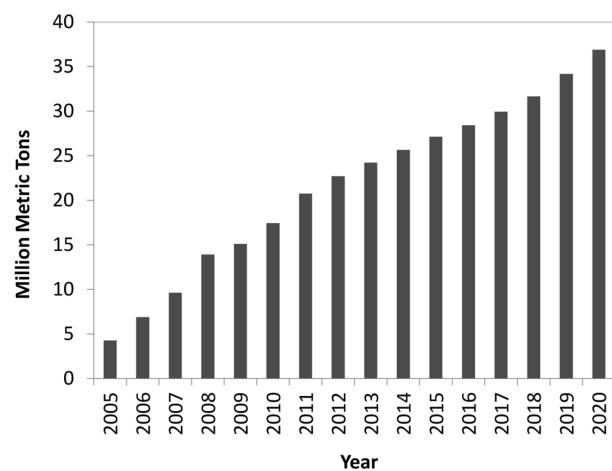


Figure 1. Annual production of biodiesel¹.

cannot absorb this glycerol considerable oversupply, whereby the price of the latter has significantly decreased. Nowadays, refined glycerol is available for 900–1000 US\$/ton, but crude glycerol can be purchased for around 150 US\$/ton.² It appears, then, that the development of glycerol valorization routes is still of interest for investors because of the versatility of its possible uses, its large availability, and a rather low spot price.³

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Nevertheless, only a few processes based on bioglycerol valorization have reached the industrial level so far. One of the most widely known is certainly the synthesis process of epichlorohydrin by SOLVAY. The corresponding facility in Tavaux (France) has produced 10 kt/year of epichlorohydrin since 2007, and two new facilities in China (Taixing) and Thailand (Map Tha Put), offering a production capacity of 100 kt/year each, were announced to start production in 2013.⁴

Another example of ongoing glycerol valorization process is the production of biomethanol. The corresponding process has been used by BioMCN since 2010 in Delfzijl (Netherlands), with a production capacity of 200 kt/year.⁵ Hereby, glycerol is converted to syngas, which is subsequently transformed to methanol using a conventional syngas conversion technology.

In addition to these commercial applications, other valorization pathways have been technologically explored at the lab scale, such as partial oxidation,⁶ hydrogenolysis,^{7,8} and etherification.⁹ Although many of these processes were claimed to be economically viable,^{10,11} they have not yet been transposed to the industrial scale. This is also the case for the dehydration of glycerol to yield acrolein, a widely used intermediate for the synthesis of polymers (poly(acrylic acid)) and feed additives (DL-methionine). Since our last review paper in 2010 on this subject,¹² the number of publications dealing with the dehydration of glycerol to acrolein has significantly increased (Figure 2), but still, no commercial

application has been launched. Nevertheless, from what can be judged from the recent papers, it is clear that glycerol dehydration is still a hot topic, and the application is moving forward, considering bioacrolein production as an intermediate step in a cascade reaction directly targeting subsequent various final products. Thus, new processes are reported in which acrolein is not isolated or purified but directly converted by oxidehydration to acrylic acid^{13–15} or by ammoniation to acrylonitrile.¹⁶ Thus, in the present paper, next to the presentation of the latest catalytic developments in the reaction of dehydration of glycerol to acrolein, we also place focus on the aforementioned cascade applications.

2. DEHYDRATION OF GLYCEROL TO ACROLEIN

Known since the 19th century, the reaction of dehydration of glycerol to acrolein is catalyzed by acids. The corresponding reaction mechanism is generally supposed to proceed via the protonation of the secondary hydroxyl group with consecutive elimination of a first water molecule, thus leading to the formation of an enol intermediate, which instantly isomerizes to yield 3-hydroxypropanal. Nevertheless, the latter is never observed because it subsequently undergoes a second dehydration step, finally leading to the formation of acrolein (Scheme 1). On the other hand, the aforementioned protonation is obviously not limited to the secondary hydroxyl group, but can also affect the terminal hydroxyl groups. In that case, the elimination of a water molecule leads to the formation of acetol, again via an enol intermediate (Scheme 1).

Whereas the pathway to acrolein is generally accepted for proton donors—namely, Brønsted acids—the formation of acetol is still a matter of debate. In 2010, Alhanash and Kinage proposed, on the basis of their observations of the catalytic activity, that the formation of acetol was catalyzed by Lewis acids, but also over basic catalysts.^{18,19} Alhanash et al. suggested that glycerol coordinates to a Lewis acid site, thus enabling a concerted rupture of the terminal C–OH bond and of the secondary C–H bond (Scheme 2A). Thereby, in addition to the formation of one acetol molecule, the reaction leaves a hydrated Lewis site at the surface of the catalyst that can further act as a pseudo-Brønsted site, which is generally accepted for zeolite catalysts.²⁰ The as-formed Brønsted sites can then either catalyze the dehydration of glycerol to acrolein, as described before, or be dehydrated, for example, by thermal activation under the reaction conditions, to regenerate the initial Lewis acid site. For zeolite catalysts, this regeneration is generally observed at elevated temperatures above 500 °C.²¹

On the other hand, Kinage et al. proposed that the formation of acetol over basic sites is also possible and proceeds via

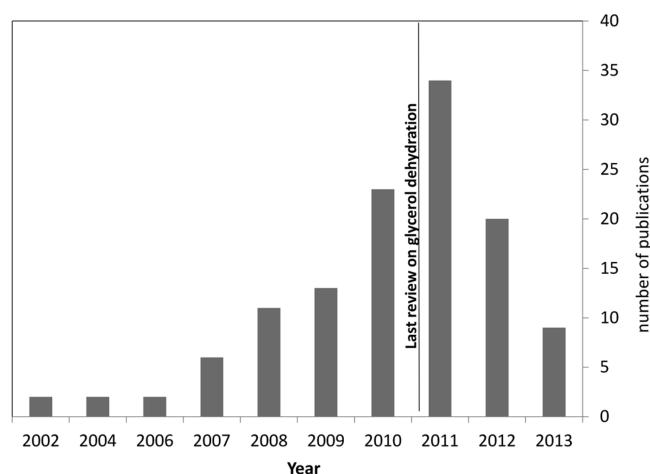
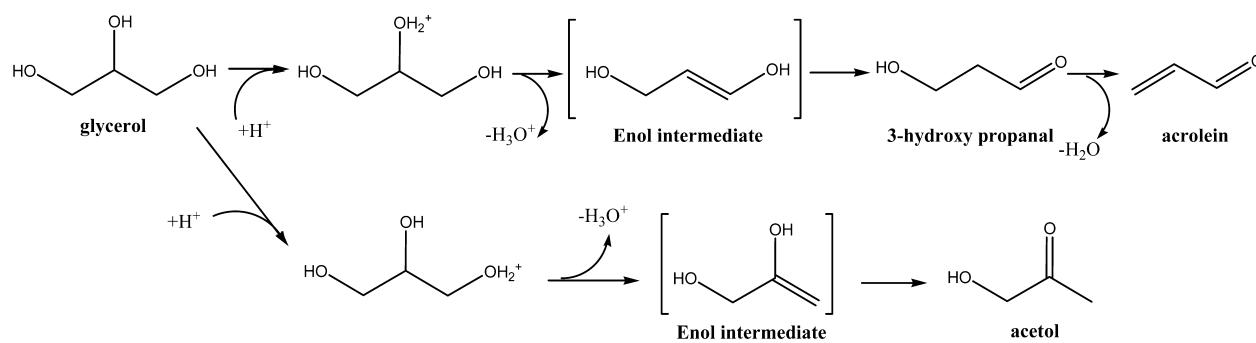
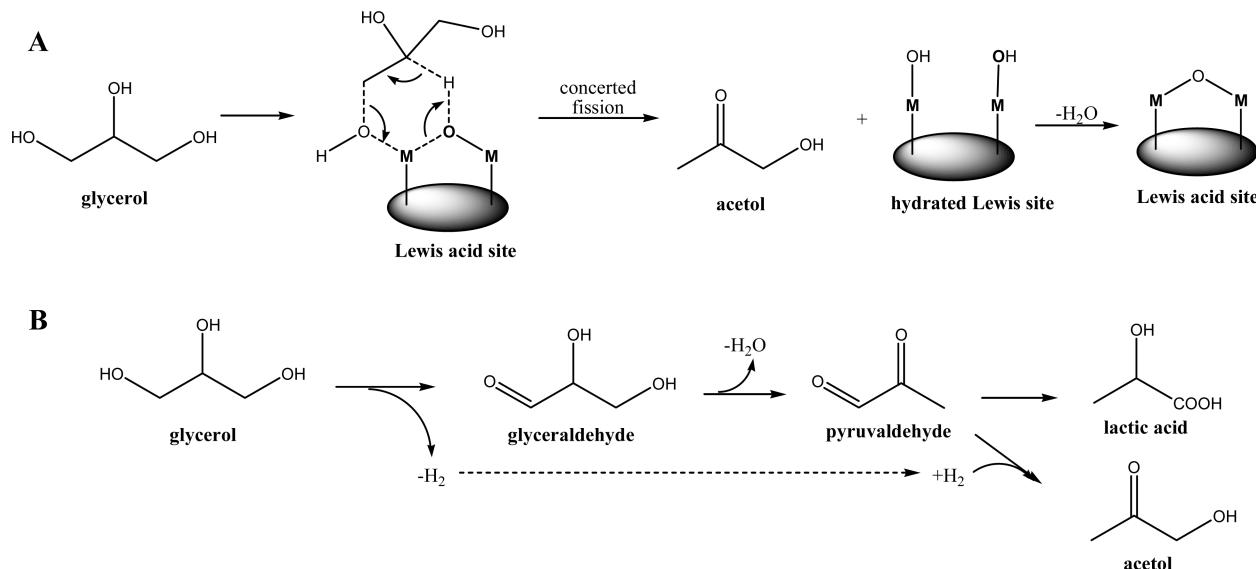


Figure 2. Evolution of the number of articles in scientific peer-reviewed journals dealing with the topic of “glycerol dehydration to acrolein”¹⁷.

