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

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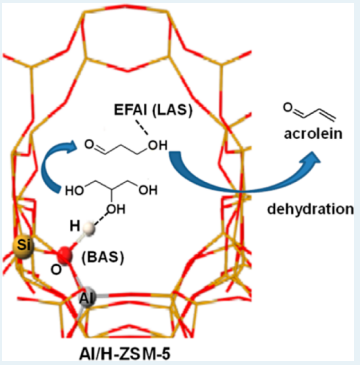
Supporting Information

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.[1] 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.[2] Valorization of such massive amounts of glycerol into value-added chemicals is resulting in increasing global concern.[3] Up to now, various routes have been developed for glycerol conversion, such as oxidation, hydrolysis, pyrolysis, dehydration, transesterification, oligomerization, and carboxylation, and so forth.[2b,3,4] 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[5] for producing acrylic acid esters, super absorber polymers, or detergents.[4d]

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.[2b] 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.[4a,b,6] 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).[2b,4a] Up to now, most attempts were made on the development of strong BAS to enhance the acrolein yield.[4a,6a,c,g]

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)

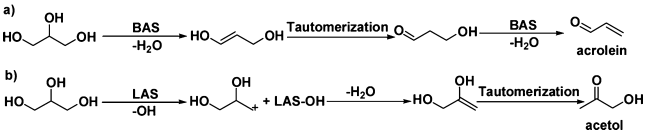


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Table 1. Concentration of Surface Sites in Various Zeolites and Their Catalytic Properties in the Selective Dehydration of Glycerol[a]

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

[a]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. [b]The total number of OH groups and BAS were determined by ^{1}H MAS NMR spectra of dehydrated samples. [c]The induced low-field resonance shift ($\Delta\delta_{1H}$) of SiOHAl groups upon adsorption of CD_3CN. [d]The conversion of glycerol (C_{Gly}), yield (Y_{acro}), and selectivity (S_{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_2/Al_2O_3 ratio, which reduces the active sites accessible for glycerol dehydration. Therefore, the optimal SiO_2/Al_2O_3 ratio of 150 was obtained for the maximum acrolein yield on zeolites H-ZSM-5 with silica/alumina ratios between 23 and 1000.[6g] 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.[7] 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 ^{29}Si MAS NMR spectra (Figure S1) indicate that all the zeolites used in this study have similar framework n_{Si}/n_{Al} ratios of 16−17, and no appreciable dealumination or damage of the zeolites framework was observed after synthesis and calcination. The ^{27}Al MAS NMR spectra (Figure S2) show most of the aluminum atoms were incorporated into the silica framework to form the Al^{IV} species, which contributes to the formation of bridging SiOHAl groups working as BAS during reaction. After quantitative evaluation of ^{1}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.[8] 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 ^{13}C MAS NMR spectra (Figure 1) after adsorption of acetone-2-^{13}C

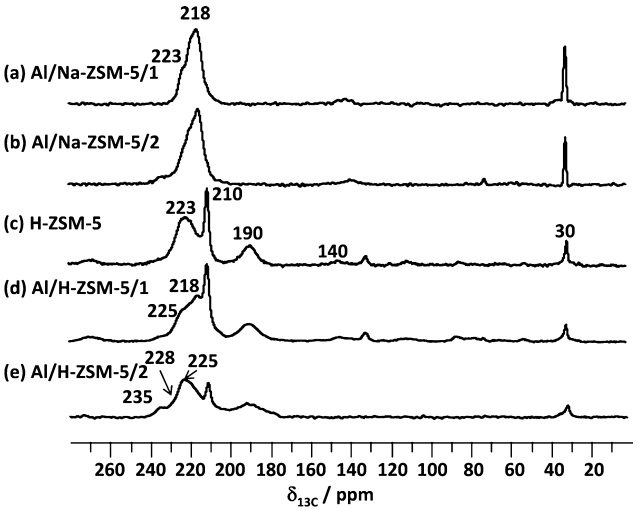

Figure 1. ^{13}C MAS NMR spectra of dehydrated (723 K) zeolites Al/Na-ZSM-5/1 (a), Al/Na-ZSM-5/2 (b), H-ZSM-5 (c), Al/H-ZSM-5/1 (d), and Al/H-ZSM-5/2 (e) recorded upon loading with acetone-2-^{13}C.

($CH_3{}^{13}COCH_3$) probe molecules on zeolites. This sequence of BAS strength was further confirmed by ^{1}H MAS NMR studies of the weak base acetonitrile-d_3 (CD_3CN) 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.[9] In addition, a weak signal at δ_{13C} = 235 ppm in Al/Na-ZSM-5/2 and Al/H-ZSM-5/2 (Figure 1b,e) is assigned to acetone adsorbed on LAS.[8b,10]

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%.

