

Article

# Low Temperature Dehydration of Glycerol to Acrolein in Vapor Phase with Hydrogen as Dilution: From Catalyst Screening via TPSR to Real-Time Reaction in a Fixed-Bed

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**Abstract:** Temperature programmed surface reaction (TPSR) was developed as a method for rapid screening of catalysts. In this study, a series of acid catalysts was screened for the low-temperature dehydration of glycerol to acrolein via TPSR. Results suggested that most catalysts show activity of glycerol conversion to acrolein at a greatly different temperature range. HY, SiO<sub>2</sub> supported H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> (STA/SiO<sub>2</sub>), SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub>, and SO<sub>4</sub><sup>2-</sup>/TiO<sub>2</sub> were observed to be efficient for the conversion of glycerol into acrolein at 210 °C, which was significantly lower than that generally reported (250–340 °C). Moreover, high selectivity of acrolein was gained at 85% and 86% over SiW/SiO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup>/TiO<sub>2</sub>, respectively. A new style catalyst, ZnCl<sub>2</sub>/SiO<sub>2</sub>, was also found to be highly selective to acrolein and evaluated in a conventional fixed-bed reactor. Especially, stability tests showed that the catalyst life was up to 300 h with no clear deactivation on ZnCl<sub>2</sub>/SiO<sub>2</sub> with hydrogen as dilution.

**Keywords:** glycerol; low temperature dehydration; acrolein; TPSR

## 1. Introduction

Recently, due to development in bio-diesel fuel, a large surplus of glycerol is produced as a byproduct [1]. In addition, glycerol can also be produced by fermentation of sugars, or as a byproduct of ethanol production from lignocellulose [2]. As a result, many research efforts have been put to convert glycerol into valued-added chemicals or fuel, and glycerol dehydration to acrolein presents an important route [3]. Acrolein is a high-demand (US capacity > 250 MMlbs) unsaturated aldehyde for production of acrylic acid esters, superabsorber polymers, and detergents [4]. The commercial production route based on the oxidation of propylene with a Bi/Mo mixed oxide catalyst [5]. Furthermore, acrolein is of particular interest as a precursor for 1,3-Propanediol, which is an important and valuable compound in polymer production [6].

Under sub-critical or super-critical water (25–35 MPa and 250–290 °C), the acrolein yield can be up to 75% with ZnSO<sub>4</sub> as a catalyst. The high cost of such severe conditions, and the difficulty in recycling the homogenous catalyst, make this process unfavorable for commercial production. Chai et al. reported the vapor-phase dehydration of glycerol over solid acid catalysts with a wide range of acid-basic properties at 315 °C, and they further demonstrated that the most effective catalysts have acid strength at  $-3 < H_0 < -8.2$  [7,8]. Tsukuda et al. reported that the heteropoly acids were effective catalysts for glycerol dehydration, and the highest acrolein selectivity can be 86.2% over the

SiO<sub>2</sub> supported silicotungstic acid at 275 °C [9]. Wang et al. reported that the H-ZSM-5 catalyst with a nano straight channel along the b-axis and medium acidity could give a high acrolein selectivity (87%) with 98% glycerol conversion at 320 °C [10].

The previous studies have mainly focused on screening catalyst types at a constant high temperature (typically at 275–325 °C) [7–9]. Actually, the suitable reaction temperatures should be various to different solid acid catalysts. Fukuoka et al. reported that mesoporous sulfated zirconia-silica catalysts bearing only Brønsted acid sites converted glycerol to acrolein in an 81% yield with 82% selectivity at 250 °C [11]. However, few research efforts have been done on optimizing the reaction temperature, and little information has been reported on the approximately suitable reaction temperature over different solid acid catalysts.

One objective of this work is to give clues of a suitable reaction temperature. Temperature programmed surface reaction (TPSR) is a powerful technique for adsorption, reaction, and desorption of the reactants and products at the catalysts' surfaces. According to the temperature range and peaks of acrolein desorption in TPSR, the qualitative data can be gained to determine the suitable reaction temperature. In this case, we present the primary TPSR results over a wide range of acid catalysts including Lewis acids, zeolites, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, super acid, and heteropoly acid.

Another objective is to develop a catalyst to perform the reaction at low temperatures with a high yield of acrolein. Generally, a milder reaction temperature is favorable for catalyst stability, operation, and economy. Furthermore, the enthalpy grows when increasing the reaction temperature for the dehydration reaction (+25.9 kJ/mol @ 210 °C, +28.3 kJ/mol @ 300 °C). Since the dehydration reaction is more facile over the catalyst with lower desorption temperature in the TPSR profiles, the catalysts with high activity can be gained based on the TPSR results. After screening via TPSR, the catalysts with low temperature desorption peaks were further investigated in a fixed-bed at 230 °C.