Scheme 1. Reaction Pathway from Glycerol to Acrolein and Acetol over Brønsted Acid Sites



Scheme 2. Reaction Mechanism for the Formation of Acetol over Lewis Acid Sites (A) and over Basic Catalysts (B)

Table 1. Catalytic Performance of Various Zeolite-Type Catalysts^a

catalyst (Si/Al ratio)	T (°C)	GHSV (h ⁻¹)	TOS (h)	X (%)	S _{acrolein} (%)	S _{acetol} (%)	ref
mordenite (18) ^b	250		10	91.8	100	0	25
ZSM-23 (51)b ^b	250		10	79.5	100	0	25
MY (5) ^b	250		10	89	100	0	25
H-Beta (350)	315	62 ^c	2	36.7	38.3	2.8	26
H-Beta (38)	315	62 ^c	2	30.1	33.1	3.6	26
nano HZSM-11	320	873	2	100	78.4	0	27
Si _{0.8} Al _{0.2} O _x (4)	315	62 ^c	2	94.7	52.2	6.7	30
Si _{0.6} Al _{0.4} O _x (1.5)	315	62 ^c	2	95.4	50	8.2	30

^aT = reaction temperature; GHSV = gas hourly space velocity; TOS = time on-stream; X = conversion of glycerol; S_{acrolein} = selectivity to acrolein; S_{acetol} = selectivity to acetol. ^bLiquid phase batch process. ^cWeight hourly space velocity.

sequential dehydrogenation, dehydration, and rehydrogenation of glycerol (Scheme 2B).¹⁸ It is worth mentioning that the same mechanism is also involved in the conversion of glycerol to lactic acid.²²

As aforementioned, the dehydration generally proceeds via a mechanism involving a transfer of a proton. Thus, the corresponding reaction can either be envisaged in the gas phase or the liquid phase, whereby the latter also involves sub- or near-critical conditions. With respect to the corrosion when combining acid catalysts and near-critical conditions, the application of a gas phase reaction is preferable for an industrial application, whereby recent publications focused on the dehydration in the gas phase. We now focus the following discussion on the latest developments in terms of the nature of the employed catalyst systems, dividing these latter into three families, namely, heteropoly acids, zeolitic materials, and metal oxides, instead of choosing a classification along possible reactor technologies. Nevertheless, the discussion concerning liquid phase processes was integrated into the corresponding catalysts' sections.

2.1. Zeolites and Silica–Alumina Materials. The use of zeolites as acid catalysts is well-known and finds a wide range of applications in isomerization²³ and cracking reactions.²⁴ Hereby, zeolites offer a unique feature: the combination of acid properties together with well-defined microporosity. Whereas their acidity can be varied via the silica to alumina molar ratio and by neutralization with cations, their micro-

porosity depends on the structure of the considered material (MFI, FAU, MOR, etc.). Thus, zeolites have also been widely studied for the reaction of dehydration of glycerol.

De Oliveira et al. studied the dehydration of glycerol in liquid phase over zeolite catalysts of various structures with thus different native Si/Al ratios (from 5 to 51).²⁵ Their results show that, as expected, the number of acid sites decreases when increasing the Si/Al ratio. Nevertheless, the catalytic performance was not directly correlated to this latter ratio. In fact, whereas the catalyst with a large Si/Al ratio of 18 (mordenite) exhibited a 91.8% yield in acrolein, the zeolite with the low ratio of 5 (HY) exhibited an 89.0% yield, and even the zeolite with a ratio of 51 (ZSM-23), still yielded 79.5% of acrolein (Table 1). It is worth mentioning that, for all these catalysts, the selectivity to acrolein was 100%, meaning that no other byproducts were observed. The authors conclude that it is not the Si/Al ratio that directly influences the performances, but that the presence of medium acid sites is the predominant parameter. Furthermore, the catalyst structure was claimed to have a significant impact: small pores and one-dimensional channels hindered mass transfer whereby the formation of carbonaceous species was increased.

Kim et al. also studied zeolite-based catalysts and especially examined the influence of the silica to alumina ratio on the catalytic performances.²⁶ In contrast to the results of De Oliveira et al.,²⁵ the influence of the acidity and the Si/Al ratio is less eye-catching in their case. For example, a H-beta zeolite

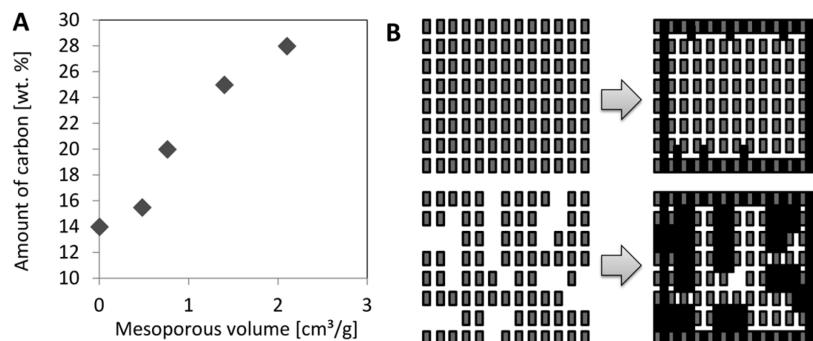


Figure 3. Correlation between the amount of carbon deposit during 8 h on-stream and mesoporous volume (A); schematics of the formation of cokes over microporous (top, B) and mesoporous zeolite (bottom, B).

with a Si/Al ratio of 350 yielded significantly more acrolein (14.2%) than a H-beta zeolite with a Si/Al ratio of 38 (9.9% Table 1). On the other hand, Kim et al. found a linear correlation between the nonporous (external) surface and the glycerol conversion. Microporous materials with a low external surface, such as H-ferrierite, H-mordenite, and H-Y, exhibited low conversion of no more than 30%. This correlation supports the hypothesis of internal mass transfer limitations, which means that the active sites inside the catalyst particle do not contribute to the reaction.

Because all the samples showed significant deactivation during the reaction by coking, the authors brought up the idea of increasing the amount of water in the feed to lower the partial pressure of glycerol, whereby the probability for C–C coupling bimolecular reactions should be decreased. Nevertheless, the observed impact was rather negligible. On the other hand, an increase in the contact time promoted the formation of acetaldehyde and also coke, supposedly due to cracking and condensation reactions, respectively.

A more fundamental study of the influences of the pore size and the channel structure of protonated zeolite catalysts was performed by Gu et al.²⁷ Therefore, they used HZSM-5, HZSM-11, HY, and H-beta zeolites. These materials show significant differences in pore size and framework structure: Whereas HZSM-5 and HZSM-11 exhibit pores of 0.51 and 0.53 nm, respectively, H-beta and HY exhibit larger pores of 0.67 and 0.74 nm, respectively. Further, HY has large cavities (also called supercage) of 1.3 nm. In terms of acidity, all the prepared samples exhibited similar values of surface acid density, between 1.25 (HZSM-11) and 1.85 $\mu\text{mol/g}$ (H-beta). In terms of catalytic performances, it was clearly observed that all the catalysts tended to deactivate, but to a different extent. Whereas the conversion of HY-zeolite dropped from 85% to 25% during the first 3 h on-stream, the conversion of HZSM-11 decreased only by 15 points (from 100% to 85%) during the same period. From these figures, the authors state that the mechanism of coke formation depends on the channel structure. In fact, small channels like in HZSM-5 and HZSM-11 sterically hinder the formation of coke via a multimolecular mechanism because the size of glycerol is in the same range as that of the pores. On the other hand, large channels and supercages, such as those in the case of HY and H-beta, enable the multimolecular formation. Another possibility to decrease the formation of coke was the dilution with inert gas (He) to lower the partial pressure of reactants and products, whereby, similarly to the strategy proposed by Kim et al.,²⁶ the multimolecular reactions were hindered.

With regard to this contrasting point of view concerning the influence of the pore size, Possato et al. performed an interesting study using MFI zeolites.²⁸ Instead of a classical synthesis for varying the Si/Al ratio, they used a parent MFI zeolite with a Si/Al ratio of 40 and desilicated the latter by treatment in NaOH solution. Correspondingly, the Si/Al ratio could be adjusted in the range of 8–40. As a second effect, the microporous structure was modified, whereby the micropore volume decreased (0.25 cm³/g for Si/Al = 40 vs 0.08 cm³/g for Si/Al = 8) giving rise to mesopores (0 cm³/g for Si/Al = 40 vs 2.1 cm³/g for Si/Al = 8). Concerning the catalytic performances, all the samples showed rather similar behavior, with a yield in acrolein of 20%. More interesting is the characterization of the samples after testing by thermogravimetric analysis, revealing that the carbon content over the desilicated catalysts after 8 h of reaction increased with the mesoporous volume. Thus, the authors could accordingly even establish a linear relationship between them (Figure 3A). The difference between the microporous catalyst and the mesoporous samples was ascribed to the formation of coke in the whole porous network in the latter case, whereas the coke formation over the microporous catalyst was strictly limited to the surface, thus only blocking the pore entrance (Figure 3B). Comparable results were also claimed by Hulteberg et al., showing that the pore condensation was the main reason for catalyst deactivation.²⁹

Next to their aforementioned work on zeolites,²⁶ common nonmicroporous silica–alumina materials were also used by Kim et al.³⁰ Thereby, they systematically studied the influence of the Si/Al ratio on the physical properties and the catalytic performances of the as-prepared solids. The corresponding samples exhibited a Si/Al ratio from 19 to 0.25. Furthermore, bare θ -alumina was used as a benchmark. The total acidity initially increased with the alumina content, reaching a maximum value of 450 $\mu\text{mol/g}$ for a ratio of 1.5. For larger values, the number of acid sites then decreased, but still showing 343 $\mu\text{mol/g}$ for bare θ -alumina. Furthermore, the authors also determined the nature of the acid sites and showed that increasing alumina content led to more Lewis acidity, as expected. In fact, the ratio of Brønsted to Lewis acid sites decreased from 2.4 for the silica–alumina with a Si/Al ratio of 19 to 0.6 for a ratio of 0.25. Bare θ -alumina exhibited exclusively Lewis acidity. Accordingly, the selectivity in acetol followed the same trend, meaning that catalysts with small Si/Al ratios promoted the formation of acetol, which was in agreement with the mechanism postulated by Alhanash et al. (Scheme 2A).¹⁹ The best performance in terms of acrolein

Table 2. Catalytic Performance of Various Heteropoly Acid-Type Catalysts^a

catalyst	T (°C)	GHSV (h ⁻¹)	TOS (h)	X (%)	S _{acrolein} (%)	S _{acetol} (%)	ref
H ₃ SiW ₁₂ O ₄₀ /TiO ₂	280	2570	nc	93.9	80	7.8	34
H ₄ PW ₁₂ O ₄₀ /TiO ₂	280	2570	nc	100	49.6	9.6	34
H ₃ PMo ₁₂ O ₄₀ /TiO ₂	300	17850	nc	95.3	42	5.2	34
H ₃ PW ₁₂ O ₄₀ /W-SBA-15	250	62 ^b	nc	100	74	nc	37
H ₃ SiW ₁₂ O ₄₀ /Si _{0.8} Al _{0.2} O _x	315	62 ^b	2	95.5	50.6	9.1	38
H ₃ SiW ₁₂ O ₄₀ /Si _{0.9} Al _{0.1} O _x	315	62 ^b	2	97.2	54.4	8.9	38
H ₃ SiW ₁₂ O ₄₀ /ZrO ₂	315	62 ^b	2	83.6	58.1	11.9	39
H ₃ SiW ₁₂ O ₄₀ /CeO ₂	315	62 ^b	2	62.4	5.1	23.4	39
H ₃ SiW ₁₂ O ₄₀ /MgO	315	62 ^b	2	24	7.1	17	39
LiSiW ₁₂ O ₄₀ /SiO ₂	300	25320	nc	99.3	70.2	7.9	40
KSiW ₁₂ O ₄₀ /SiO ₂	300	25320	nc	100	64.7	6.9	40
CsSiW ₁₂ O ₄₀ /SiO ₂	300	25320	nc	96.6	57.2	8.4	40
CsSiW ₁₂ O ₄₀	250	24000	3	100	96	4	41
RbSiW ₁₂ O ₄₀	250	24000	3	100	94	4	41
CsSiW ₁₂ O ₄₀ /Al ₂ O ₃	250	24000	10	100	84	11	41

^aT = reaction temperature; GHSV = gas hourly space velocity; TOS = time on-stream; X = conversion of glycerol; S_{acrolein} = selectivity to acrolein; S_{acetol} = selectivity to acetol; nc = not communicated. ^bWeight hourly space velocity.

yield (49%) was obtained over the catalyst with a Si/Al ratio of 4 (Table 1).

