

# Cooperativity of Brønsted and Lewis Acid Sites on Zeolite for Glycerol Dehydration

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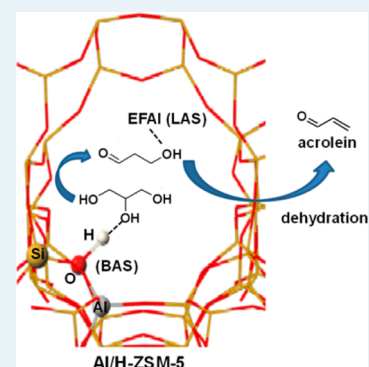
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## S Supporting Information

**ABSTRACT:** Selective dehydration of glycerol, a byproduct from the biodiesel industry, on solid acids is an important reaction in the production of the value-added chemical acrolein for economic-sustainable biorefinery. Most efforts have been made on the development of strong Brønsted acid sites (BAS) to improve the production of acrolein, because the Lewis acid sites (LAS) generally promote the generation of the byproduct acetol. However, exclusively tuning the properties of BAS or LAS did not well-promote the acrolein production from glycerol as indicated in this work. We provide a new route for efficient and selective glycerol transformation to acrolein via the cooperative dehydration between the BAS and LAS. The role of LAS (extra-framework aluminum species on zeolites) was altered from competition with BAS to generate the byproduct acetol to cooperation with the neighboring BAS. It is very beneficial for the sequential two-step dehydration of the internal and terminal hydroxyl groups of glycerol to value-added acrolein. This cooperativity of BAS and LAS significantly improved the yield of acrolein from the selective glycerol dehydration.

**KEYWORDS:** glycerol dehydration, zeolite H-ZSM-5, solid-state NMR, Brønsted acid sites, Lewis acid sites



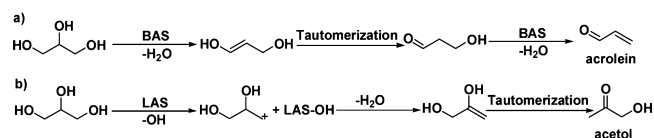
To fulfill carbon neutral production, modern biorefinery industries are developing rapidly and are accompanied with a large quantity of byproducts.<sup>1</sup> Especially in biodiesel production, a million tons of glycerol have been produced every year, and this keeps increasing with the growing market of renewable energy.<sup>2</sup> Valorization of such massive amounts of glycerol into value-added chemicals is resulting in increasing global concern.<sup>3</sup> Up to now, various routes have been developed for glycerol conversion, such as oxidation, hydrolysis, pyrolysis, dehydration, transesterification, oligomerization, and carboxylation, and so forth.<sup>2b,3,4</sup> Among them, the dehydration of glycerol to acrolein is very attractive, because acrolein currently produced by selective oxidation of the petrochemical propylene is an important chemical intermediate<sup>5</sup> for producing acrylic acid esters, super absorber polymers, or detergents.<sup>4d</sup>

Glycerol dehydration is a typical acid-catalyzed reaction, which has been investigated using both liquid and solid acids. The homogeneously catalytic dehydration of glycerol using liquid acids offers high yields of acrolein, whereas the corrosive acids and separation difficulties cause serious environmental issues and high investment/operation costs.<sup>2b</sup> Therefore, many efforts have been devoted to the gas-phase dehydration on solid acids, such as zeolites, niobia, metal sulphates and phosphates, heteropolyacids, and metal oxides.<sup>4a,b,6</sup> Particularly, the glycerol dehydration on zeolites is a promising process for emerging application due to its relatively low costs, wide availability of commercial zeolites, and widespread in-depth knowledge of

zeolite-mediated reactions. However, a significant challenge for zeolite-catalyzed dehydration reactions is how to improve the production of the desired acrolein.

The mechanistic studies of glycerol dehydration reported two proposed reaction pathways based on the type of acid sites: (a) The two-step reaction starts with the dehydration of the internal secondary hydroxyl groups of glycerol followed by the terminal primary hydroxyl groups both occurring at Brønsted acid sites (BAS) to form acrolein (Scheme 1a). (b) The one-step dehydration occurs exclusively for the primary hydroxyl groups of glycerol at Lewis acid sites (LAS) to produce acetol (Scheme 1b).<sup>2b,4a</sup> Up to now, most attempts were made on the development of strong BAS to enhance the acrolein yield.<sup>4a,6a,c,g</sup>