## 2. Result and Discussion

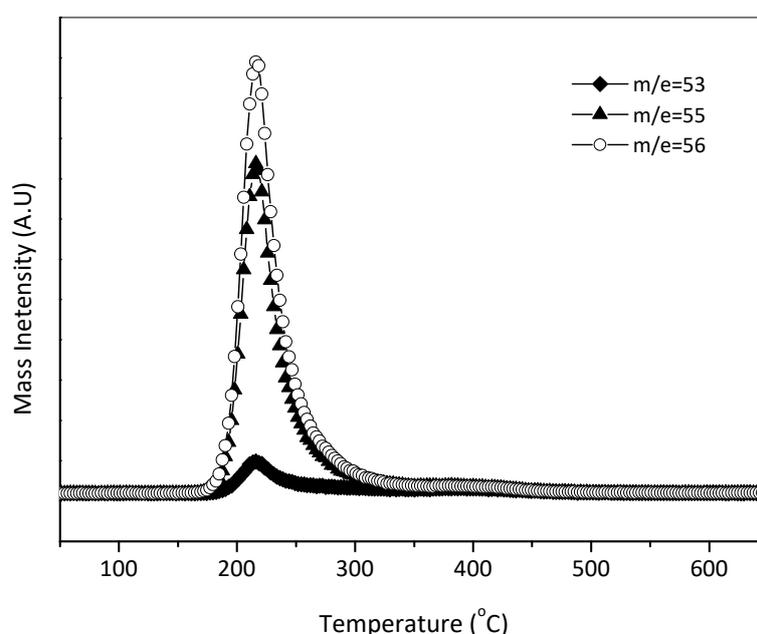
### 2.1. TPSR Results

TPSR results showed the desorption temperature of the products, which indicates the most appropriate reaction temperature [12–14]. In this way, a catalyst with low-temperature activity could be easily obtained when the corresponding products showed desorption at low temperatures. However, it is task-intensive conducting the reaction at various temperatures. Therefore, TPSR was used herein to efficiently screen catalysts for the dehydration of glycerol.

Scheme 1 shows the reaction pathway of glycerol hydrogenolysis to 1,3-propanediol. 3-hydroxy propanal was the intermediate for the production of 1,3-propanediol. However, it suffered from thermal instability and tended to decompose into acrolein and water at 40 °C. In other words, the 3-hydroxy propanal derived from glycerol dehydration during TPSR would decompose completely [15,16]. No 3-hydroxy propanal was observed during the dehydration or the hydrogenolysis process of glycerol [17]. Therefore, it is difficult to determine the selectivity of 3-hydroxy propanal from glycerol dehydration. Considering the fact that the consecutive dehydration of 3-hydroxy propanal gave acrolein, catalysts effective for the conversion of glycerol to acrolein would be certainly efficient for the dehydration of glycerol to 3-hydroxy propanal as well. In this way, the current study focused on the development of solid acid catalysts efficient for the selective dehydration of glycerol to acrolein at low temperatures so as to settle bases for the development of metal-acid bifunctional catalysts for the cascade dehydration and hydrogenolysis reactions of glycerol to 1,3-propanediol.



The  $M/e$  of fragment ions of acrolein included 56, 55, and 53, and their corresponding percentage of relative intensities were 100, 72, and 11, respectively [18]. Figure 2 showed the typical mass spectrometry spectra of acrolein over SAPO-11 and STA/SiO<sub>2</sub>. The  $M/e$  values of 56, 55, and 53 fit well with the corresponding intensities of acrolein, showing that acrolein was produced from absorbed glycerol. The well fit is observed in these three  $M/e$  values on the other catalysts investigated. Thus, it is reasonable that the  $M/e$  value of 56 was assigned to represent the acrolein desorption. The value has already been used during the reaction of acrolein over TiO<sub>2</sub> [19].



**Figure 2.** A typical mass spectrometry profile of acrolein in TPSR of glycerol absorbed SAPO-11.

**Table 1.** The main fragment ions of the products from glycerol dehydration.

Substance	Molecular Weight	Main Fragment Ions (Relative Intensity)
Glycerol	92	61(100), 44(43), 43(78), 31(39), 29(30)
Acrolein	56	56(100), 55(72), 53(11), 29(56)
3-Hydroxypropanal	74	45, 44, 30, 29
Acetol	74	43(100), 31(17)
Acetaldehyde	44	44(83), 43(47), 29(100)
Formaldehyde	30	30(58), 29(100), 28(24)
Glycidol	74	44(100), 43(90), 31(59), 29(42), 28(44)
Water	18	18(100), 17(21)
CO <sub>2</sub>	44	44(100)
CO	28	28(100)
CH <sub>4</sub>	16	16(100), 15(89), 14(20)

The TPSR spectra of all catalysts are listed in the supporting information. The range and peak of acrolein desorption temperature are summarized in Table 2, and the main desorption peaks are marked in bold. Most of the catalysts show an ability to convert glycerol to acrolein, but the desorption temperature is various. For example, acrolein can be produced below 100 °C over TPA/SiO<sub>2</sub> and 250ZnCl<sub>2</sub>/SiO<sub>2</sub>, while above 190 °C over Al<sub>2</sub>O<sub>3</sub>.

**Table 2.** Desorption temperature peak and temperature range of acrolein in the TPSR of glycerol dehydration on solid acid catalysts <sup>a</sup>.

Group	Catalysts	Peak 1		Peak 2		Peak 3	
		Range	Maximum	Range	Maximum	Range	Maximum
Heteropolyacid	PW/SiO <sub>2</sub>	75–162	120	170–351	245	322–507	376
	SiW/SiO <sub>2</sub>	<b>141–261</b>	<b>189</b>				
Zeolites/Al <sub>2</sub> O <sub>3</sub>	PMO/SiO <sub>2</sub>	<b>85–320</b>	<b>231</b>	224–409	312		
	SAPO-11	<b>165</b>	<b>220</b>				
	HZSM-5	<b>275</b>	<b>400</b>				
	Al <sub>2</sub> O <sub>3</sub>	<b>190–320</b>	<b>260</b>				
	SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	145–260	175	223–460	341		
	HY	<b>116–237</b>	<b>160</b>	150–414	250		
Lewis acid	Hβ	180–207	195	<b>180</b>	<b>235</b>	180	305
	250ZnCl <sub>2</sub> /SiO <sub>2</sub>	72–160	115	<b>183–315</b>	<b>216</b>		
	300ZnCl <sub>2</sub> /SiO <sub>2</sub>	73–170	119	<b>185–310</b>	<b>220</b>		
	350ZnCl <sub>2</sub> /SiO <sub>2</sub>	<b>175–306</b>	<b>220</b>				
	450ZnCl <sub>2</sub> /SiO <sub>2</sub>	<b>183–319</b>	<b>220</b>				
Super acid	SO <sub>4</sub> <sup>2-</sup> /TiO <sub>2</sub>	<b>129–265</b>	<b>205</b>				
	SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub>	<b>126–233</b>	<b>190</b>				

<sup>a</sup> The bold stands for the main temperature range of acrolein desorption.