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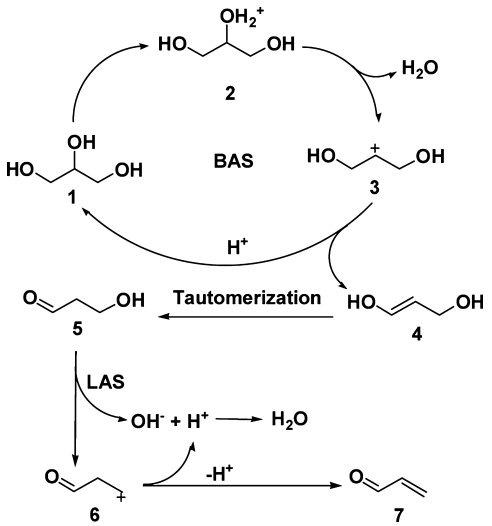
Hence, the enhanced BAS strength of H-ZSM-5 and the increased number of BAS could not dramatically enhance the catalytic performance in the glycerol dehydration in comparison with the Al/Na-ZSM-5. Also, the selectivity to acrolein was only slightly increased from 62 to 63% on the Al/Na-ZSM-5 to 78% on 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 β position.[4a] The primary OH groups of glycerol are available for LAS to perform dehydration.[11] 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-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**.

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)



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.

■ REFERENCES

(1) Ragauskas, A. J.; Williams, C. K.; Davison, B. H.; Britovsek, G.; Cairney, J.; Eckert, C. A.; Frederick, W. J.; Hallett, J. P.; Leak, D. J.; Liotta, C. L.; Mielenz, J. R.; Murphy, R.; Templer, R.; Tschaplinski, T. *Science* **2006**, *311*, 484.

(2) (a) Biofuels for Transport: An International Perspective. *International Energy Agency*, Paris, France, 2005, p 169. (b) Katryniok, B.; Paul, S.; Capron, M.; Dumeignil, F. *ChemSusChem* **2009**, *2*, 719.

(3) Zhou, C.-H.; Beltramini, J. N.; Fan, Y.-X.; Lu, G. Q. *Chem. Soc. Rev.* **2008**, *37*, 527−.

(4) (a) Alhanash, A.; Kozhevnikova, E. F.; Kozhevnikov, I. V. *Appl. Catal., A* **2010**, *378*, 11. (b) Atia, H.; Armbruster, U.; Martin, A. *J. Catal.* **2008**, *258*, 71. (c) Clacens, J. M.; Pouilloux, Y.; Barrault, J. *Appl. Catal., A* **2002**, *227*, 181. (d) Pagliaro, M.; Ciriminna, R.; Kimura, H.; Rossi, M.; Della Pina, C. *Angew. Chem., Int Ed.* **2007**, *46*, 4434. (e) Brett, G. L.; He, Q.; Hammond, C.; Miedziak, P. J.; Dimitratos, N.; Sankar, M.; Herzing, A. A.; Conte, M.; Lopez-Sanchez, J. A.; Kiely, C. J.; Knight, D. W.; Taylor, S. H.; Hutchings, G. J. *Angew. Chem., Int Ed.* **2011**, *50*, 10136.