### Scheme 1. Proposed Reaction Pathways of Glycerol Dehydration on Brønsted Acid Sites (BAS, a) and Lewis Acid Sites (LAS, b) Reported in the Literature (Ref 4a)



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**Table 1. Concentration of Surface Sites in Various Zeolites and Their Catalytic Properties in the Selective Dehydration of Glycerol<sup>a</sup>**

zeolites <sup>a</sup>	total amount of OH groups <sup>b</sup> (mmol/g)	no. of BAS <sup>b</sup> (mmol/g)	$\Delta\delta_{\text{IH}}^c$ ppm	$C_{\text{Gly}}^d$ %	$S_{\text{acro}}^d$ %	$Y_{\text{acro}}^d$ %
Al/Na-ZSM5/1	$43.4 \times 10^{-2}$	$36.7 \times 10^{-2}$	4.2	36	63	22.7
Al/Na-ZSM5/2	$54.1 \times 10^{-2}$	$37.8 \times 10^{-2}$	7.3	39	62	24.2
H-ZSM-5	$82.2 \times 10^{-2}$	$76.0 \times 10^{-2}$	7.5	46	78	35.9
Al/H-ZSM5/1	$95.6 \times 10^{-2}$	$77.5 \times 10^{-2}$	7.8	85	64	54.4
Al/H-ZSM5/2	$78.1 \times 10^{-2}$	$62.4 \times 10^{-2}$	8	87	58	50.5

<sup>a</sup>The nomenclature indicates 1- or 2-fold aluminum exchange with parent materials (Na-ZSM-5 or H-ZSM-5). Reaction conditions: an aqueous glycerol solution (36.2 wt.%, 5 mL/h) with nitrogen (30 mL/min) dehydrated over 50 mg of catalyst at 315 °C under atmospheric pressure. <sup>b</sup>The total number of OH groups and BAS were determined by <sup>1</sup>H MAS NMR spectra of dehydrated samples. <sup>c</sup>The induced low-field resonance shift ( $\Delta\delta_{\text{IH}}$ ) of SiOHAl groups upon adsorption of CD<sub>3</sub>CN. <sup>d</sup>The conversion of glycerol ( $C_{\text{Gly}}$ ), yield ( $Y_{\text{acro}}$ ), and selectivity ( $S_{\text{acro}}$ ) of acrolein were obtained after 2 h of reaction.

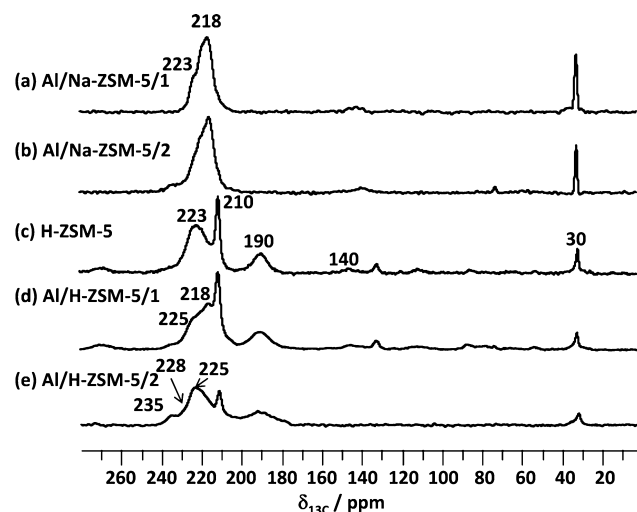
For zeolites, increasing the framework silica/alumina ratio could improve the Brønsted acid strength of bridging OH groups without introducing LAS. However, the density of BAS will dramatically drop down for the high SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio, which reduces the active sites accessible for glycerol dehydration. Therefore, the optimal SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 150 was obtained for the maximum acrolein yield on zeolites H-ZSM-5 with silica/alumina ratios between 23 and 1000.<sup>6g</sup> Nevertheless, one significant question was raised as to whether tuning the Brønsted acidity is the only way to improve the glycerol dehydration and acrolein yield.