Some catalysts in Group 1 shows more than two desorption peaks such as SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, which possibly implies several kinds of active sites. Taking into account that the reaction should predominantly carry out on the active sites attributing to the main desorption peaks, we only consider the main desorption peaks. Among Group 1, HY shows a low desorption temperature at 160 °C, and this indicates that HY may be active at a low temperature. Moreover, it is found that no simple correlation is observed with the acidity strength and desorption temperature. Berteau and Delmon proposed that the catalysts with moderate acid centers have relatively high activities for a catalytic dehydration of alcohol [20]. The heteropoly acids in Group 2 are typical Brønsted acid catalysts. The temperature of acrolein desorption follows the following trend STA/SiO<sub>2</sub> > MPA/SiO<sub>2</sub> > TPA/SiO<sub>2</sub>, while Varisli et al. and Tsukuda et al. reported that the activity follows STA/SiO<sub>2</sub> > TPA/SiO<sub>2</sub> > MPA/SiO<sub>2</sub> for ethanol and glycerol dehydration [21]. In this work, the calcined temperature (350 °C) is much higher than the decomposition temperature (180 °C) of TPA. Thus, the low activity of TPA/SiO<sub>2</sub> might be ascribed to thermal stability. The catalysts in Group 3 are of exclusively a Lewis type with weak acid strength. The main desorption peak is at 220 °C, and it does not evidently change when the calcined temperature increased from 250 °C to 450 °C. Trasarti et al. proved that ZnO/SiO<sub>2</sub> mainly contains weak Lewis acid sites [22]. From Table 1, the activity of ZnO/SiO<sub>2</sub> is similar to that of SAPO-11, and the latter one mainly contains Brønsted acid sites. Accordingly, the results strongly suggest that the activity was irrespective of the acid nature. The temperatures of desorption peaks are observed to be low on two kinds of super acid in Group 4, which implies that the super acids may be highly active. In brief, it is found that HY, SO<sub>4</sub><sup>2-</sup>/TiO<sub>2</sub>, SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub>, and STA/SiO<sub>2</sub> show the high activity at a lower temperature, and they were further tested in the fixed-bed. No correlation is found between the activity and the acid strength (or nature).

Figure 3 shows the mass spectrometry signal (M/e = 56) for acrolein desorption in the TPSR of each group of acidic catalysts. The intervals and peaks of the acrolein desorption peaks on each catalyst are summarized in Table 2. The main desorption temperature range of acrolein on the Lewis acid catalyst ZnCl<sub>2</sub>/SiO<sub>2</sub> is about 190–310 °C, the peak top temperature is about 245 °C, and the dehydration temperature is almost unaffected by the catalyst calcination temperature. From the results of TPSR, the dehydration of glycerol on ZnCl<sub>2</sub>/SiO<sub>2</sub> catalyst to acrolein is suitable for a reaction temperature higher than 220 °C. Therefore, the Lewis acid catalyst cannot be used as a suitable low-temperature dehydration catalyst.

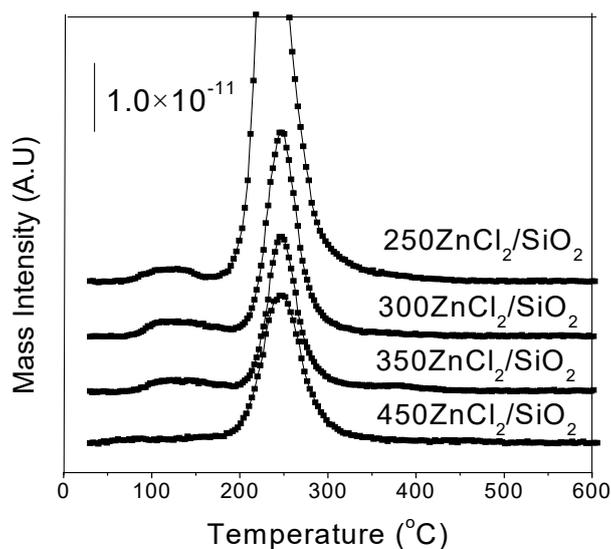


Figure 3. Acrolein in the TPSR of Lewis acid catalysts.

At a reaction temperature of 290 °C, the heteropoly acid catalyst exhibited good glycerol dehydration catalytic performance, but the activity and selectivity of the catalyst at low temperature were not investigated (Figure 4). For the three different heteropoly acid catalysts, according to the TPSR results, the dehydration activity was STA/SiO<sub>2</sub> > MPA/SiO<sub>2</sub> > TPA/SiO<sub>2</sub>. For these three catalysts, the order of activity obtained by TPSR is consistent with the results obtained by Varislia et al. for the dehydration of bioethanol to ethylene [21]. The desorption peak of acrolein on STA/SiO<sub>2</sub> is 190 °C, and the desorption peak range is 140–240 °C. Most of the acrolein is desorbed below 220 °C, which indicates that STA/SiO<sub>2</sub> has high dehydration performance at relatively low temperatures.