One can conclude that the use of zeolites is a very promising way for high performance in the reaction of glycerol dehydration, notably due to the possibility to tune acidity and pore size via the Si/Al ratio. Furthermore, the outstanding performances of zeolites in terms of selectivity is a significant advantage compared with other catalyst families. On the other hand, the formation of coke is the major drawback, and the blocking of the pores is a strong hint, suggesting the presence of internal diffusion limitations in the micropores.

2.2. Heteropoly Acid-Based Catalysts. Heteropoly acids (HPAs) are widely studied in catalysis and especially in the field of the valorization of biomass-derived molecules.³¹ These compounds, under their native nonneutralized/partially neutralized form, are well known Brønsted acids of a strong to a very strong strength. Like zeolites, heteropoly acids offer the possibility to modify their acidity and, thereby, their catalytic properties. This can be done by tuning their composition: namely, the nature of the central atom, the addenda atoms, and the counterions.³² Thus, these compounds are ideal candidates for the dehydration of glycerol, which needs fine-tuned acidic properties. Nevertheless, because of their rather low specific surface area, which might be a drawback for surface-catalyzed reactions, heteropoly acids are either supported on carriers (silica, alumina, titania, zirconia, etc.) or used as partially neutralized salts (cesium, or potassium), whereby their specific surface area is strongly increased. A recent review on the use of heteropoly acids in the dehydration of glycerol was published by Martin et al.³³

Titania (rutile)-supported heteropoly acids (notably, silicotungstic, phosphotungstic, and phosphomolybdc acid) were studied by Shen et al.³⁴ Except for the molybdenum-based HPA, all the catalysts exhibited high catalytic activity (90–100% conversion), which is consistent with the acid strength of the corresponding HPAs, decreasing in the following order: phosphotungstic acid, silicotungstic acid, phosphomolybdc acid. The selectivity to acrolein followed a similar trend whereby the catalyst based on silicotungstic acid exhibited the best performances, with 76% yield in acrolein (50% for H₃PW₁₂O₄₀ and 42% for H₃PMo₁₂O₄₀; Table 2). Nevertheless, it is worth mentioning that the selectivity to acrolein

significantly dropped over the silicotungstic acid catalyst when the temperature exceeded 300 °C, giving rise to undesired byproducts, such as acetic acid, acetaldehyde, acetol, and small amounts of phenol (6.8%, 8.3%, 7.8%, and 1.3%, respectively). The authors, however, did not state if any deactivation was observed.

Alumina-supported and nonsupported silicotungstic acid was studied by Armbruster et al.³⁵ They claimed that, for supported catalysts, the selectivity to acrolein initially increases from around 18% to 68% with an increase in the conversion from 22% to 90%. A further increase in the latter (>90%) results in a decrease in acrolein selectivity to 60%. Thereby, the authors used different reaction temperatures for adjusting the conversion level because the influence of the contact time was too low. Thus, the results confirmed the previous study of Deleplanque et al., who explained the low selectivity at low temperature by the formation of acetals from glycerol and acrolein, whereas the decreased selectivity observed at high temperature was explained by the promotion of cracking reactions.³⁶

Finally, Armbruster et al. also studied the regeneration either by replacing the reactant feed with oxygen or by cofeeding of oxygen. Both possibilities enabled preventing the blocking of the active sites by carbonaceous species.

In a following study, the same group used tungsten-incorporated SBA-15 as a support for phosphotungstic acid.³⁷ The corresponding support was prepared by adding the tungsten precursor directly into the gel containing the silica precursor (tetraethyl-*ortho*-silicate) and the structuring agent (Pluronic P123). Finally, the as-prepared support was impregnated with the active phase (phosphotungstic acid) and calcined at 400 °C. From the characterization of the samples, a quite large difference between the properties of the support (WO₃–SBA-15) and the final catalyst (containing 19.2 wt % phosphotungstic acid) was shown. Whereas the latter exhibited a rather low surface area (322 m²/g), but a high number of acid sites (2.21 mmol/g; 6.8 μmol/m²), the W-doped support revealed a large surface area (570 m²/g), but a considerably lower number of acid sites (1.26 mmol/g; 2.2 μmol/m²). Thus, the additional acidic sites could only originate from the HPA active phase. Surprisingly, the catalytic performances of the solids were quite similar: whereas the

support showed 88% conversion, the final catalyst gave full conversion at an identical selectivity in acrolein of 74%. Using IR-spectroscopy, it was not fully clear whether the active phase was preserved upon the thermal treatment (400 °C) or decomposed into tungsten oxide. This fact may explain the rather small difference in terms of catalytic performance (100% vs 88% conversion), which could simply be related to the larger numbers of active sites.

Following their work on silica–alumina,³⁰ Kim et al. further used their solids as supports for silicotungstic acid.³⁸ The characterization of the catalysts showed that supporting silicotungstic acid did not yield much difference in acidity compared with the bare support, which can be explained by the relatively low loading of silicotungstic acid they used (15 wt %). Consequently, the performances were essentially quite close to those of the nonimpregnated supports, whereby the best performance was obtained over the catalyst based on a support with a Si/Al ratio of 9 (53% yield in acrolein; Table 2). Thereby, it is noteworthy that the corresponding catalyst did not exhibit the highest specific surface among all samples, but a rather reasonable value of 110 m²/g compared to a maximal value of 273 m²/g (θ -alumina). As in the case of bare silica–alumina,³⁰ the selectivity to acetol increased with the alumina content, which can be again attributed to the Lewis acidity of alumina.

Because these catalysts suffered from deactivation by coke formation, the authors again studied the influence of water on the amount of carbon deposit. As in the previous studies by Kim et al. and Gu et al.,^{26,27} it was found that large amounts of inert (vapor or helium) decreased the formation of products with high molecular weight and, thereby, the amount of carbon deposit as a result of the lower partial pressure of glycerol, which decreased the probability for multimolecular reactions.

Furthermore, Kim et al. also performed a more fundamental study on the influence of the support on the performance of silicotungstic acid-based catalysts.³⁹ They then used different support materials, such as γ -alumina, silica–alumina, titania, silica, zirconia, cerium oxide, magnesium oxide, and active carbon. The support had a significant impact on the activity and selectivity of the final catalysts. The catalysts based on basic supports, such as cerium oxide and magnesium oxide, showed pronounced selectivity to acetol (23% and 17%, respectively; Table 2). On the other hand, those based on acidic and amphoteric supports such as alumina, zirconia, and silica–alumina promoted the formation of acrolein (46%, 58%, and 58%, respectively). Nevertheless, the formation of coke remained the major drawback of these catalysts on the basis of acid and amphoteric supports. In fact, the catalyst exhibiting the highest amount of strong acid sites (silicotungstic acid on silica–alumina) also exhibited the largest amount of coke deposit (23.6 wt % after 12 h of reaction).

Following the idea of Alhanash et al. who used salts of phosphotungstic acid, Atia et al. and Haider et al. studied supported alkaline salts of silicotungstic acid.^{40,41} Whereas Atia et al. focused on lithium, potassium, and cesium as counterions using silica and alumina-silicates as support, Haider et al. chose to study cesium and rubidium salts over alumina. Whereas Atia et al. claimed that the supported lithium salts are superior in terms of catalytic performances, the other authors found that cesium salts were the best systems. In detail, silica-supported lithium silicotungstate gave 70% of yield in acrolein, whereas the corresponding potassium salt yielded 65%, and the cesium salt, only 55% (Table 2).⁴⁰ The authors explained this

trend with the increasing hydrophobicity of the salts (Cs > K > Li). In fact, a high hydrophobicity can hinder the transformation of Lewis acid sites into more selective Brønsted acid sites, as postulated by Alhanash et al. (Scheme 2A).¹⁹ Nevertheless, Atia et al. also admitted that the preparation method also had a significant influence. In fact, when the catalyst was prepared in a reversed manner (first impregnated with cesium and then with silicotungstic acid), the acrolein yield increased from 55% to 67%. This difference was notably explained by the higher number of Brønsted acid sites present in the case of this inverse preparation technique (86 vs 66 μ mol/g).

In the first part of their work, Haider et al. studied nonsupported cesium and rubidium salts of silicotungstic acid, thereby confirming the previous results of Alhanash et al. Indeed, these samples exhibited an outstanding acrolein selectivity (up to 96%).¹⁹ By varying the amount of counterion, they stated that a partial substitution of the protons (50%) was the most favorable feature for yielding high catalytic performances. In the second part, they then supported these salts on two types of alumina: namely, a mixture of theta/delta phase alumina and an alpha alumina. Whereas the latter is more stable than the former, it exhibited a significantly higher specific surface of 88 vs 2 m²/g. Thus, the samples supported over α -alumina exhibited significantly lower activity but, at the same time, rapid deactivation. For example, the yield observed for cesium silicotungstate (50% substitution of protons) supported on α -alumina dropped from 91% to 31% after 10 h of testing, whereas the sample supported over θ - δ -alumina still yielded 84% (vs 85% initially), which is remarkable. In all the cases, the rubidium salt showed similar but slightly lower performances than those of the cesium salt (Table 2).