In this work, we explore a new possibility for efficient and selective dehydration of glycerol via the cooperativity of BAS and LAS. The strategy herein is to alter the negative role of LAS in competing with BAS and generating byproduct acetol during glycerol dehydration (Scheme 1b) to the positive role for associating BAS to enhance acrolein production. By dealumination, impregnation, and ion exchange, it is possible to obtain multifunctional active sites on zeolites. It is best to tune these active centers and let them work together to promote the desired reaction.<sup>7</sup> In this work, we found that increasing acidity of either BAS or LAS on ZSM-5 zeolites only slightly enhanced the glycerol dehydration. While introducing extra-framework aluminum cations (EFAl, acting as LAS) into H-ZSM-5 with a significant amount of BAS, a remarkable enhancement of glycerol conversion and acrolein yield was achieved. BAS were proposed to initiate the first-step dehydration of the secondary hydroxyl group of glycerol, and the neighboring LAS collaborated to complete the second-step dehydration of the primary hydroxyl groups to form acrolein. This work focuses on the cooperative effect of various acid sites on the glycerol transformation, but the concepts are applicable to a wide range of catalyst design.

Al/Na-ZSM-5, H-ZSM-5, and Al/H-ZSM-5 zeolites were prepared for glycerol dehydration (see both preparation and characterization methods in Supporting Information). The number of EFAl species per gram of zeolites (Table 1) was calculated on the basis of Al exchange degree. Nearly no EFAl species were observed for H-ZSM-5. The <sup>29</sup>Si MAS NMR spectra (Figure S1) indicate that all the zeolites used in this study have similar framework  $n_{\text{Si}}/n_{\text{Al}}$  ratios of 16–17, and no appreciable dealumination or damage of the zeolites framework was observed after synthesis and calcination. The <sup>27</sup>Al MAS NMR spectra (Figure S2) show most of the aluminum atoms were incorporated into the silica framework to form the Al<sup>IV</sup> species, which contributes to the formation of bridging SiOHAl groups working as BAS during reaction. After quantitative

evaluation of <sup>1</sup>H MAS NMR spectra in Figure S3, the densities of BAS are summarized in Table 1.

The aluminum species introduced inside zeolite pores (EFAl) contribute to surface Lewis sites and enhance the acid strength of BAS in their vicinity.<sup>8</sup> A sequence of BAS strength of Al/H-ZSM-5/2 > Al/H-ZSM-5/1 > H-ZSM-5 > Al/Na-ZSM-5/2 > Al/Na-ZSM-5/1 has been determined by <sup>13</sup>C MAS NMR spectra (Figure 1) after adsorption of acetone-2-<sup>13</sup>C



**Figure 1.** <sup>13</sup>C MAS NMR spectra of dehydrated (723 K) zeolites Al/Na-ZSM-5/1 (a), Al/Na-ZSM-5/2 (b), H-ZSM-5 (c), Al/H-ZSM-5/1 (d), and Al/H-ZSM-5/2 (e) recorded upon loading with acetone-2-<sup>13</sup>C.

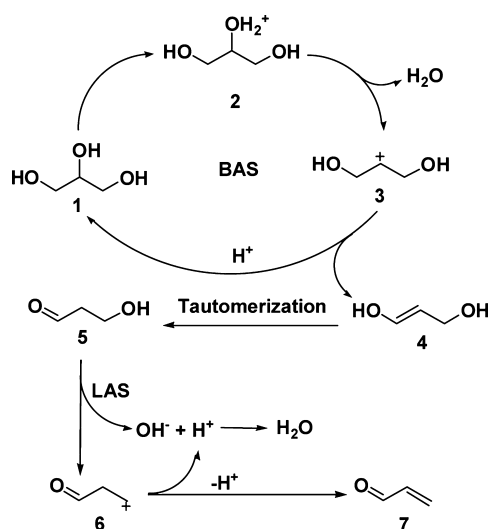
(CH<sub>3</sub><sup>13</sup>COCH<sub>3</sub>) probe molecules on zeolites. This sequence of BAS strength was further confirmed by <sup>1</sup>H MAS NMR studies of the weak base acetonitrile-*d*<sub>3</sub> (CD<sub>3</sub>CN) on zeolites (Figure S4). Hence, a higher Al exchange degree resulted in an enhanced acid strength, which was also observed in the previous report on Al-exchanged zeolites X and Y.<sup>9</sup> In addition, a weak signal at  $\delta_{13\text{C}} = 235$  ppm in Al/Na-ZSM-5/2 and Al/H-ZSM-5/2 (Figure 1b,e) is assigned to acetone adsorbed on LAS.<sup>8b,10</sup>

The catalytic performance of the ZSM-5 catalysts under study was evaluated via the selective dehydration of glycerol to acrolein at 588 K. As shown in Table 1, the conversion of glycerol slightly increases from 36% on Al/Na-ZSM-5/1 to 39% on Al/Na-ZSM-5/2 with increasing number of BAS from  $36.7 \times 10^{-2}$  mmol/g to  $37.8 \times 10^{-2}$  mmol/g. On H-ZSM-5 with  $76 \times 10^{-2}$  mmol/g BAS (two times higher than Al/Na-ZSM-5/2), however, the glycerol conversion was gently improved to 46%.