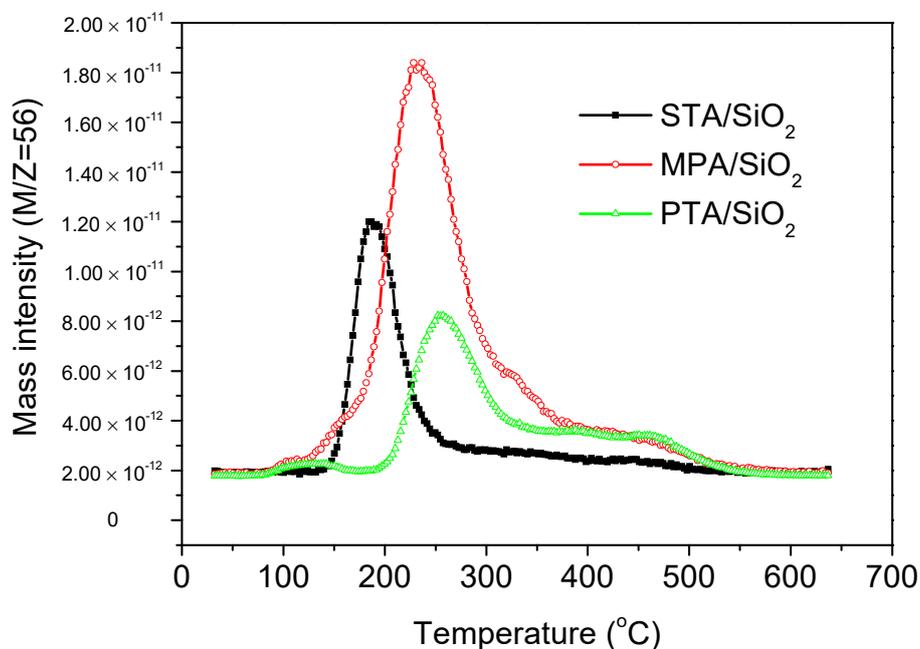


Figure 4. Acrolein in the TPSR of supported heteropoly acid catalysts.

Molecular sieves and acidic oxides are widely used as catalysts in the dehydration reaction of alcohols (Figure 5). It has been reported that molecular sieves such as H-ZSM-5 have extremely high activity and selectivity for the dehydration of glycerol to acrolein (reaction temperature is generally higher than 250 °C) [10]. The results of TPSR characterization indicate that the glycerol dehydration

activity on different molecular sieves is quite different. Although there is a desorption peak of acrolein below 220 °C, the acrolein desorption interval on most molecular sieves is mainly above 240 °C, so these catalysts are not suitable. The acrolein desorption temperature (>275 °C) on the HZSM-5 catalyst provided by two different manufacturers was higher than the reaction temperature reported in the literature, and the activity test results showed that the HZSM-5 (Chocolate Institute of Shanxi Institute of Chinese Academy of Sciences, Taiyuan, China) was 270 °C. The glycerol conversion was 99.6% and the acrolein selectivity was 86%. This may be because the glycerol adsorption temperature in the TPSR is room temperature, and the pore size of HZSM-5 ( $0.53 \times 0.56$  nm) is so small that glycerol could not diffuse into the catalyst pores during adsorption. The acrolein desorbed at the time of TPSR characterization is produced by dehydration of glycerol adsorbed outside the pores, while the active sites outside the pores have lower glycerol activity so that acrolein desorption is only at higher reaction temperatures. At temperatures above the adsorption temperature (room temperature), such as 270 °C, glycerol diffuses into the pores and dehydrates to acrolein. HY exhibits extremely high glycerol dehydration activity. On HY, the desorption temperature of most of the acrolein produced is between 115 °C and 235 °C, which indicates the low temperature dehydration activity of HY.

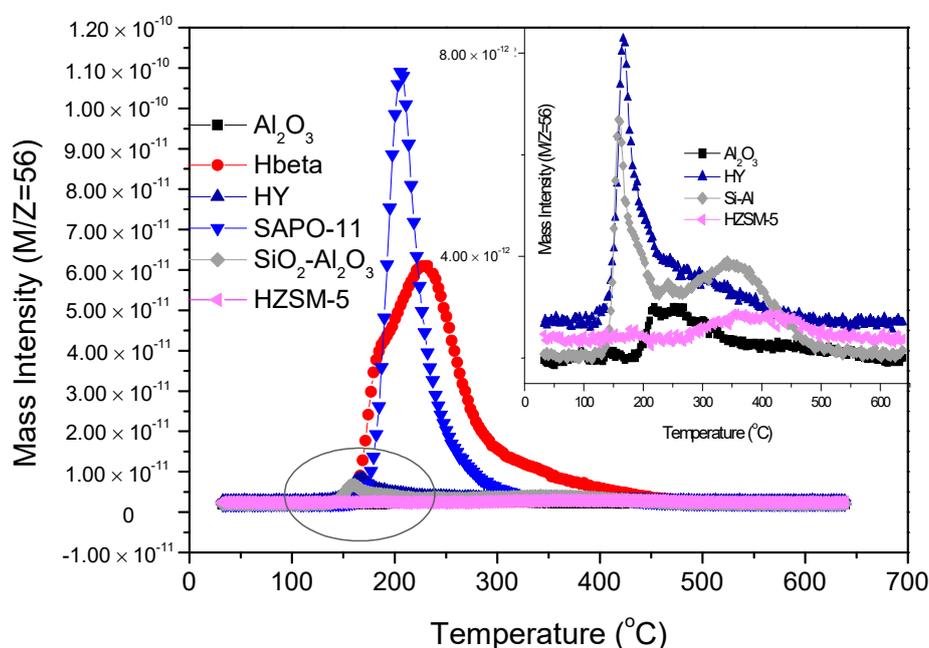


Figure 5. Acrolein in the TPSR of zeolites and oxides.