The idea of using silica-supported salts of heteropoly acids was also caught up by Böhmer et al. who used high-throughput equipment, allowing them to screen runs of 48 catalysts in parallel.⁴² The corresponding catalysts were prepared using silicotungstic, phosphotungstic, silicomolybdc, and phosphomolybdc acid with lithium, potassium, cesium, zinc, or nickel as counter cations. According to the authors, the nature of the used counter cations had no impact on the catalytic performances, which was generally in the range of 45% yield in acrolein. Because of the absence of characterization of the catalysts, the corresponding results are rather difficult to explain with regard to those of Atia et al.,⁴⁰ Haider et al.⁴¹, or Alhanash et al.¹⁹

The possibility for increasing the long-term performance of supported heteropoly acids and, notably, phosphotungstic acid on carbon was studied by Park et al.⁴³ To avoid the deposition of coke on the active sites of the catalysts, the authors proposed to use highly dispersed palladium to capture the carbonaceous species. An amount of 1 wt % palladium enabled increasing the long-term catalytic performances of carbon-supported phosphotungstic acid by more than a factor 2. In fact, whereas the nondoped catalyst lost 60% in activity during 8 h of testing (40% conversion after 8 h), the corresponding doped sample still exhibited 90% conversion. On the other hand, when using silica as a support, no beneficial effect was observed. The positive effect of palladium was explained by the formation of Pd₆C species, thus capturing the coke and maintaining the active sites' integrity. On the other hand, the regeneration showed that the formation of the corresponding carbide species was nonreversible under mild regeneration conditions (350 °C in steam), whereby the regenerated catalysts rapidly lost its

Table 3. Catalytic Performance of Various Mixed Oxide Type Catalysts^a

catalyst	T (°C)	GHSV (h ⁻¹)	TOS (h)	X (%)	S _{acrolein} (%)	S _{acetol} (%)	ref
CeZrO	250	38 ^e	10	93.5	nc	42	49
CeZrCoO	250	34000	nc	80	40	60	50
Cu/Al (30/70 wt %) ^b	220		3	26	nc	92	52
10 wt % Ag/Al ₂ O ₃ ^c	240	6350	5	85	0	60	53
ZrSiO _x activated	325	37400	5	97	40	13	54
ZrSiO _x	325	37400	5	89	26	21	54
ZrNbO _x	290	1900	nc	93	71	16.3	57
WO ₃ /ZrO ₂ + SiO ₂	300	380	75	96	78	8.2	60
WO ₃ /Nb ₂ O ₅ (700 °C)	300	4280	1	98	70.1	3	61
WO ₃ /Nb ₂ O ₅ (400 °C)	300	4280	1	98	74.4	0.4	61
WO ₃ /TiO ₂	280	11220	nc	78.6	73.7	6.4	63
WO ₃ /TiO ₂ ^d	280	11220	nc	90	71.4	1.3	63
SBA-SO ₃ H	275	30420	3	100	82.9	4.2	68
29 wt % NiSO ₄ /SiO ₂	340	22225	3	66	63	16.5	69
29 wt % NiSO ₄ /SiO ₂ ^d	340	22225	3	89	62	8	69
Ta ₂ O ₅ calcd 350 °C	315	4580	10	39	75	19	62

^aT = reaction temperature; GHSV = gas hourly space velocity; TOS = time on-stream; X = conversion of glycerol; S_{acrolein} = selectivity to acrolein; S_{acetol} = selectivity to acetol; nc = not communicated. ^bLiquid phase batch process. ^cUnder H₂ flow. ^dCo-feeding of O₂. ^eWeight hourly space velocity.

performances. Thus, the doping with palladium has rather limited interest for commercial catalysts, notably with regard to the price of palladium.

As we have seen, the use of heteropoly acid catalysts has the disadvantage of significant coke formation. Furthermore, a commonly admitted weak point of this family of catalysts consists of a rather low thermal stability of the active compound. In a previous work, Katryniok et al. introduced the use of zirconia-grafted silica as a support for silicotungstic acid, whereby they claimed an increased thermal stability of the active phase.⁴⁴ In a recent work, they further studied the regeneration of these supported heteropoly acid catalysts using alternating feed technique.⁴⁵ As a first point, it was found that the cofeeding of steam during the regeneration cycle had a positive impact on the catalytic performance afterward, which was explained by the mechanism of the HPA decomposition proceeding via the cleavage of constitutional water. Thus, an increase in the partial pressure of water was claimed to shift the decomposition reaction in favor of the stabilization of the heteropolyanion.

Furthermore, the authors also studied the influence of the cycle length on the catalytic performance. Thus, they claimed that Brønsted acid catalysts were optimally regenerated when employing short reaction/regeneration cycles of typically 2 min. On the other hand, Lewis acid catalysts required rather long cycles, which was explained by the significant activation period of the latter. This again confirmed the mechanism postulated by Alhanash et al. for Brønsted and Lewis acid catalysts (Scheme 2A).¹⁹

The use of heteropoly acids for the dehydration in the liquid phase was finally studied by Shen et al.⁴⁶ using silicotungstic, phosphotungstic, and phosphomolybdic acid as homogeneous catalysts in a semibatch mode. The reaction was performed with pure glycerol, whereby the products could be directly removed from the reaction mixture under the employed conditions (260–320 °C). It is noteworthy that such high temperatures may also lead to thermal decomposition of glycerol (normally starting from 272 °C). From the catalytic results, one can see that silicotungstic acid was the most active catalyst, followed by phosphotungstic acid and—far behind—

by phosphomolybdic acid. The same trend was observed for the formation of acrolein, which was the highest over silicotungstic acid (79% of yield in acrolein). Nevertheless, it is noteworthy that the latter promoted the formation of acetic acid when used in high concentration amounts (0.3 mmol/L), whereby the yield in acrolein dropped. The corresponding effect that was not observed when using phosphorus-based HPAs. Finally, the authors also mentioned the formation of carbon residues, supposedly issued from the condensation or polymerization of reactant or products.

From the recent works on heteropoly acid catalysts, one can thus see that research is still under progress in that field. The large versatility of these catalysts and the numerous possibilities for tuning their acidity via their variations in composition, the selection of the counter cations and also of the support, still leaves room for optimization. On the other hand, the major disadvantage of these catalysts is notably their low thermal stability, which generates problems for oxidative regeneration (burning of the coke) that must be taken into account to build smart regeneration strategies.

2.3. Metal Oxides. Some metal oxides, such as alumina, niobium oxide, and tungsten oxide, are well known solid acids, which are used as catalysts in the metathesis of olefins.⁴⁷ The synthesis of metal oxides, as well as of their binary and tertiary mixtures, is varicolored and strongly influences the chemical and physical properties of the final materials. One may mention the well-known example of the influence of the calcination temperature on the acidity of niobium-V-oxide.⁴⁸ Thus, the study of metal oxides and their mixtures offers many parameters for optimizing the catalytic performance.

Vasconcelos et al. studied the use of binary cerium–zirconium mixed oxides in the dehydration of glycerol.⁴⁹ The corresponding samples were prepared using a silica template. The latter was then dissolved in HF for obtaining well dispersed nanoparticles (10–200 nm particle size). Next to this binary oxide, the authors also used a bare cerium oxide. The as-prepared catalyst exhibited a significant amount of basic sites of up to 0.36 mmol_{CO₂}/g (bare cerium oxide), whereby the main product was acetol (39% yield over CeZrO; Table 3), which confirms the previous results of Kinage et al. It is noteworthy

that the conversion was strongly dependent on the catalyst and the time on-stream. Whereas the activity over the cerium oxide rapidly decreased with the reaction time (30% conversion after 10 h), the binary CeZr oxide exhibited increasing conversion (>90% conversion after 10 h).

De Sousa et al. continued the work of Vasconcelos et al.,⁴⁹ studying this time ternary mixtures of metal oxide catalysts in the glycerol dehydration reaction.⁵⁰ They prepared mixed oxides based on ceria (CeO_2) with zirconia (ZrO_2), nickel oxide (NiO), and cobalt oxide (Co_3O_4), also using the aforementioned technique based on a silica template for obtaining well-dispersed nanoparticles (10–200 nm particle size). The authors admit that the preparation method had a significant influence on the particle size and the homogeneous distribution. The as-prepared catalysts exhibited acidic as well as basic properties, whereby notably the sample based on ceria–zirconia–cobalt oxide (CZC) showed pronounced basicity of 0.75 $\text{mmol}_{\text{CO}_2}/\text{g}$. Correspondingly, the CZC catalyst was found quite selective in the dehydration of glycerol, but rather toward acetol (60%; Table 3) instead of acrolein (40%), which is in agreement with the previous results from Kinage et al. and Vasconcelos et al.^{18,49}

The use of basic mixed oxides was also studied by Lima et al., who used a combination of tin oxide, titania, zirconia, manganese oxide, and the aforementioned nickel/cobalt oxide as catalysts.⁵¹ All the catalysts exhibited basic and weak acid sites in different proportions and quantities. Whereas the amount of the latter was well balanced for SnMnO_x (base/acid ratio of 1), the catalysts based on nickel–cobalt and zirconia–manganese exhibited significantly more basic sites (ratio of 7 and 2, respectively), and those based on tin–zirconia and SnTiO_x , more acidic sites (ratios of 0.5 and 0.6, respectively). Nevertheless, no clear trend could be observed for the catalytic performances. In fact, all the catalysts exhibited pronounced formation of acetol (selectivity ranging from 11 to 22%), but in all cases, the major product was either acrolein (selectivity between 12 and 34%) or acetaldehyde (selectivity 14–28%), this latter being supposedly easily obtained by decomposition of acetol. Thus, the results again confirmed that basic sites catalyze the formation of acetol,¹⁸ but when accompanied by acid sites, the formation of acrolein was always promoted.

Recently, Mane et al. studied the dehydration of glycerol, but with the focus on the selective synthesis of acetol, which they further transformed to 1,2-propanediol.⁵² The catalysts they used were based on copper chromite or copper–alumina and tested in the liquid phase using either water or 2-propanol as a solvent. Under inert atmosphere, all the catalysts selectively promoted the formation of acetol with selectivity between 89 and 100% when used in water. In 2-propanol, the selectivity was generally lower, but the catalytic activity was increased (maximum conversion of 86% vs 26% in water). Thus, the best performance was observed over a copper–alumina catalyst with 26% yield in acetol (92% selectivity at 26% conversion; Table 3). The main byproducts, even under inert atmosphere, were ethylene glycol and 1,2-propanediol. This latter may be formed with hydrogen from the reforming of glycerol under reaction conditions yielding CO/H_2 . Nevertheless, the results are difficult to compare because the reaction was performed in the liquid phase, and the catalysts were not characterized to evaluate either their acidity or their basicity.

Another type of metal catalysts was described by Sato et al. using metallic silver over different supports, namely, alumina,

silica, zirconia, ceria, and titania.⁵³ All the tests were performed in hydrogen flow, whereby the best performance was observed over an alumina-supported catalyst with 85% conversion of glycerol and 91% selectivity to acetol. On the other hand, in the absence of hydrogen or when using diluted hydrogen, the catalytic performance was very low (7% conversion and 63% selectivity to acetol).