(5) (a) Grasselli, R. K. In *Handbook of Heterogeneous Catalysis*; G.Ertl, Knozinger, H., Weitkamp, J., Eds.; Wiley-VCH: Weinheim, Germany, 1997, p 2303. (b) Grasselli, R. *Top. Catal.* **2002**, *21*, 79.
(6) (a) Gu, Y.; Liu, S.; Li, C.; Cui, Q. *J. Catal.* **2013**, *301*, 93. (b) Possato, L. G.; Diniz, R. N.; Garetto, T.; Pulcinelli, S. H.; Santilli, C. V.; Martins, L. *J. Catal.* **2013**, *300*, 102. (c) Massa, M.; Andersson, A.; Finocchio, E.; Busca, G.; Lenrick, F.; Wallenberg, L. R. *J. Catal.* **2013**, *297*, 93. (d) Choi, Y.; Park, D. S.; Yun, H. J.; Baek, J.; Yun, D.; Yi, J. *ChemSusChem.* **2012**, *5*, 2460. (e) Martin, A.; Armbruster, U.; Atia, H. *Eur. J. Lipid Sci. Technol.* **2012**, *114*, 10. (f) Kim, Y. T.; Jung, K. D.; Park, E. D. *Appl. Catal., B* **2011**, *107*, 177. (g) Kim, Y. T.; Jung, K.-D.; Park, E. D. *Microporous Mesoporous Mater.* **2010**, *131*, 28. (h) Lauriol-Garbey, P.; Millet, J. M. M.; Loridant, S.; Bellière-Baca, V.; Rey, P. *J. Catal.* **2011**, *281*, 362. (i) Chai, S.-H.; Wang, H.-P.; Liang, Y.; Xu, B.-Q. *J. Catal.* **2007**, *250*, 342. (j) Cavani, F.; Guidetti, S.; Marinelli, L.; Piccinini, M.; Ghedini, E.; Signoretto, M. *Appl. Catal., B* **2010**, *100*, 197. (k) Kim, Y. T.; Jung, K.-D.; Park, E. D. *Appl. Catal., A* **2011**, *393*, 275. (l) Gu, Y.; Cui, N.; Yu, Q.; Li, C.; Cui, Q. *Appl. Catal., A* **2012**, *429*−*430*, 9.
(7) (a) Huang, J.; Jiang, Y.; Marthala, V. R. R.; Hunger, M. *J. Am. Chem. Soc.* **2008**, *130*, 12642. (b) Luzgin, M. V.; Rogov, V. A.; Arzumanov, S. S.; Toktarev, A. V.; Stepanov, A. G.; Parmon, V. N. *Angew. Chem., Int. Ed.* **2008**, *47*, 4559. (c) Brunelli, N. A.; Didas, S. A.; Venkatasubbaiah, K.; Jones, C. W. *J. Am. Chem. Soc.* **2012**, *134*, 13950. (d) Macht, J.; Carr, R. T.; Iglesia, E. *J. Am. Chem. Soc.* **2009**, *131*, 6554. (e) Corma, A.; Diaz, U.; Garcia, T.; Sastre, G.; Velty, A. *J. Am. Chem. Soc.* **2010**, *132*, 15011. (f) Zhao, C.; Lercher, J. A. *Angew. Chem., Int. Ed.* **2012**, *51*, 5935. (g) de Clippel, F.; Dusselier, M.; Van Rompaey, R.; Vanelderen, P.; Dijkmans, J.; Makshina, E.; Giebeler, L.; Oswald, S.; Baron, G. V.; Denayer, J. F. M.; Pescarmona, P. P.; Jacobs, P. A.; Sels, B. F. *J. Am. Chem. Soc.* **2012**, *134*, 10089. (h) Xu, J.; Zheng, A.; Wang, X.; Qi, G.; Su, J.; Du, J.; Gan, Z.; Wu, J.; Wang, W.; Deng, F. *Chem. Sci* **2012**, *3*, 2932. (i) Scherzer J. In *Catalytic Materials: Relationship Between Structure and Reactivity*; Comstock, M. J., Eds; ; ACS Symposium Series 248; American Chemical Society: Washington, DC, 1984; pp 157−200 (j) Sulikowski, B. *Heterogeneous Chem. Rev.* **1996**, *3*, 203.
(8) (a) Almutairi, S. M. T.; Mezari, B.; Filonenko, G. A.; Magusin, P.; Rigutto, M. S.; Pidko, E. A.; Hensen, E. J. M. *ChemCatChem* **2013**, *5*, 452. (b) Li, S.; Zheng, A.; Su, Y.; Zhang, H.; Chen, L.; Yang, J.; Ye, C.; Deng, F. *J. Am. Chem. Soc.* **2007**, *129*, 11161.
(9) Huang, J.; Jiang, Y.; Marthala, V. R. R.; Thomas, B.; Romanova, E.; Hunger, M. *J. Phys. Chem. C* **2008**, *112*, 3811.
(10) Haw, J. F.; Nicholas, J. B.; Xu, T.; Beck, L. W.; Ferguson, D. B. *Acc. Chem. Res.* **1996**, *29*, 259.
(11) Abbaslou, R. M. M.; Tavasoli, A.; Dalai, A. K. *Appl. Catal., A* **2009**, *355*, 33.

Supporting Information

The cooperativity of Brønsted and Lewis acid sites on zeolite for glycerol dehydration

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Experimental Section

Catalyst preparation

All chemicals used for ZSM-5 synthesis, such as NaOH (> 99.99 %), tetrapropylammonium hydroxide (TPAOH, 1.0 M in H_2O), silicic acid (> 99.9 %), sodium aluminate (Al_2O_3 content 50 - 56 %), ammonium hydroxide solution (28 % NH_3 in H_2O) and $Al(NO_3)_3$ (≥ 98 %) were obtained from Sigma-Aldrich.