On the two super acid catalysts tried, the desorption temperature of acrolein was low, so super acid may also become a catalyst for dehydration of glycerol to acrolein at a low temperature (Figure 6). Based on the above description, we can conclude that each catalyst can convert glycerol to acrolein, but the difference in activity is large, among which STA/SiO<sub>2</sub>, HY, SO<sub>4</sub><sup>2-</sup>/TiO<sub>2</sub>, and SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> have dehydrated glycerol at low temperatures. Since the TPSR can only characterize the activity of dehydration of glycerol to acrolein qualitatively and the selectivity of the catalyst cannot be obtained, the acrolein selectivity of the four low-temperature dehydration of glycerol was evaluated on a fixed bed.

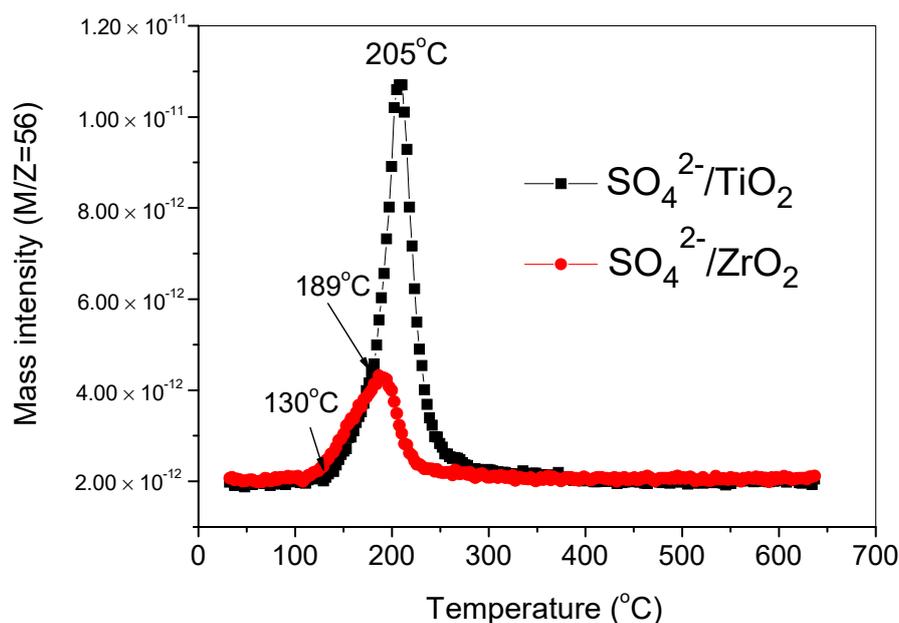


Figure 6. Acrolein in the TPSR of super acid.

## 2.2. Catalytic Performance of Different Catalysts and Fixed-Bed Reactions

Table 3 lists the catalytic activity of the solid acid catalysts at 210 °C, and the selectivity to acrolein was low with several by-products such as acetol, propanal, and acetaldehyde. Among them, STA/SiO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup>/TiO<sub>2</sub> showed high yields of acrolein over 80%. Four solid acid catalysts with low temperature activity selected by TPSR were evaluated under 210 °C and hydrogen conditions. On HY and SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> catalysts, the material balance is much lower than the reasonable range (<50%) due to two reasons. The first reason is the formation of a large amount of carbon on the catalyst surface and the second reason is that the formed brown viscous liquid sample was too viscous to flow out when entering the cold trap. The viscous liquid was washed by deionized water and analyzed by GC-MS, which were mostly unknown high boiling products and glycerol, but no acrolein. Considering that a part of the glycerin is present in the viscous liquid, which is not collected, only the yield (the amount of acrolein detected/the amount of glycerin fed) is calculated for the two catalysts. Although HY and SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> have a certain acrolein yield, their main products are unknown high-boiling products obtained by side reactions such as glycerol polymerization.

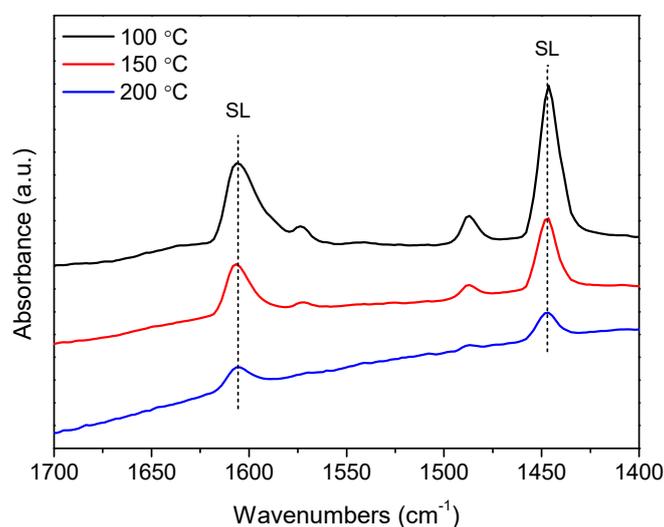
For STA/SiO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup>/TiO<sub>2</sub>, the acrolein selectivity (>85%) was high in the initial stage of the reaction, but, in the latter stage of the reaction, some of the viscous liquids could not flow out. The STA/SiO<sub>2</sub> showed higher stability. No significant deactivation was observed during the initial 42 h of operation. Atia et al. has screened solid acidic catalysts at different temperatures [15]. Their results also showed that the silicotungstic acid catalyst had a higher acrolein yield at 230 °C. In summary, according to the evaluation experiment on a fixed bed, STA/SiO<sub>2</sub> can dehydrate glycerol to acrolein at low temperature, so it is selected as the acid group in the metal-acid bifunctional catalyst for hydrogenolysis of glycerol to produce 1,3-propanediol.