Mixed oxides based on zirconia and silica were further studied by García-Sancho et al., who used MCM-4-incorporated zirconia catalysts.⁵⁴ The authors prepared catalysts with Zr/Si ratios of 4, 5, and 10 and also compared the so-obtained samples with one sample based on a common impregnation technique. As expected, the acidity increased with an increasing amount of zirconia. The catalytic performances and, notably, the selectivity were found rather low, whereby three main products were observed: acrolein, acetol, and acetaldehyde. Here, it is noteworthy that the carbon balance increased with the Zr/Si ratio, meaning that the formation of unknown products and/or carbonaceous species was suppressed. This was also confirmed by TGA analysis of the spent catalysts, which showed that the sample with a Zr/Si ratio of 4 exhibited the largest amount of coke deposition. Finally, the authors also studied a pretreatment technique to convert Lewis acid sites to Brønsted sites. Therefore, the catalyst with a Zr/Si ratio of 5 was activated in the presence of water at 315 °C. The as-prepared sample showed an increased conversion (97% vs 89% after 5 h; Table 3), an increased selectivity to acrolein (40% vs 26% after 5 h), and an increased long-term stability (80% vs 47% of conversion after 24 h), which is remarkable, and further confirmed the mechanism postulated by Alhanash et al. for the in situ transformation of Lewis acid sites into Brønsted acid sites in the presence of water (Scheme 2A).¹⁹

Silica-supported niobium oxides were used by Shiju et al.⁵⁵ With regard to results previously reported by Chai et al.,⁵⁶ the authors prepared catalysts with different amounts of niobium oxide (5–40 wt %) and calcined the as-prepared samples at 400–800 °C. The performances over catalysts prepared using different niobia loadings (at the constant calcination temperature of 400 °C) increased with the amount of active phase, with the best result over the catalyst containing 20 wt % niobium oxide (68% yield in acrolein). A further increase to 40 wt % resulted in a drop in conversion (from 98% to 71%). A similar trend was observed when maintaining a constant loading of 20 wt % of active phase but applying higher calcination temperatures. In this case, the conversion dropped from 100% to 78% when changing the calcination temperature from 400 to 800 °C, respectively. The authors performed microcalorimetry experiments with ammonia as a probe molecule to determine the acidity of the catalysts. They could correlate the acrolein formation rate to the observed heat of adsorption, meaning that strong acid sites were favorable for obtaining large yields in acrolein. On the other hand, these catalysts also suffered from pronounced deactivation by coking, whereby they lost half of their initial activity within 10 h of time on-stream.

Lauriol-Garbay et al. also studied the use of silica–zirconia-based catalysts, but used niobia as an additive. They thus prepared ZrNbO_x mixed oxides with a Zr/Nb ratio ranging from 12 to 31.⁵⁷ Increasing the amount of zirconia led to a significant decrease in the selectivity to acrolein, to the benefit of acetol formation. In fact, whereas the catalyst with a Zr/Nb ratio of 12 exhibited 71% selectivity to acrolein (16.3% to acetol), the catalyst with a Zr/Nb ratio of 31 gave 51% selectivity to

acrolein, but 24% to acetol (Table 3). From comparative examples using triclinic and monoclinic zirconia, one can understand that the latter promotes selectivity to acetol (26% and 36%, respectively). Taking into account the results of the characterizations performed on the catalysts, the authors claimed that the formation of polymeric NbO_x on the catalyst surface resulted in the coverage of the nonselective zirconia, thus explaining the observed selectivity to acrolein. Furthermore, the corresponding catalyst (Zr/Nb ratio of 12) was only slightly affected by deactivation (still 90% of conversion after 200 h on stream). Finally, it is noteworthy that the authors also studied the role of acetol under the reaction conditions. Like Suprun et al.,⁵⁸ they injected acetol into the reactor and analyzed the reaction products. As a result, acetone, acetylaldehyde, acetic acid, and carbon oxides were detected as the main products with selectivity of 39%, 20%, 18%, and 11%, respectively.

In their following study, the same authors performed a detailed study on the influence of the acidity to get a more fundamental understanding of the aforementioned catalysts.⁵⁹ It was found that the sample with a large Zr/Nb ratio of 31 exhibited strong acid and basic sites. With regard to the mechanism proposed by Kinage et al.,¹⁸ the latter were responsible for the pronounced formation of acetol, whereas the strong acid sites yielded pronounced formation of coke and, thus, a rapid deactivation of the corresponding catalyst. On the other hand, the catalysts with low Zr/Nb ratios of 12 and 19 exhibited only medium and weak acid sites, whereby the deactivation was suppressed. It is finally noteworthy that all the catalysts needed a significant activation period of 1–2 h. During this time, the selectivity to acrolein increased considerably from no more than 40% to about 70%, which is in agreement with the reaction mechanism proposed by Alhanash et al. for the activation of Lewis acid catalysts by conversion to Brønsted sites.¹⁹

Lauriol-Garbay et al. continued their work on zirconia-based catalysts but with tungsten oxide as an additive.⁶⁰ In contrast to García-Sancho et al.,⁵⁴ they incorporated silica not as a support but as a doping agent. Thus, the preparation method was based on the extraction of silica from the glassware used for the synthesis. Similarly to their work on zirconia-niobia catalysts,^{57,59} the coverage of tetragonal silica was found crucial for yielding high selectivity and increased long-term performance. Thus, the optimum surface density of tungsten oxide was found between 2.5 and 3.8 W atoms/nm². A lower density resulted in less selective catalysts as a result of the poor coverage of the zirconia. Finally, the authors explained the positive effect of the silica doping by the same mechanism, that is, by the coverage of the nonselective zirconia. The as-prepared catalysts exhibited a remarkable long-term performance with 70–72% yield in acrolein after 75 h, against 75% initially (Table 3).

To complete the puzzle, the group of Ueda studied the combination of tungsten and niobium mixed oxides for the dehydration of glycerol.⁶¹ The corresponding samples were prepared using hydrothermal synthesis, whereby rod-like crystals with a layered structure were obtained. According to the final calcination temperature, the specific surface area ranged from 43 to 100 m²/g, and the amount of acid sites, from 0.016 to 0.19 mmol/g (calcination performed at 700 and 400 °C, respectively). A higher calcination temperature of 1000 °C resulted in the collapse of the layered structure, yielding the $\text{Nb}_8\text{W}_9\text{O}_{47}$ phase, which was accompanied by a significant loss in surface and specific acidity (2 vs 100 m²/g and 0.003 vs

0.016 mmol/g, respectively). From the catalytic results, it appeared that the samples calcined at low temperature exhibited better performance, yielding 74% and 70% acrolein (calcination temperature of 400 and 700 °C, respectively; Table 3). Nevertheless, both catalysts significantly lost their performances with time on-stream, yielding ~60% and 50% acrolein, according to the calcination temperature (400 and 700 °C, respectively). It is noteworthy that a commonly prepared $\text{WO}_3/\text{Nb}_2\text{O}_5$ catalyst exhibited significantly lower yield in acrolein (38%), thus suggesting that the planar structure of the mixed oxide was responsible for the catalytic performances.

Another type of catalyst was proposed by Tao et al., who used tantalum-(V)-oxide as a catalyst.⁶² Similarly to niobium-(V)-oxide, the authors modified the acidity via the calcination temperature. Nevertheless, in contrast to niobium-based catalysts, no clear trend could be observed, as for calcination temperatures between 110 and 350 °C, the total number of acid sites increased (from 175 μmol/g for a calcination temperature of 110 °C to 302 μmol/g for a calcination temperature of 350 °C) and then decreased again for calcination temperatures between 350 and 700 °C (70 μmol/g for a calcination at 700 °C). It is noteworthy that the relative amount of strong acid sites followed the same trend. Accordingly, the best performance was obtained over the catalyst calcined at 350 °C, yielding 29% acrolein (Table 3). As a typical feature for this kind of Lewis acid catalyst, the selectivity to acetol was rather significant, generally in the range of 20%.

The use of titania-supported tungsten oxide was studied by Ulgen et al.⁶³ Thereby, the authors employed commercial titania carriers at a constant loading of ~18 wt % tungsten oxide. The catalytic performance observed over the various supports was quite similar, with a glycerol conversion in the range of 76–89% and a selectivity to acrolein of 74–77%. The observed slight differences were ascribed to the presence of sulfate ions in some carriers, increasing the acidity of the catalyst. Because the catalytic activity was affected by deactivation due to the development of carbonaceous species, the cofeeding of oxygen was also studied. From the corresponding results, the selectivity to acrolein was only slightly affected (71% vs 74% without oxygen; Table 3), whereas the selectivity to acetol decreased by at least four times (1.3% vs 6.4% without oxygen). Nevertheless, even with cofeeding of oxygen, the deactivation was only slightly slowed down, meaning that the conversion dropped to 50% after 350 h on-stream (instead of 40% in the absence of O₂). Finally, it is worth mentioning that the corresponding optimized catalyst was recently described by Liebig et al. for use in a tandem reactor with consecutive ammonoxidation of the intermediately formed acrolein to acrylonitrile.¹⁶

The use of sulfated zirconia was intensively studied by Cavani et al. and Yang et al.^{64–66} Whereas the latter authors used supported catalysts in the liquid phase, the first group used bulk samples in the gaseous phase. Hereby, Cavani et al. especially studied the impact of the sulfate amount and the possibility to cofeed oxygen (aerobic conditions). From their results, it can be deduced that the family of sulfated zirconia shows rather low selectivity to acrolein (in the range of 20–30%) but a pronounced formation of heavy products. The authors explained this effect by internal mass transfer limitations inside the catalyst particles. Thus, the type of the deposited carbonaceous species depends on the reaction conditions: whereas anaerobic conditions yielded graphitelike coke, the presence of oxygen in the feed led to amorphous

coke. Nevertheless, the deposition of carbonaceous species was found to be only one of the factors responsible for the deactivation of the catalysts. In fact, the loss of sulfur and the autoreduction of the sulfate groups were also identified as parameters contributing to the deactivation of the catalysts with time on stream. Whereas autoreduction could be eliminated under oxidative conditions, the leaching of sulfur was still present. Nevertheless, the authors stated that the latter was limited to a small extent and also mentioned the possibility of cofeeding SO_3 gas to replenish the depleted sites, as previously proposed by Dubois et al.⁶⁷

Sulfonated SBA-15 was recently described by Lourenco et al.⁶⁸ The as-prepared catalysts exhibited mesopores of a diameter of 6 nm and a medium amount of Brønsted acid sites (0.6 mmol/g). The initial yield in acrolein was between 93% (300 °C) and 83% (275 °C; Table 3), whereby higher reaction temperatures caused increased deactivation (25% vs 40% yield in acrolein after 140 h on stream at 300 °C). It is noteworthy that the selectivity remained highly stable at about 80% when the reaction was performed at 275 °C.

Finally, Gu et al. reported the use of silica-supported nickel sulfate as a promising catalyst for the dehydration of glycerol.⁶⁹ The initial idea of using nickel sulfate was based on the presence of basic sites when using sulfated zirconia, which could result in increased formation of acetol. The authors meticulously studied the influence of the amount of nickel sulfate as well as the calcination temperature of the catalyst. The total acidity decreased with the calcination temperature (i.e., 3.1 mmol_{NH₃}/g for a calcination temperature of 350 °C vs 0.1 mmol_{NH₃}/g for a calcination temperature of 750 °C). Correspondingly, the catalytic performances, observed in the presence of oxygen, decreased with the calcination temperature showing 97% conversion and 68% selectivity to acrolein over the NiSO_4 catalyst calcined at 350 °C against 58% conversion and 31% selectivity to acrolein for the nickel-sulfate catalyst calcined at 750 °C (Table 3). It is noteworthy that the active phase was identified as a hydrate of nickel sulfate ($\text{NiSO}_4 \cdot x\text{H}_2\text{O}$) with an amount of coordination water (x) between 0 and 1. Furthermore, the authors claimed that the main problem of deactivation was due to the loss of sulfate, resulting in the irreversible degradation of the active phase.