High aluminum content Na-ZSM-5 was synthesized via a hydrothermal route.[1] Firstly, seeding gel was prepared by thoroughly mixing deionized water, NaOH, TPA-OH and silicic acid solution together in the molar ratio of 116:1.6:1:5, accordingly. Stirring of the resulting mixture for 1 h at ambient temperature, followed by aging at 100 °C for 16 h, were performed. A mixture consisting of water, sodium hydroxide, sodium aluminate, silicic acid and seeding gel with the respective molar ratio of 375:1.7:1:9.4:1 was stirred at ambient temperature for 1 h. Then the resulting gel was placed into an autoclave and aged at 180 ^oC for 40 h. The products were recovered by filtration, washing and drying at 105 ^oC for 24 h. Finally, to completely remove organic compounds, the as-synthesized samples were calcined in a flow of synthetic air (58 L/h, 20 vol.% oxygen) at 550 ^oC with a heating rate of 1 ^oC/min for 5 h. The n_{Si}/n_{Al} ratio of obtained Na-ZSM-5 was 17, as determined by ICP-AES.

Ammonium exchange was performed with Na-ZSM-5 by adding certain amount of 0.1 M NH_4NO_3 aqueous solution. The mixture was stirred at 80 ^oC for 3 h. Subsequently, this solution was filtered and washed with deionized water until no nitrate ions can be detected. Then the obtained product was dried at room temperature overnight. After repeating the above mentioned processed for 4 times, NH_4-ZSM-5 (ion-exchange degree > 99 %) was obtained.

Aluminum exchange was carried out with Na-ZSM-5 or H-ZSM-5 mixed with a certain amount of 1.0 M $Al(NO_3)_3$ aqueous solution. To avoid dealumination or destruction of the framework, the pH value of the solution was adjusted to 4. Then the mixture was stirred at room temperature for 4 h. The obtained products were washed by deionized water until no nitrate ions were detected and then dried at 80 ^oC. Both

one-fold and two-fold aluminum-exchanged Na-ZSM-5 and H-ZSM-5 were prepared, respectively. The number of extraframework aluminum species (EFAl) was 13.4×10^{-2} mmol/g for Al/Na-ZSM-5/1, 17.6×10^{-2} mmol/g for Al/Na-ZSM-5/2, 12.1×10^{-2} mmol/g for Al/H-ZSM-5/1 and 16.4×10^{-2} mmol/g for Al/H-ZSM-5/2.

Solid-state NMR investigation

For the ^{27}Al and ^{29}Si MAS NMR investigations, all samples were fully hydrated by exposure to the saturated vapour of $Ca(NO_3)_2$ solution at ambient temperature overnight in a desiccator. Before the ^{1}H and ^{13}C MAS NMR experiments, the samples filled in glass tubes were dehydrated for 12 h at 723 K under a pressure of less than 10^{-2} mbar. These dehydrated samples were sealed in the glass tubes or directly loaded with ammonia, acetonitrile-d_3 or acetone-2-^{13}C (99.5 % ^{13}C-enriched, Sigma-Aldrich) on a vacuum line. Subsequently, the loaded samples were evacuated at 393 K for 1 h (for ammonia) or at room temperature (10 min for acetonitrile-d_3, 2 h for acetone) to remove weakly physisorbed molecules. Subsequently, the samples were transferred into the MAS NMR rotors under dry nitrogen gas inside a glove box.

^{1}H, ^{27}Al, and ^{13}C MAS NMR investigations were carried out on a Bruker Avance III 400 WB spectrometer at resonance frequencies of 400.1, 104.3, and 100.6 MHz, respectively, and with the sample spinning rate of 8 kHz using 4 mm MAS rotors. The spectra were recorded after single-pulse $\pi/2$ and $\pi/6$ excitation with repetition times of 20 s and 0.5 s for studying ^{1}H and ^{27}Al nuclei, respectively. Quantitative ^{1}H MAS NMR measurements were performed using zeolite H,Na-Y (35 % ion-exchanged) as an external intensity standard. ^{13}C cross-polarization (CP) MAS NMR spectra were recorded with the contact time of 4 ms and the repetition time of 4 s. ^{29}Si MAS NMR measurements were performed on the same spectrometer at the resonance frequency of 79.5 MHz and with the sample spinning rate of 4 kHz using a 7 mm MAS rotor. For ^{29}Si MAS NMR, single-pulse $\pi/2$ excitation, high-power proton decoupling, and the recycle delay of 20 s were applied.