ZnCl<sub>2</sub> modified SiO<sub>2</sub> could serve as promising catalysts for the production of acrolein from glycerol. Clearly, there is an optimum calcination temperature (350 °C) with the acrolein selectivity of 88.0% at glycerol conversion of 54.9% at 210 °C. Most importantly, the conversion of glycerol increased dramatically to 94.4% when the reaction temperature was up to 230 °C and the corresponding selectivity of acrolein increased slightly to 89.1%, which indicates that 350ZnCl<sub>2</sub>/SiO<sub>2</sub> was highly selective for the conversion of glycerol to acrolein. The FTIR analysis after pyridine chemisorption revealed the strong Lewis acidity (1450 cm<sup>-1</sup>) of 350ZnCl<sub>2</sub>/SiO<sub>2</sub>, which indicates that Lewis acidity was more significant for the conversion of glycerol to acrolein (Figure 7) [23]. The catalyst life was up to 300 h with no clear deactivation on 350ZnCl<sub>2</sub>/SiO<sub>2</sub> with hydrogen as dilution (Figure 8).

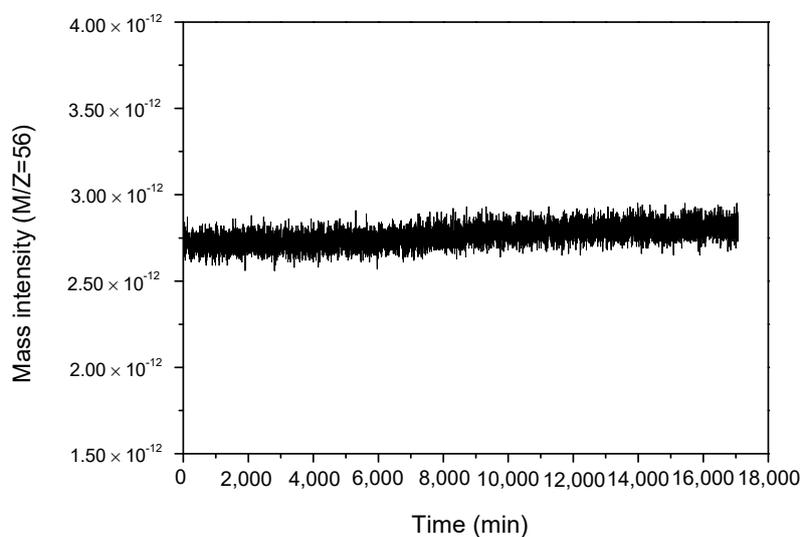
**Table 3.** The results of glycerol dehydration over acid catalysts at 210 °C.

Catalyst	Conv. (%)	Yield (%)	Selectivity (%)			
			Acrolein	Acetol	Acetaldehyde	Others
30STA/SiO <sub>2</sub>	65.5	58.1	88.7	2.6	1.8	6.6
	66.3	59.6	89.9	1.3	2.2	5.8
	-	44.8	-	-	-	-
	-	17.4	-	-	-	-
HY SO <sub>4</sub> /TiO <sub>2</sub>	-	17.0	-	-	-	-
	86.9	76.7	88.2	6.2	0.5	5.1
SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub>	77.4	64.4	83.2	6.3	0.5	10.0
	-	15.6	-	-	-	-
SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub>	-	5.1	-	-	-	-
250ZnCl <sub>2</sub> /SiO <sub>2</sub>	33.1	25.1	75.8			
300ZnCl <sub>2</sub> /SiO <sub>2</sub>	42.1	36.9	87.6			
350ZnCl <sub>2</sub> /SiO <sub>2</sub>	54.9	48.3	88.0			
350ZnCl <sub>2</sub> /SiO <sub>2</sub> *	94.4	84.1	89.1			
450ZnCl <sub>2</sub> /SiO <sub>2</sub>	40.9	35.3	86.3			

Reaction conditions: WHSV = 0.08 h<sup>-1</sup>, catalysts weight = 12.0 g, H<sub>2</sub>/glycerol = 110. \* reaction temperature = 230 °C.



**Figure 7.** FTIR spectra of 350ZnCl<sub>2</sub>/SiO<sub>2</sub> in the fingerprint domain after pyridine sorption and evacuation at various temperatures. Absorbance peaks characteristic of strong Lewis (SL) is indicated.



**Figure 8.** Time on stream stability of 350ZnCl<sub>2</sub>/SiO<sub>2</sub> for the conversion of glycerol to acrolein at 230 °C.