Among the three different catalyst systems presented, the mixed oxides are the largest family. In fact, the combination of various elements offers a multitude of parameters to be adjusted. Thus, the optimal catalyst may consist of more than 5 elements, such as in the case of industrial catalysts for oxidation or ammonoxidation (the SOHIO catalyst for the ammonoxidation of propylene contains 12 different elements). The major drawback of the mixed oxide catalysts is notably the relatively lower selectivity to acrolein, supposedly due to the presence of Lewis acid or even basic sites (amphoteric oxides). Thus, it is interesting to note that some groups have even focused on the development of mixed oxide catalysts for the selective synthesis of acetol.

2.4. Others. A new family of catalysts, namely, silica-supported ionic liquids, was described for the dehydration of glycerol by Munshi et al.⁷⁰ The corresponding ionic liquids were based on imidazole, pyrrolidone, triphenyl phosphine, and picoline and exhibited initial yields in acrolein between 15 and 49%. Nevertheless, all the catalysts significantly lost activity even during the first 4 h of testing. In fact, the best catalyst, based on 1-methyl-3-(3-sulfopropyl)-1*H*-imidazol-3-ium 4-

methylbenzenesulfonate, exhibited 20% yield in acrolein after 4 h vs the aforementioned 49% after 2 h of reaction. The authors ascribed this significant decrease to the thermal decomposition of the ionic liquids, which are generally stable up to 350 °C, a temperature close to the reaction conditions (275 °C). Thus, contrary to the liquid phase, ionic liquid catalysts seem rather unfavorable for the dehydration in the gaseous phase.

3. OXIDEHYDRATION OF GLYCEROL

As aforementioned, the dehydration of glycerol to yield acrolein is only one step in the process workflow. As a matter of fact, acrolein is only an intermediate and is, thus, generally converted on-site. In fact, because of the toxicity as well as the flammability of acrolein, it is preferentially neither stored nor transported, but rapidly converted to either DL-methionine or acrylic acid in the most advanced technologies in the field. In contrast to the synthesis of DL-methionine, the formation of acrylic acid is another 1-step process whereby, already in 2010, the group of Ueda proposed a combination using a multifunctional catalyst: acidic for the dehydration and redox for the oxidation.³⁶

Recently, the oxidehydration of glycerol yielding acrylic acid via intermediate formation of acrolein was studied by Kampe et al., Soriano et al., and Chieregato et al. using mixed oxides based on tungsten, niobium, vanadium, and molybdenum.^{13–15} Whereas the former group focused rather on the mechanistic aspects of WMoV catalysts, the two latter groups studied the influence of vanadium and niobium doping on the catalytic performances of tungsten oxides. From the study of Kampe et al., it could be concluded that the oxidehydration proceeds via a Mars–van Krevelen mechanism for yielding acrolein. Furthermore, the authors concluded that the presence of tungsten was beneficial because it increases the oxygen mobility.

The work of Soriano et al. was focused on the use of tungsten–vanadium catalysts with different V/W ratios ranging from 0.12 to 0.24.¹⁴ As expected, the redox properties increased with the amount of vanadium in the catalyst. This notably finds expression in the decreasing selectivity to acrolein and increasing formation of acrylic acid and carbon oxides. In fact, whereas a vanadium-free catalyst yielded 67% acrolein but only 1% acrylic acid, the catalyst with a V/W ratio of 0.21 yielded 11% acrolein but 26% acrylic acid (Table 3). Nevertheless, a further increase in the vanadium content favored the overoxidation to carbon oxides, which reached up to 63% yield for the catalyst with a V/W ratio of 0.24. As a conclusion, the redox properties have to be well balanced to enable the selective oxidation of intermediately formed acrolein without promoting overoxidation. It is also noteworthy that the catalysts were strongly affected by deactivation, which was ascribed to the irreversible formation of V^{5+} species.

Later on, Chieregato et al. studied the same family of tungsten–vanadium catalysts, but further introduced niobium to increase the acidity of the catalysts.¹³ In fact, the aforementioned pronounced formation of carbon mono- and dioxide, over vanadium-based catalysts can originate from the over oxidation of acrolein or glycerol. In the case that glycerol was the source of carbon oxides, an increase in acidity would promote the dehydration reaction, whereby the over oxidation decreased. Furthermore, the addition of Nb is known to stabilize the V^{4+} oxidation state, whereby the deactivation issue was reduced. It was found that a combination of tungsten and niobium (W/Nb) resulted in a catalyst with high selectivity to

Table 4. Catalytic Performance in the Oxidehydration of Glycerol^a

catalyst (atomic ratio)	T (°C)	GHSV (h ⁻¹)	TOS (h)	X (%)	S _{acrolein} (%)	S _{acrylic acid} (%)	S _{CO_x} (%)	ref
WNbO _x (W/Nb 0.2)	290	9470	2	>99	73	2.5	1.5	13
WVNbO _x	290	9470	2	>99	19	24	38	13
WO _x	290	9470	2	>99	76	1	12	14
WVO _x (W/V 0.21)	290	9470	2	>99	11	26	47	14
HZSM-5 (Si/Al 13)	300	800	7	100	81	nc	nc	71
HZSM-5, VMoO _x ^b	300	800	7	100	28	46	13	71
WZrO _x	305	12260	3	98	77	nc	7.4	72
WZrO _x , WVMo ^b	305	12260	3	100	7.8	44.1	20.2	72
WZrO _x , WVMo mix	305	12260	3	100	19.5	0.5	23.8	72

^aT = reaction temperature; GHSV = gas hourly space velocity; TOS = time on-stream; X = conversion of glycerol; S_{acrolein} = selectivity to acrolein; S_{acrylic acid} = selectivity to acrylic acid; S_{CO_x} = selectivity to carbon oxides; nc = not communicated. ^bTwo-step process.

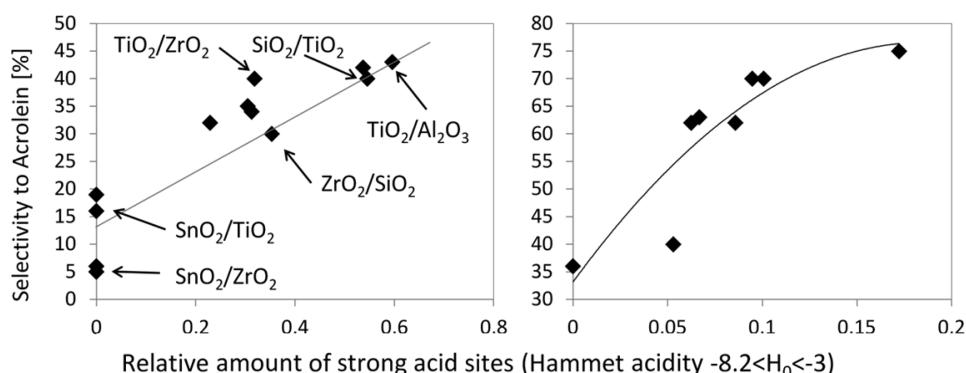


Figure 4. Correlation between the ratio of strong acid sites (Hammett acidity) and the selectivity to acrolein over different mixed oxides (left) and over tantalum oxide calcined at different temperatures (right).^{75,62}

acrolein (40%), whereby no acrylic acid was observed, which was ascribed to the absence of redox properties (Table 3). On the other hand, the aforementioned tungsten–vanadium catalyst (W/V) promoted the formation of oxidation products, such as acrylic acid (20% selectivity), and carbon oxides (55% selectivity). When niobium was added to the W/V catalyst, the formation of CO_x significantly decreased (35% selectivity), to the benefit of acrolein and acrylic acid (17% and 34% selectivity, respectively). Then the balance between redox and acid properties is a key to obtaining high yields in acrylic acid and avoiding nonselective oxidation to carbon oxides.

The previous results about oxidehydration show that the yield in acrylic acid is generally low. Thus, the concept of using bifunctional catalysts combining acidity and redox-properties in a single reactor is not favorable. Therefore, Witsuthammakul et al. and Massa et al. studied the use of a two-step process in a single reactor containing two catalytic beds. Thus, the intermediately formed acrolein could be directly converted to acrylic acid in the second bed.^{71,72} Correspondingly, the authors employed two different catalysts: an acid catalyst for the dehydration step (namely, HZSM-5 zeolite in the case of Witsuthammakul et al. and tungsten oxide on zirconia in the case of Massa et al.) and a vanadium–molybdenum oxide for the oxidation step. Whereas the reaction temperature had to be identical for both reactions (300–305 °C) because of the use of a single reactor, the contact time for each reaction was adjusted via the amount of catalyst in the corresponding bed. Whereas Witsuthammakul et al. found that the contact time for the second reaction (oxidation) had to be chosen twice as long as for the first reaction (dehydration), Massa et al. stated that a similar contact time in both catalytic beds was a good compromise. Both groups obtained nearly identical yields in

acrylic acid of 44% and 45%, respectively (Table 4). Nevertheless, in both cases, the conversion of the intermediately formed acrolein was still incomplete, suggesting that the reaction conditions or the catalyst for the second step were still not optimized. In fact, the commercial synthesis used for the conversion of propene to acrylic acid also proceeds via the oxidation of acrolein over V–Mo–O catalysts at around 270 °C but at a pressure of 2 atm.⁷³ Thus, one can assume that the last-mentioned parameter was responsible for the observed low yield in acrylic acid.

The combination of dehydration and oxidation over a multicomponent catalyst seems rather difficult with respect to the good balance of acidity and redox properties. Thus, the use of a well established oxidation catalyst combined with an efficient dehydration catalyst seems much more promising from the current point of view.

4. EFFECT OF ACIDITY

From the work of Chai et al.⁷⁴ in 2007, it was first concluded that the acid strength had a strong impact on the catalytic performance. To summarize this pioneer work, one can draw up two main theses: (i) the selectivity to acrolein is highest over strong acid catalysts (meaning with a Hammett acidity between -3 and -8.2) and (ii) the conversion is not affected by the acidity.

Following this pioneer work, the influence of the acid strength on the catalytic performance was studied by Tao et al. also using the Hammett acidity as an indicator for ranking the catalysts.^{62,75} In their first work, they used combinations of mixed oxides, such as tin oxide, titania, zirconia, alumina, and zinc oxide, similar to Lima et al.,⁵¹ and in their second article, they used tantalum oxide calcined at different temperatures.