Catalytic reaction

Dehydration of glycerol on zeolites were carried out according to the literature[2]. Briefly, a constant weight of 50 mg catalyst was placed in a fixed-bed quartz reactor with a thermal couple monitoring. Prior to the reaction, the NH_4-ZSM-5 or Al-exchanged ZSM-5 catalysts was preheated in dry nitrogen flow (30 ml/min) at 400 ^oC overnight (NH_4/Na-ZSM-5) or 2 h (Al/Na-ZSM-5), respectively. Then an aqueous glycerol solution (36.2 wt.%) was fed into the reactor by a syringe pump at a rate of 5 ml/h with nitrogen (30 ml/min) as carrier gas. The reactions were performed at 315 ^oC and the products were analyzed by Shimadzu GC-2010 Plus GC-FID or GC-MS-QP2010 Ultra. The selectivity to specific product(s) (S_i) was calculated as S_i (%) = 100 × (i) / [$C_{GLY0} - C_{GLY}$], where (i) is the molar concentration of the product(s), and C_{GLY0} and C_{GLY} are corresponding to the molar concentration of glycerol before and after reaction, respectively.

^{29}Si MAS NMR

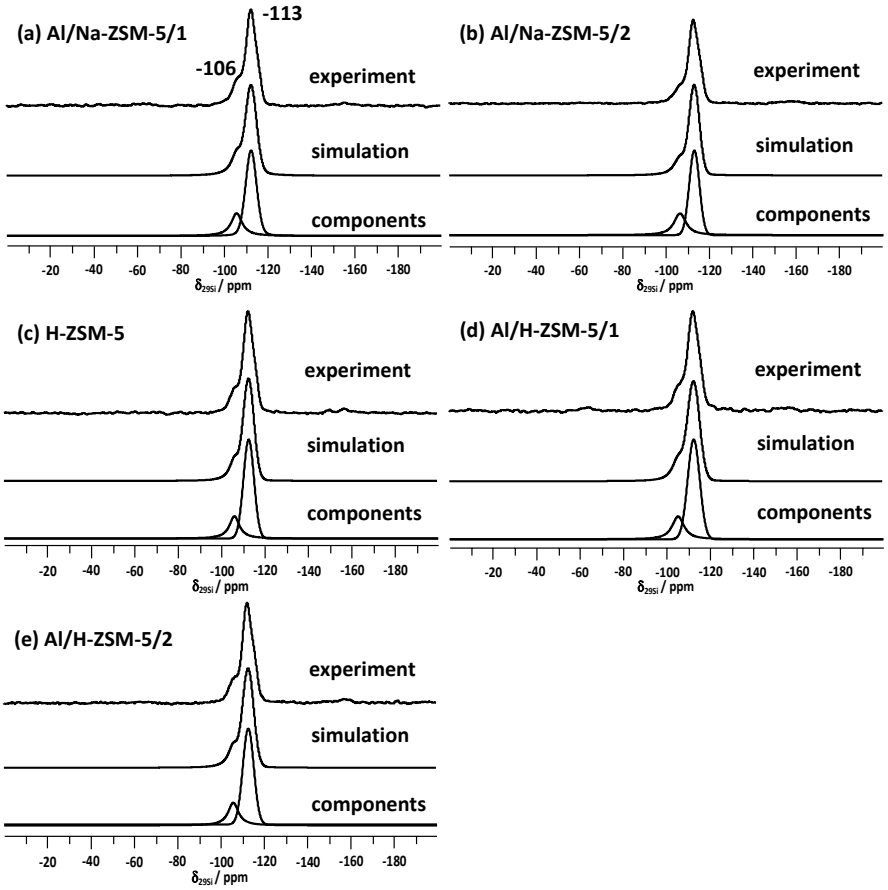

Figure S1. ^{29}Si MAS NMR spectra of Al/Na-ZSM-5/1 (a), Al/Na-ZSM-5/2 (b), H-ZSM-5 (c), Al/H-ZSM-5/1 (d) and Al/H-ZSM-5/2 (e).

As shown in Fig. S1 (top), the ^{29}Si MAS NMR spectra of all zeolites were dominated by a strong signal at -113 ppm caused by silicon atoms without neighbouring framework aluminium atoms in the first coordination sphere of T atoms Si(0Al) and a weak shoulder at -106 ppm due to silicon atoms with neighbouring framework aluminum atom Si(1Al), respectively. According to the deconvolution of the spectra (Fig. S1, bottom), these two Si signals caused by Si(0Al) and Si(1Al) species, respectively, showed similar intensities for all the zeolites. The relative intensities in Fig. S1 gave the framework n_{Si}/n_{Al} ratios of 16-17 for all the zeolites. It indicates that all the zeolites used in this study have similar framework n_{Si}/n_{Al} ratios, and no obvious dealumination and damage of the zeolites framework were observed after synthesis and calcination.