### 3. Experimental

#### 3.1. Catalysts

SiO<sub>2</sub> (Qingdao Haiyang Chemical Co., Ltd., Qingdao, China), Al<sub>2</sub>O<sub>3</sub> (CHALCO Shandong branch, Zibo, China), ZrO<sub>2</sub>, and TiO<sub>2</sub> (Shanghai Aladdin Bio-Chem Technology Co., Ltd., Shanghai, China) were used as received. The heteropoly acid supported catalysts were prepared by the incipient wetness impregnation with 30 wt% loading. The impregnated samples were dried at 120 °C overnight and then reduced in H<sub>2</sub> at 350 °C for 3 h. The SiO<sub>2</sub> supported tungstophosphoric acid, silicotungstic acid, and molybdophosphoric acid catalysts were designated as TPA/SiO<sub>2</sub>, STA/SiO<sub>2</sub>, and MPA/SiO<sub>2</sub>, respectively. The sulfate ions were introduced by impregnation of pure oxides by titrated aqueous solutions of 1 N H<sub>2</sub>SO<sub>4</sub>. The samples were then dried at 120 °C and calcined at 550 °C. The series of ZnCl<sub>2</sub>/SiO<sub>2</sub> was prepared according to previous reports [24], and these catalysts are named in the form of xZnCl<sub>2</sub>/SiO<sub>2</sub> in which x stands for the calcination temperature. SAPO-11, H-beta, and HY were supplied by Fushun Research Institute of Petroleum and Petrochemicals, and H-ZSM-5 and SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> were kindly supplied by Assistant Prof. Jing Xian Hu in the Institute of Coal Chemistry, Chinese Academy of Science. SAPO-5 and SAPO-34 were provided by Dr. Lijun Wang in Fudan University. All the samples were smashed into 20–40 mesh.

#### 3.2. TPSR

The TPSR studies were carried out in a thermogravimetric analyzer (TGA92) connected to an on-line quadrupole mass spectrometer (MS). The absorption of glycerol was performed by a stream of glycerol vapor at ambient temperature for 30 min (the molar ratio of Ar to glycerol was approximately 300–350:1, while the estimated partial pressure of glycerol was 0.34–0.29 kPa), in which the glycerol was diluted with a great amount of argon. The glycerol-absorbed catalyst (about 20 mg) was placed into the chamber of TG and purged with argon to remove any physically adsorbed oxygen or background gases at 30 °C until the detected M/e values were constant. The TPSR experiments were then performed with a heating rate of 10 °C/min under flowing argon (50 mL/min), and the desorbed products were monitored by online MS. For each sample, the TPSR measurement was generally performed three times, and the results showed effective reproducibility.

#### 3.3. Catalyst Activity

The glycerol dehydration reaction was performed in a fixed-bed reactor (length of 900 mm and i.d. of 13 mm) at 210 °C or 300 °C. Generally, 12 g (20–40 mesh) of catalysts was packed. Considering the differences in catalyst density, inert silica (20–40 mesh) was added to keep the catalyst bed at a constant volume (20 mL). The catalysts were pre-treated at 300 °C for 2 h. After pretreatment, glycerol and hydrogen were introduced into the fixed-bed reactor through a heated saturator, and the downstream flow lines of the saturator were maintained at 230 °C to prevent condensation of vaporized glycerol. Typically, the liquid samples were collected in a trap immersed in ice-water, and the tail gas products were periodically analyzed. Both liquid and gaseous samples were analyzed using a GC-950 gas-chromatograph (GC, Shanghai Huaai chromatogram analysis Co., Ltd., Shanghai, China) equipped with a flame ionization detector (FID) and a capillary column (OV-101, 60 m × 0.25 μm). Gas phase products consist of a large amount of acrolein, a small amount of acetaldehyde and acetol, and a trace amount of propane, propanal, and two unidentified products. In liquid phase, a large amount is water and the rest are unreacted glycerol or side products.

### 4. Conclusions

Temperature-programmed surface reaction was used as a rapid screening method to screen catalysts for dehydration of glycerol to produce acrolein at low temperatures. Several acidic catalysts, such as Lewis catalysts, molecular sieves, and metal oxides, supported heteropoly acids and super acids, which were screened. Four catalysts with low temperature (210 °C) dehydration activity were

evaluated by a gas-solid fixed bed reactor at a much lower temperature than those reported previously. STA/SiO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup>/TiO<sub>2</sub> have higher acrolein yield in the initial stage of the reaction, and STA/SiO<sub>2</sub> is relatively more stable. Therefore, STA/SiO<sub>2</sub> was selected as the acidic carrier of the metal-acid bifunctional catalyst. Especially, stability tests showed that the catalyst life was up to 300 h with no clear deactivation on ZnCl<sub>2</sub>/SiO<sub>2</sub> with hydrogen as dilution.