With the help of the different Hammett indicators, the catalysts were classified according to the number of strong acid sites (meaning a Hammett acidity between $-8.2 < H_0 \leq -3$). The catalysts without any strong acid site, such as tin-titania oxide or tin-zirconia, showed only poor selectivity to acrolein (6–20%). With an increasing ratio of strong acid sites, the selectivity increased to 43% for a relative amount of 60% strong sites (titania–alumina catalyst; Figure 4). The same result was also obtained over tantalum oxide catalysts calcined at different temperatures (Figure 4). Thus, the first hypothesis of Chai was confirmed: namely, that the selectivity to acrolein was highest over strong acid catalysts. On the other hand, it is surprising that the catalytic activity was correlated neither to the total amount of acid sites (Figure 5), nor to the absolute amount of

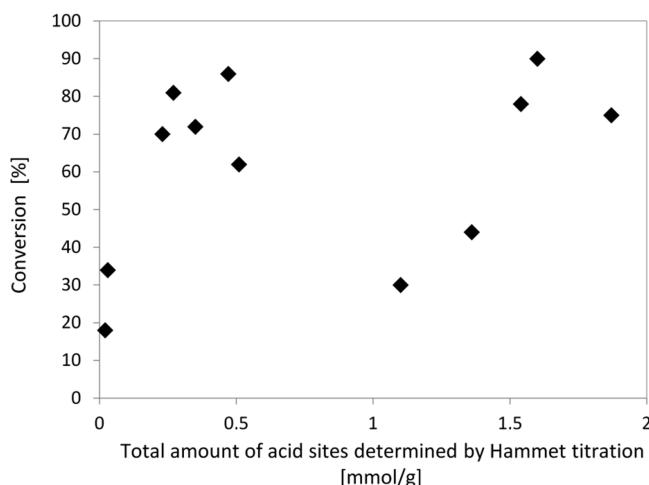


Figure 5. Conversion as a function of the total amount of acid sites (Hammett acidity) using data from ref 75.

strong sites (Figure 6), as one would expect for a surface-catalyzed reaction. In fact, the increase in the number of acid sites is equal to the increase in the number of active sites, whereby the reaction rate (or conversion) should increase significantly.

Thus, the influence of the acidity on the catalytic activity (conversion) was still not clear, when Suprun et al. performed

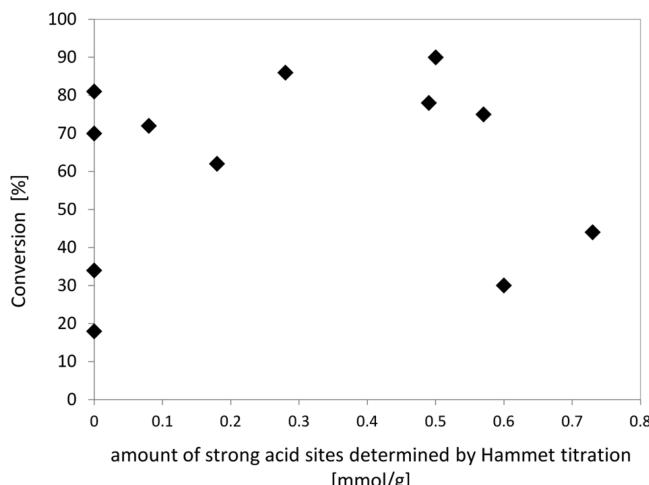


Figure 6. Conversion of glycerol as a function of the amount of strong acid sites (Hammett acidity) using data from ref 75.

their work on supported phosphoric acid doped with various metals (Cr, Mn, Mo, ...).^{76–78} The catalysts were prepared by simultaneous impregnation of γ -alumina with phosphoric acid and a corresponding metal. The as-prepared samples were characterized by ammonia TPD, and the catalytic performance was evaluated during 30 h of testing. Hereby, Suprun et al. found that the overall dehydration activity, yielding acrolein and acetol, as well as the catalytic activity were correlated to the amount of acid sites and the density of the acid sites, respectively (Figures 9 and 10), which could be expected for a surface-catalyzed reaction.^{77,78}

When correlating the selectivity to acrolein to the surface acid density, no clear picture was observed for short reaction times (1 h, Figure 7), which was ascribed to the Lewis acid

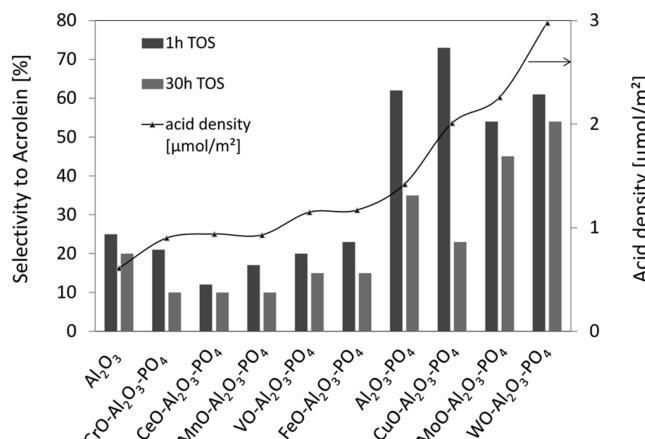


Figure 7. Correlation between surface acid density and selectivity to acrolein over various catalysts (plotted from ref 76).

character of the support (γ -alumina), necessitating an activation period.¹⁹ But for an increased reaction time of 30 h, the selectivity to acrolein increases with the surface acid density (Figure 8). This result is rather surprising because the selective dehydration of glycerol does not require two closely localized acid sites.

To understand the influence of the density of the acid sites on the selectivity to acrolein, one has to take a look at the work

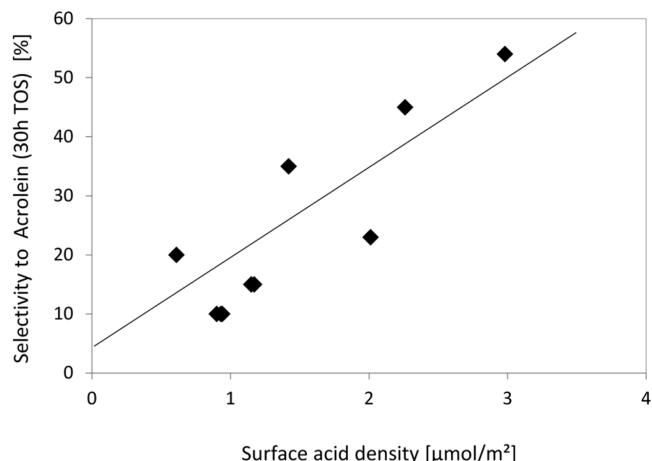


Figure 8. Selectivity to acrolein as a function of the surface acid sites' density for 30 h of time of reaction (time on-stream; TOS) (plotted using data from ref 78).

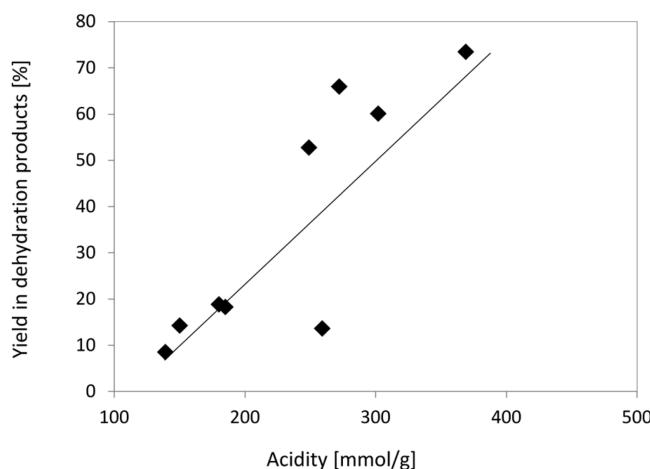


Figure 9. Yield in acetol and acrolein as a function of the total amount of acid sites (plotted using data from ref 77).

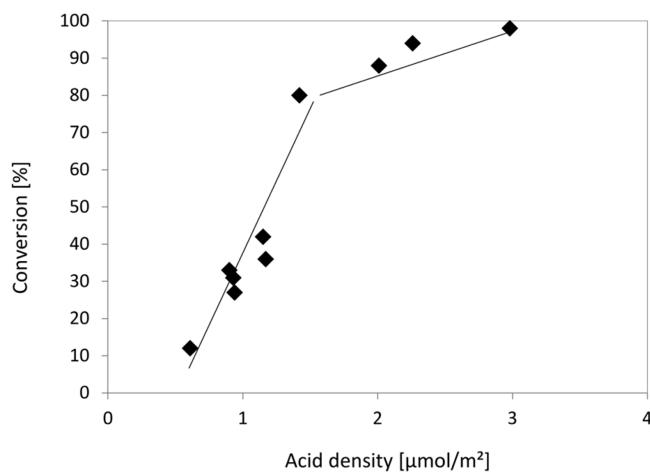


Figure 10. Conversion of glycerol as a function of the acid sites density (plotted using data from ref 78).

of Stojić et al.⁷⁹ characterizing the acidity together with the basicity. In contrast to the previous works of Chai et al. and of Tao et al.,^{74,75} the authors did not classify the catalysts according to the Hammett acidity, but used the very powerful technique of microcalorimetry with SO_2 and NH_3 as probe molecules to determine the acid strength and amount. Thus, they characterized eight catalysts—namely, zirconia, tungsten–zirconia, ceria–zirconia, lanthanum oxide–zirconia, and titania (anatase and rutile) as well as phosphotungstic acid supported on titania and tungsten–zirconia—and further evaluated their catalytic performances. As expected, the strong acid catalysts, such as tungsten–zirconia and the samples containing phosphotungstic acid, exhibited the highest performances in the range of 72–74% yield in acrolein. On the other hand, the amphoteric and basic samples exhibited low performance of no more than 4% yield in acrolein. Finally, the authors were able to establish a correlation between the selectivity to acrolein and the surface density of basic sites (Figure 11). In fact, the highest selectivity to acrolein (>70%) was obtained over the catalysts exhibiting extremely low amounts (<0.5 $\mu\text{mol}/\text{m}^2$) or a total absence of basic sites, such as in the case of the phosphotungstic acid-based catalysts. Furthermore, the selectivity to acrolein was the highest when the ratio of the surface acid density to the surface density of basic sites was higher than

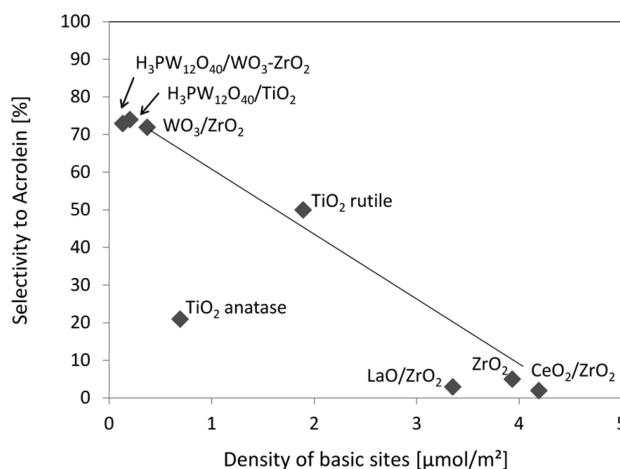


Figure 11. Correlation between selectivity to acrolein and density of basic sites (determined by microcalorimetry) using data from ref 79.