^{27}Al MAS NMR

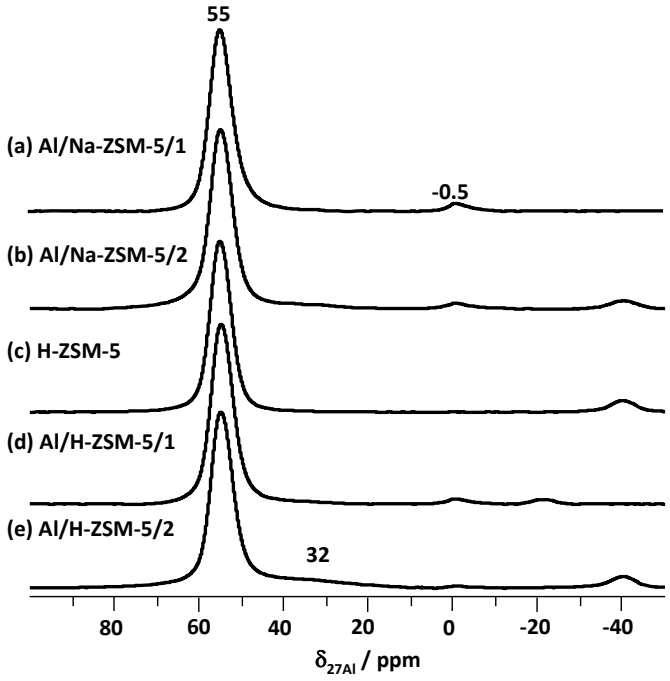

Figure S2. ^{27}Al MAS NMR spectra of Al/Na-ZSM-5/1 (a), Al/Na-ZSM-5/2 (b), H-ZSM-5 (c), Al/H-ZSM-5/1 (d) and Al/H-ZSM-5/2 (e).

The ^{27}Al MAS NMR spectra of all ZSM-5 samples (Fig. S2) were dominated by a signal of tetrahedrally coordinated aluminum (Al^{IV}) species at δ_{27Al} = 55 ppm.[3,4] It indicates most of the aluminum atoms were incorporated into the silica framework to form the bridging SiOHAl groups and Brønsted acid sites. The weak signals at $\delta_{27Al} \approx$ - 0.5 ppm for all Al exchanged zeolites were caused by the octahedrally coordinated aluminum (Al^{VI}) species, which were proposed to be the extra-framework aluminum species.[5,6] For those zeolites with high contents of extra-framework Al (EFAl) species (Al/Na-HZSM-5/2 and Al/H-ZSM-5/2), the ^{27}Al MAS NMR spectra showed a weak and broad peak at 32 ppm, which are due to pentacoordinated extra-framework aluminum species (Al^{V}). These EFAl species could work as LAS during reaction, and enhance the acidity of nearby Brønsted acid sites by withdrawing electron density from neighboring bridging OH groups.[7,8] However, nearly no extra-framework aluminum species were observed for H-ZSM-5.