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## References

1. Kim, Y.C.; Moon, D.J. Sustainable process for the synthesis of value-added products using glycerol as a useful raw material. *Catal. Surv. Asia* **2019**, *23*, 10–22. [[CrossRef](#)]
2. Wang, Z.; Zhuge, J.; Fang, H.; Prior, B.A. Glycerol production by microbial fermentation: A review. *Biotechnol. Adv.* **2001**, *19*, 201–223. [[CrossRef](#)]
3. Adeniyi, A.G.; Ighalo, J.O. A review of steam reforming of glycerol. *Chem. Pap.* **2019**, *73*, 2619–2635. [[CrossRef](#)]
4. Corma, A.; Huber, G.W.; Sauvinaud, L.; O'Connor, P. Biomass to chemicals: Catalytic conversion of glycerol/water mixtures into acrolein, reaction network. *J. Catal.* **2008**, *257*, 163–171. [[CrossRef](#)]
5. Katryniok, B.; Paul, S.; Belliere-Baca, V.; Rey, P.; Dumeignil, F. Glycerol dehydration to acrolein in the context of new uses of glycerol. *Green Chem.* **2010**, *12*, 2079–2098. [[CrossRef](#)]
6. Saxena, R.K.; Anand, P.; Saran, S.; Isar, J. Microbial production of 1,3-propanediol: Recent developments and emerging opportunities. *Biotechnol. Adv.* **2009**, *27*, 895–913. [[CrossRef](#)]
7. Chai, S.H.; Wang, H.P.; Liang, Y.; Xu, B.Q. Sustainable production of acrolein: Investigation of solid acid–base catalysts for gas-phase dehydration of glycerol. *Green Chem.* **2007**, *9*, 1130–1136. [[CrossRef](#)]
8. Tao, L.Z.; Chai, S.H.; Zuo, Y.; Zheng, W.T.; Liang, Y.; Xu, B.Q. Sustainable production of acrolein: Acidic binary metal oxide catalysts for gas-phase dehydration of glycerol. *Catal. Today* **2010**, *158*, 310–316. [[CrossRef](#)]
9. Tsukuda, E.; Sato, S.; Takahashi, R.; Sodesawa, T. Production of acrolein from glycerol over silica-supported heteropoly acids. *Catal. Commun.* **2007**, *8*, 1349–1353. [[CrossRef](#)]
10. Qureshi, B.A.; Lan, X.; Arslan, M.T.; Wang, T. Highly active and selective nano H-ZSM-5 catalyst with short channels along b-Axis for glycerol dehydration to acrolein. *Ind. Eng. Chem. Res.* **2019**, *58*, 12611–12622. [[CrossRef](#)]
11. Kobayashi, H.; Ito, S.; Hara, K.; Fukuoka, A. Conversion of glycerol to acrolein by mesoporous sulfated zirconia-silica catalyst. *Chin. J. Catal.* **2017**, *38*, 420–425. [[CrossRef](#)]
12. Gambaro, L.A.; Briand, L.E. In situ quantification of the active acid sites of H<sub>6</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> center dot nH<sub>2</sub>O heteropoly-acid through chemisorption and temperature programmed surface reaction of isopropanol. *Appl. Catal. A Gen.* **2004**, *264*, 151–159. [[CrossRef](#)]
13. Wang, H.; Liu, Z.M.; Shen, J.H.; Liu, H.C.; Zhang, J.L. High-throughput screening of HZSM-5 supported metal-oxides catalysts for the coupling of methane with CO to benzene and naphthalene. *Catal. Commun.* **2005**, *6*, 343–346. [[CrossRef](#)]
14. Sakakini, B.H.; Verbrugge, A.S. Temperature-programmed surface reaction as a means of characterizing supported-metal catalysts and probing their surface reactivity. *J. Chem. Soc. Trans.* **1997**, *93*, 1637–1640. [[CrossRef](#)]
15. Atia, H.; Armbruster, U.; Martin, A. Dehydration of glycerol in gas phase using heteropolyacid catalysts as active compounds. *J. Catal.* **2008**, *258*, 71–82. [[CrossRef](#)]
16. Zhao, H.; Zhou, C.H.; Wu, L.M.; Lou, J.Y.; Li, N.; Yang, H.M.; Tong, D.S.; Yu, W.H. Catalytic dehydration of glycerol to acrolein over sulfuric acid-activated montmorillonite catalysts. *Appl. Clay Sci.* **2013**, *74*, 154–162. [[CrossRef](#)]

17. Liu, Q.; Cao, X.F.; Wang, T.J.; Wang, C.G.; Zhang, Q.; Ma, L.L. Synthesis of shape-controllable cobalt nanoparticles and their shape-dependent performance in glycerol hydrogenolysis. *RSC Adv.* **2015**, *5*, 4861–4871. [[CrossRef](#)]
18. Castle, L.W.; Gross, M.L. The cycloaddition of the 1,3-butadiene radical cation with acrolein and methyl vinyl ketone. *Org. Mass Spectrom.* **1989**, *24*, 637–646. [[CrossRef](#)]
19. Sherrill, A.B.; Idriss, H.; Barteau, M.A.; Chen, J.G. Adsorption and reaction of acrolein on titanium oxide single crystal surfaces: Coupling versus condensation. *Catal. Today* **2003**, *85*, 321–331. [[CrossRef](#)]
20. Berteau, P.; Delmon, B. Modified aluminas: Relationship between activity in 1-butanol dehydration and acidity measured by NH<sub>3</sub>-TPD. *Catal. Today* **1989**, *5*, 121–137. [[CrossRef](#)]
21. Varisli, D.; Dogu, T.; Dogu, G. Ethylene and diethyl-ether production by dehydration reaction of ethanol over different heteropolyacid catalysts. *Chem. Eng. Sci.* **2007**, *62*, 5349–5352. [[CrossRef](#)]
22. Bertero, N.M.; Trasarti, A.F.; Apesteguía, C.R.; Marchi, A.J. Liquid-phase dehydration of 1-phenylethanol on solid acids: Influence of catalyst acidity and pore structure. *Appl. Catal. A Gen.* **2013**, *458*, 28–38. [[CrossRef](#)]
23. Wang, X.C.; Song, Y.J.; Huang, L.; Wang, H.; Huang, C.P.; Li, C.Q. Tin Modified Nb<sub>2</sub>O<sub>5</sub> as an efficient solid acid catalyst for the catalytic conversion of triose sugars to lactic acid. *Catal. Sci. Technol.* **2019**, *9*, 1669–1679.
24. Ammari, F.; Milone, C.; Touroude, R. Selective hydrogenation of crotonaldehyde on Pt/ZnCl<sub>2</sub>/SiO<sub>2</sub> catalysts. *J. Catal.* **2005**, *235*, 1–9. [[CrossRef](#)]



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