6 (Figure 12). Thus, it is not the surface acid density, but rather, the simultaneous presence of basic sites that is responsible for a decreased selectivity to acrolein.

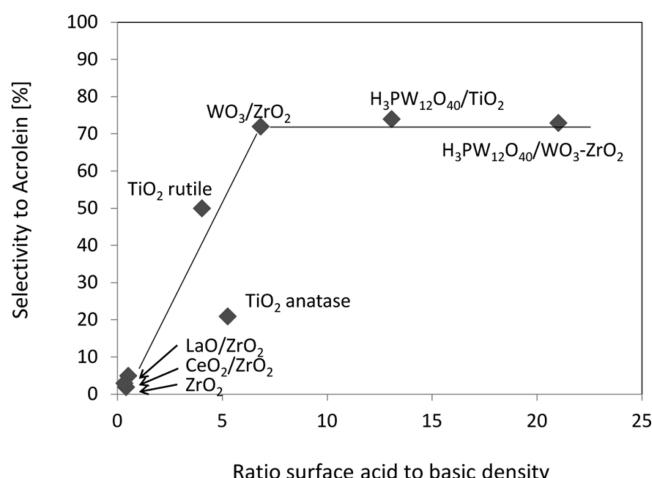


Figure 12. Correlation between selectivity to acrolein and ratio of surface acid to basic density (determined by microcalorimetry) using data from ref 79.

To conclude, the acid strength is effectively the key parameter to high selectivity in acrolein, whereas the catalytic activity depends on the number of active sites at the catalyst surface (surface acid density). Furthermore, the selectivity to acrolein can be strongly altered in the case of the simultaneous presence of basic sites, which favor the formation of acetol (cf. Scheme 2B).

5. THEORETICAL CHEMISTRY AND MECHANISM

The mechanism of the dehydration of protonated glycerol in aqueous media was studied by Caratzoulas et al. using quantum mechanics and molecular dynamics calculations.⁸⁰ The main difference compared with the previous works of Nimlos et al.⁸¹ lies notably in the consideration of the presence of water molecules in the reaction mechanism. Hereby, the authors state that both dehydration steps were mediated by water, which facilitated the protonation (Figure 13). In fact, for the first dehydration step (yielding 1,3-propenol), the authors

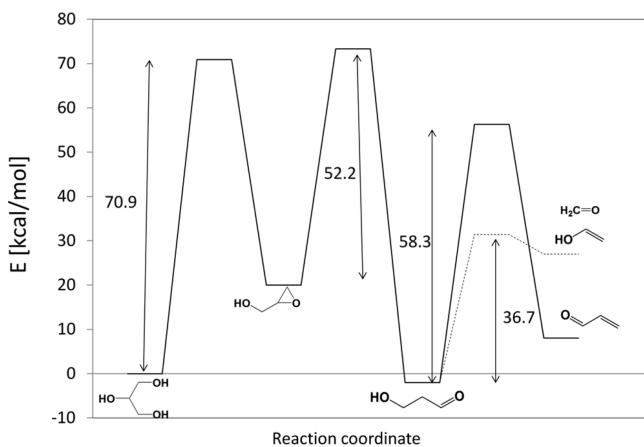


Figure 13. Energy profile for the glycerol dehydration in protic environment (plotted using data from refs 80 and 81).

calculated an activation energy of 21.7 kcal/mol when assuming hydrogen transfer before scission of the secondary C–O bond and 19.2 kcal/mol for the reverse order (C–O bond scission before hydrogen transfer). The thus obtained values are only slightly higher than those obtained for the water-free mechanism (16.7 kcal/mol). On the other hand, the second dehydration was found to be strongly favored in the presence of water, with an activation energy of 13.0 kcal/mol against 33.9 kcal/mol in the absence of water. From these figures, the authors notably state that, in the absence of water, the C–C bond scission was much more probable because it exhibited an activation energy of no more than 28.5 kcal/mol, which is lower than that required for the second dehydration step. On the other hand, in the presence of water, the C–C scission was rather improbable because it exhibited an activation energy of 84.0 kcal/mol. The overall reaction was found to be slightly exothermic, by -8.0 kcal/mol. From these figures, one can conclude that even the gas-phase reaction over acid catalysts most probably involves a hydrated environment to facilitate the second protonation step.

Following their previous work,⁸² Kongpatpanich et al. performed DFT calculations to determine the differences between the dehydration pathway leading to acrolein and acetol over an H-ZSM-5 zeolite.⁸³ As in the case of acrolein, the authors considered the stepwise mechanism more favorable than the concerted one (Figure 14). In fact, whereas the

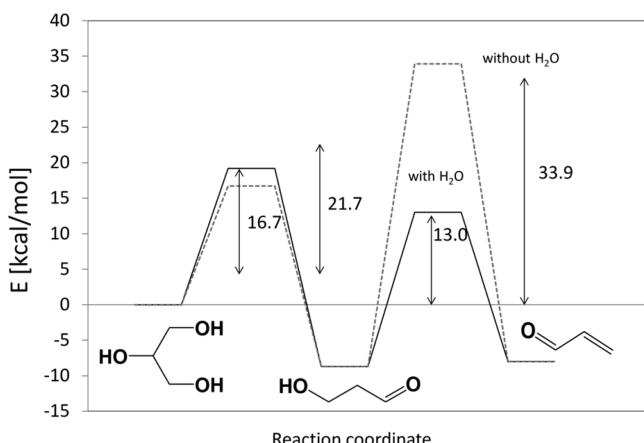


Figure 14. Multistep reaction mechanism toward acrolein and acetol.⁸³

concerted dehydration to acrolein exhibited an activation barrier of 72.0 kcal/mol for the first dehydration step, the activation energy via the stepwise mechanism was calculated as 42.5 kcal/mol.

The formation of acrolein and acetol proceeds via the same mechanism, except that the latter involves the protonation of the primary hydroxyl group, not the secondary one. Following the cleavage of the hydroxyl group, an alkoxide is formed in both cases. The activation barrier is comparable in both cases (42.3 kcal/mol for acetol; 42.5 kcal/mol for acrolein). In the following step, the alkoxide returns the proton, yielding the enol form, which is associated with an activation energy of 26.8 kcal/mol in the case of acetol and 19.7 kcal/mol in the case of acrolein. The difference of 7.1 kcal/mol explains why the formation of acrolein is kinetically favored over the formation of acetol. The final step in both cases consists of the tautomerization to the keto species (acetol and 3-hydroxypropanal, respectively). Hereby, it is noteworthy that the final energy state observed for acetol formation is significantly lower (-27.2 vs -17.1 kcal/mol), meaning that acetol is thermodynamically more stable. As a conclusion, the formation of acetol is thermodynamically favored, whereas the reaction pathway toward acrolein is kinetically less hindered.

The neutral mechanism for the decomposition of glycerol, initially studied by Nimlos et al.,⁸¹ was revisited by Liano et al., who proposed glycidol as an intermediate (Figure 15).⁸⁴ Thus,

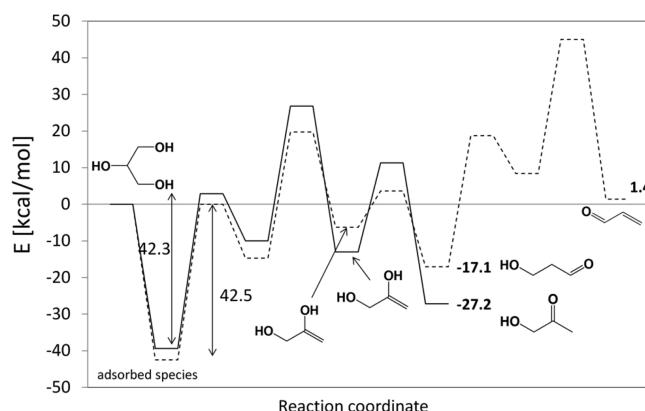


Figure 15. Reaction pathway toward acrolein via glycidol as intermediate.⁸⁴

the authors evoke a multistep mechanism resulting in the first step to the formation of glycidol, followed by the conversion to 1-hydroxypropanal that finally converts to acrolein or decomposes to formaldehyde and vinyl alcohol. The corresponding activation energies are 70.9, 52.2, 58.3, and 36.7 kcal/mol, respectively. Notably, the difference between the two last mentioned energies suggested that the decomposition to formaldehyde and vinyl alcohol was favored over the formation of acrolein. Finally, compared with the activation energy proposed by Nimlos et al. (70.9 kcal/mol), the new mechanism via glycidol seems energetically equivalent, meaning that glycidol is a potential intermediate when considering a neutral mechanism. Nevertheless, for the moment, no experimental data is available to verify the corresponding mechanisms because the dehydration is generally not performed in aprotic conditions, and the protic conditions have a crucial effect on reactivity, as aforementioned.

6. CONCLUSION

As we have seen in the previous sections, the research for new catalysts and new regeneration techniques, but also the fundamental research for understanding the mechanism behind the dehydration of glycerol, is still in progress. From the current point of view, it is rather surprising that the corresponding technologies have still not reached industrial application. In fact, apart from some rumors about the upscaling of the process by ARKEMA in Pierre- Bénite (France) and Nippon Shokubai in Japan, it seems that the corresponding process has not even been evaluated at the pilot scale. This is even more amazing because the economical aspects clearly show the feasibility and viability of the process. Posada et al. already calculated that the valorization of glycerol to acrolein would present a sales price-to-production price ratio of 1.3, meaning that the corresponding process is profitable.¹¹ More recently, Liu et al. benchmarked the conventional acrolein synthesis, based on the oxidation of propylene, against the glycerol route.⁸⁵ From the obtained figures, it was concluded that the glycerol dehydration, including a previous purification of glycerol, can be viable even for crude glycerol prices higher than 350 \$/t. As a matter of fact, it is clear that existing propylene oxidation plants will not be converted to glycerol dehydration plants. Nevertheless, the demand in acrolein (or more precisely, in the final products manufactured from acrolein) is increasing in Asia because the increasing income in this part of the world has doped the meat consumption, which requires DL-methionine for rapid growth. As a second scenario, the demand from consumers for biobased materials, notably in Western Europe and in the US, may also drive industry to introduce “green” products, such as superabsorbents for baby diapers based on poly(acrylic acid).

Finally, the high price of propylene will also play an important role in the economical equation. In fact, Dubois et al. already proposed a coinjection of glycerol into the propylene feed of an oxidation unit.⁸⁶ The latter can enable varying the reactants ratio (glycerol/propylene) and thereby decreasing the dependence on the propylene feedstock availability and its market spot price potential volatility. In addition, the tendency to couple glycerol dehydration with successive reactions (ammonoxidation to acrylonitrile; oxidation to acrylic acid) clearly demonstrates that the obtained acrolein can already meet the specifications required for the following steps (especially in terms of purity). Thus, it is most probably just a question of time until we see more processes on glycerol dehydration technology in the near future.

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Notes

The authors declare no competing financial interest.

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