^{1}H MAS NMR investigation of surface OH groups

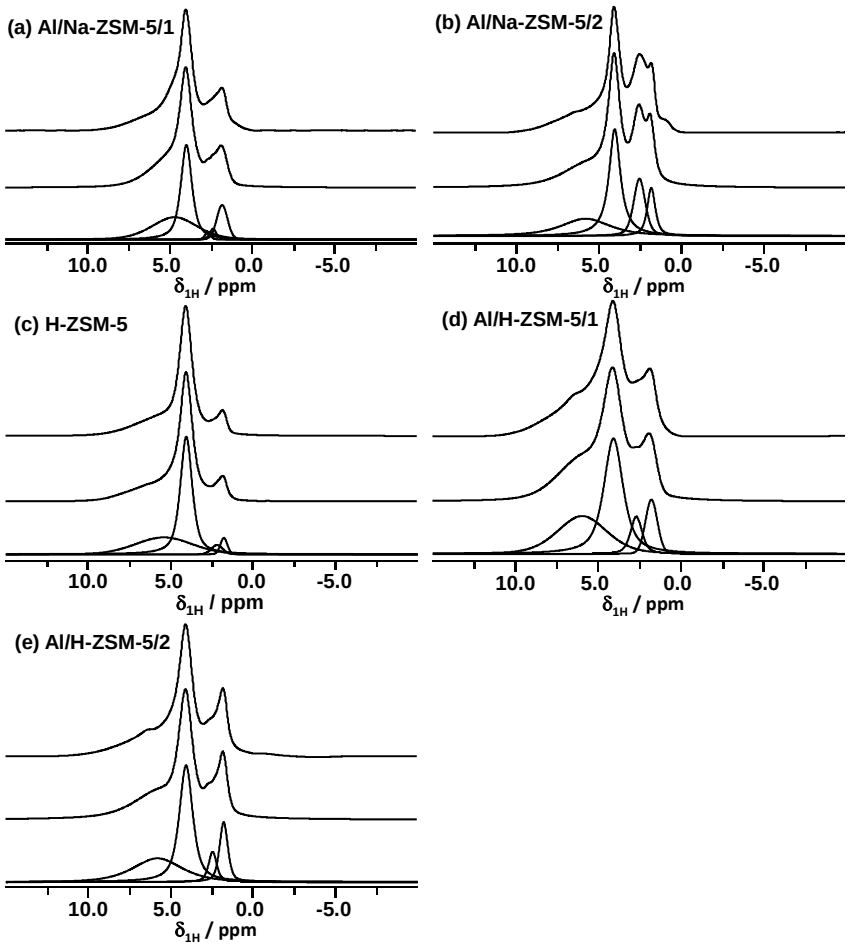

Figure S3. ^{1}H MAS NMR spectra of the dehydrated (723 K) zeolites Al/Na-ZSM-5/1 (a), Al/Na-ZSM-5/2 (b), H-ZSM-5 (c), Al/H-ZSM-5/1 (d) and Al/H-ZSM-5/2 (e) and their simulations (bottom).

Fig. S3 shows the experimental (top) and simulated ^{1}H MAS NMR spectra (middle and bottom) of all the zeolites under study. For all the samples, the main peak at ca. 4 ppm is due to the bridging SiOHAl groups in the ZSM-5 channels, while the broad hump in low-field at 5.4-6 ppm is assigned to the disturbed bridging SiOHAl groups.[4,9] The signals at ca. 2 ppm and 2.7 ppm are due to the SiOH groups and hydrogen bonded non-framework AlOH groups, respectively.[4] After evaluation of the signal intensities in the simulated spectra, the densities of BAS are determined.

^{13}C CP/MAS NMR investigation of acid strength

As shown in Fig. 1, the Al-exchanged Na-ZSM-5 zeolites are dominated by a peak at δ_{13C} = 218 ppm with a shoulder at δ_{13C} = 223 ppm (Figs. 1a and 1b), while the main peak in the ^{13}C MAS NMR spectrum of H-ZSM-5 is at δ_{13C} = 223 ppm. Acetone molecules adsorbed on Al/H-ZSM-5/1 cause two signals at 218 ppm and 225 ppm. EFAl species influence neighboring SiOHAl groups and also enhance their acid strength, as indicated by the shift of ^{13}C signal of acetone molecules from 223 to 225 ppm adsorbed on them (a stronger low-field shift indicates a higher acid strength *and vice versa.*). Further increase of EFAl species on Al/H-ZSM-5/2, the ^{13}C MAS NMR spectrum of acetone molecules adsorbed on this material is dominated by a signal at 225 ppm with a shoulder at 228 ppm (Fig. 1e). A weak signal at δ_{13C} = 235 ppm in zeolites Al/Na-ZSM-5/2 and Al/H-ZSM-5/2 (Fig. 1b and 1e) hints to acetone adsorbed on LAS.[7,10] A peak at δ_{13C} = 210 ppm hints to physisorbed acetone or acetone adsorbed at SiOH groups and the signal δ_{13C} = 190 ppm is due to the formation of mesityl oxide from acetone on strong acidic H-ZSM-5 and Al/H-ZSM-5.[8,11]