Hence, the enhanced BAS strength of H-ZSM-5 and the increased number of BAS could not dramatically enhance the catalytic performance in the glycerol dehydration in comparison with the Al/Na-ZSM-5. Also, the selectivity to acrolein was only slightly increased from 62 to 63% on the Al/Na-ZSM-5 to 78% on H-ZSM-5.

Although Al/H-ZSM5/1 has a similar number of BAS as H-ZSM-5, interestingly, it could significantly increase the glycerol conversion up to 85%, 1.85 times higher than that on H-ZSM-5. The selectivity to acrolein decreased from 78% to 64%, but the acrolein yield grew from 35.9% for H-ZSM-5 to 54.4% for Al/H-ZSM-5/1. As described above, increasing the BAS strength on ZSM-5 could not strongly enhance the glycerol conversion. The possible reason for highly active Al/H-ZSM-5/1 is that the existence of EFAl inside zeolite pores may be acting as LAS and promoting the glycerol conversion. If exclusively LAS (see signals at 235 ppm in Figures 1d,e) were responsible for the greatly increased catalytic performance of Al/H-ZSM-5, the acrolein yield should be significantly decreased in comparison with zeolite H-ZSM-5, because LAS favor the production of acetol during the glycerol dehydration. However, the yield to acrolein is sharply increased to 50.5–54.4% for the Al/H-ZSM-5 in comparison with 35.9% for H-ZSM-5 and 22.7–24.2% for Al/Na-MZS-5. Therefore, exclusively increasing the density and strength of BAS or the density of LAS on zeolites ZSM-5 does not promote the acrolein production from glycerol. The significantly high activity of Al/H-ZSM-5 may be attributed to the collaboration of BAS and LAS during the glycerol dehydration. The conversion of glycerol to acrolein involves two dehydration steps at the secondary and primary hydroxyl groups of glycerol, respectively. The highly mobile protons of the BAS are not hindered by steric constraints and are able to selectively protonate the secondary hydroxyl group of glycerol, which is supported by the relatively high negative charge of the OH group at  $\beta$  position.<sup>4a</sup> The primary OH groups of glycerol are available for LAS to perform dehydration.<sup>11</sup> The proposed reaction pathways are summarized in Scheme 2. The protonated glycerol **2** is not stable and readily dehydrated to form a carbenium ion **3**. After deprotonation of **3**, 1,3-

**Scheme 2. Proposed Reaction Pathway for the Cooperativity of Brønsted and Lewis Acid Sites in Glycerol Dehydration (BAS: Brønsted Acid Sites; LAS: Lewis acid sites)**



dihydroxypropene **4** is formed and further converted into 3-hydroxypropanal **5** via tautomerization. The proton moves back to the BAS for the new glycerol molecule and a next catalytic cycle. When the hydroxyl group of **5** reacts with a nearby LAS, the C–OH bond is activated to form the carbenium ion **6**. The deprotonation of unstable **6** generates the desired acrolein **7**. Meanwhile, an  $H^+$  releases from **6** and combines with an  $OH^-$  on the LAS to a water molecule. Then, the LAS can contribute again to the next catalytic cycle with a new species **5**.

In summary, this work reports a highly efficient and low-cost route for the transformation of the biodiesel byproduct glycerol to value-added acrolein. During the glycerol dehydration, exclusively tuning BAS or LAS did not well-promote the acrolein production from glycerol. When the zeolites ZSM-5 contain BAS with neighboring LAS, these two types of acid sites are proposed to collaborate in a two-step dehydration of glycerol to acrolein: BAS starts the reaction via the dehydration of the secondary hydroxyl groups of glycerol and LAS prefers to complete the reaction by the second reaction step consisting of the dehydration of the primary hydroxyl groups to form acrolein. This kind of cooperative action of BAS and LAS greatly improves the catalytic performance of Al-exchanged zeolites H-ZSM-5 and results in a significant increase in the yield of acrolein. Our strategy to tune the negative role of LAS in the byproduct generation to a positive contribution to target products in reactions via site–site cooperation sheds new light on a rational design of efficient catalysts. Further investigations are in progress for optimizing the cooperative effect of BAS and LAS in the glycerol dehydration on various zeolites and other solid acids.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experiment section, solid-state NMR characterization, and acidity investigation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interests.

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