^{1}H MAS NMR investigation of acid strength

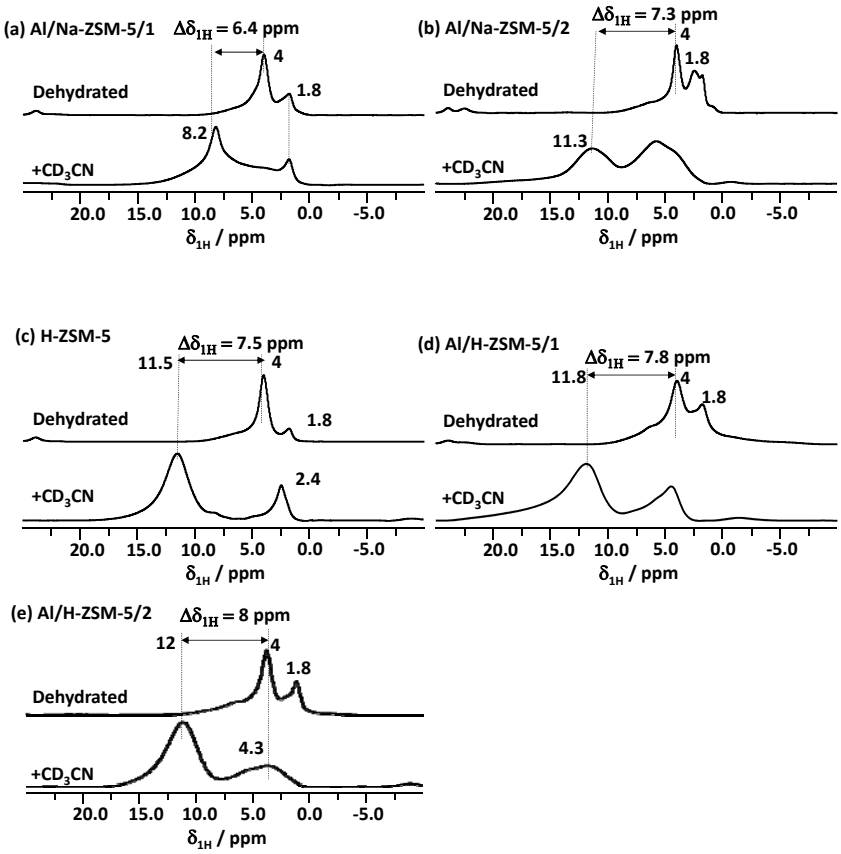

Figure S4. ^{1}H MAS NMR spectra of dehydrated (723 K) zeolites Al/Na-ZSM-5/1 (a), Al/Na-ZSM-5/2 (b), H-ZSM-5 (c), Al/H-ZSM-5/1 (d) and Al/H-ZSM-5/2 (e) recorded upon loading with CD_3CN and evacuation at room temperature for 10 min.

The $\Delta\delta_{1H}$ values observed for bridging OH groups of zeolites Al/Na-ZSM-5/1 (4.2 ppm), Al/Na-ZSM-5/2 (7.3 ppm), H-ZSM-5 (7.5 ppm), Al/H-ZSM-5/1 (7.8 ppm), and Al/H-ZSM-5/2 (8.0 ppm) give 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. This sequence correlates very well with the acid strength of zeolites obtained by acetone adsorption and ^{13}C MAS NMR spectroscopy. Hence, a higher Al exchange degree results in an enhanced acid strength, which was also observed in a previous report on Al-exchanged zeolites X and Y.[5] However, even containing similar amounts of EFAl species, zeolite Al/H-ZSM-5/2 shows a significant higher BAS strength than zeolite Al/Na-ZSM-5/2. This may be due to the much lower electronegativity of the remaining sodium cations in zeolite Al/Na-ZSM-5/2 in comparison with the same

number of hydroxyl protons in zeolite Al/H-ZSM-5/2.

Reference

1 Huang, J.; Jiang, Y. J.; Marthala, V. R. R.; Wang, W.; Sulikowski, B.; Hunger, M. *Microporous Mesoporous Mater.,* 2007, **99**, 86

2 Almutairi, S. M. T.; Mezari, B.; Filonenko, G. A.; Magusin, P.; Rigutto, M. S.; Pidko, E. A.; Hensen, E. J. M. *ChemCatChem,* 2013, **5**, 452.

3 Hunger, M.; Ernst, S.; Steuernagel, S.; Weitkamp, J. *Microporous Mater.,* 1996, **6**, 349.

4 Huang, J.; Jiang, Y.; Marthala, V. R. R.; Thomas, B.; Romanova, E.; Hunger, M. *J. Phys. Chem. C,* 2008, **112**, 3811.

5 Luan, Z. H.; Cheng, C. F.; He, H. Y.; Klinowski, J. *J. Phys. Chem.,* 1995, **99**, 10590.

6 Li, S.; Zheng, A.; Su, Y.; Zhang, H.; Chen, L.; Yang, J.; Ye, C.; Deng, F. *J. Am. Chem. Soc.,* 2007, **129**, 11161.

7 Huang, J.; van Vegten, N.; Jiang, Y.; Hunger, M.; Baiker, A. *Angew. Chem.-Int. Edit.,* 2010, **49**, 7776.

8 Huang, J.; Jiang, Y.; van Vegten, N.; Hunger, M.; Baiker, A. *J. Catal.,* 2011, **281**, 352.

9 Jiao, J.; Kanellopoulos, J.; Wang, W.; Ray, S. S.; Foerster, H.; Freude, D.; Hunger, M. *Phys. Chem. Chem. Phys.,* 2005, **7**, 3221.

10 Haw, J. F.; Nicholas, J. B.; Xu, T.; Beck, L. W.; Ferguson, D. B. *Accounts Chem. Res.,* 1996, **29**, 259.

11 Biaglow, A. I.; Gorte, R. J.; White, D. *J. Catal.,* 1994, **150**, 221.