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Mild Dealumination of H-ZSM-5 Zeolite for Enhanced Conversion of Glucose into 5-Hydroxymethylfurfural in a Biphasic Solvent System

Oluwaseyi Ojelabi [1,2], Satit Yousatit [2], Umer Rashid [2,3] and Chawalit Ngamcharussrivichai [2,4,*]

[1] Program in Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University, Pathumwan, Bangkok 10330, Thailand; 6470076323@student.chula.ac.th
[2] Center of Excellence in Catalysis for Bioenergy and Renewable Chemicals (CBRC), Faculty of Science, Chulalongkorn University, Pathumwan, Bangkok 10330, Thailand; y.satit@hotmail.com (S.Y.); umer.rashid@upm.edu.my (U.R.)
[3] Institute of Nanoscience and Nanotechnology (ION2), Universiti Putra Malaysia, Serdang 43400, Selangor, Malaysia
[4] Center of Excellence on Petrochemical and Materials Technology (PETROMAT), Chulalongkorn University, Pathumwan, Bangkok 10330, Thailand
* Correspondence: chawalit.ng@chula.ac.th; Tel.: +66-2218-7528; Fax: +66-2255-5831

Abstract: Transformation of lignocellulosic biomass into high-value chemicals is a viable strategy for sustainable development of a bio-based economy. 5-Hydroxymethylfurfural (HMF) is one of potential platform bio-chemicals for the manufacture of various renewable products. In this work, a commercial H-ZSM-5 zeolite was used as a starting material for preparing a series of acid catalysts with bifunctionality for direct dehydration of glucose to HMF in a biphasic water/tetrahydrofuran system. The pristine H-ZSM-5 was mildly dealuminated by refluxing with dilute nitric acid solutions to adjust its acid properties. Although the acid treatment slightly altered the elemental composition, textural properties, and morphology of zeolite, the total acidity and distribution of acid sites were significantly modified. Some non-framework aluminum (Al) oxide clusters were removed from the parent H-ZSM-5 simultaneously with a partial hydrolysis of zeolitic framework. An increased fraction of coordinatively unsaturated framework Al species enhanced the number of Lewis acid sites. Using 0.1 M solution in the treatment provided the suitable catalyst (0.1DeAl.H-ZSM-5), giving a glucose conversion and HMF yield of >99% and 64.7%, respectively, and a good reusability under the optimized reaction conditions. These results show the industrial potential of the proposed method for simple but efficient preparation of H-ZSM-5 catalysts for producing HMF via the catalytic dehydration of glucose.

Keywords: glucose; 5-hydroxymethylfurfural; H-ZSM-5; dealumination; acid leaching

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Citation: Ojelabi, O.; Yousatit, S.; Rashid, U.; Ngamcharussrivichai, C. Mild Dealumination of H-ZSM-5 Zeolite for Enhanced Conversion of Glucose into 5-Hydroxymethylfurfural in a Biphasic Solvent System. *Catalysts* **2023**, *13*, 982. https://doi.org/10.3390/catal13060982

Academic Editor: Tomás García

Received: 28 April 2023
Revised: 31 May 2023
Accepted: 5 June 2023
Published: 8 June 2023

1. Introduction

Petroleum-based hydrocarbons mainly contribute to our socio-economic lives as fuels and energy, as well as feedstock for producing petrochemicals and materials. However, a rapid growth in manufacturing industries and urbanization in the past few decades has accelerated the consumption of coal and crude oil [1–3], and, thus, has inevitably brought about serious environmental problems and climate change. To develop a more sustainable future, the utilization of abundant and affordable renewable resources for energy and chemical feedstocks has attracted a lot of attention in both academic and industrial sectors. Transformation of lignocellulosic biomass into high-value chemicals is a viable strategy for the successful development of a sustainable bio-based economy. 5-Hydroxymethylfurfural (HMF), being listed as a top biomass-derived platform chemical according to the US Department of Energy [4], can be utilized for the production of fuel additives, bio-based polymers, plasticizers, biodegradable herbicides, and fragrances [5,6].

Production of HMF via acid-catalyzed dehydration of glucose is an economic route due to the abundance and low cost of cellulose-based feedstock [7]. The application of heterogeneous catalysts, such as proton-form beta and Y zeolites [8], heteropolyacid salts [9], metallic oxides [10,11], mesoporous silica [12], sulfates, and phosphates [13], instead of homogeneous counterparts, in the synthesis of HMF has been investigated extensively. The developed process benefits not only from non-corrosive, more selective, and recyclable solid catalysts, but also from the lower amount of waste discharged [14]. However, owing to the existence of mass transfer limitation, the heterogeneously catalyzed reaction required more severe operating conditions than the HMF synthesis catalyzed by soluble acids [15]. This has raised serious concerns regarding the chemical and thermal stability of the catalysts used. Furthermore, some of the heterogeneous acid catalysts developed so far were synthesized using hazardous chemicals and/or complicated procedures [16], which limit their potential application in the industrial-scale production of HMF. Therefore, more scalable solid acids with superior catalytic performance, prepared via simplified methods, are in high demand and worthy of investigation.

H-ZSM-5 is a proton-form MFI-type zeolite with a high silica/alumina (SiO_2/Al_2O_3) molar ratio, which finds outstanding application as a solid acid catalyst in the petroleum and petrochemical industries due to its well-defined three-dimensional microporous channels providing shape-selective properties, high number of strong Brønsted acid sites, and good thermal and chemical stability. There have been some efforts to apply H-ZSM-5 in the catalytic conversion of glucose into HMF. Yang et al. [17] compared the catalytic performance of different acidic solids in HMF synthesis, among which H-ZSM-5 was the best zeolite-based catalyst, giving an HMF yield of 12%. The H-ZSM-5 with a high SiO_2/Al_2O_3 ratio exhibited moderate acidity and shifted the product selectivity towards HMF [18,19]. Moreno-Recio and co-workers [20] modified the acid properties of a commercial H-ZSM-5 by introducing iron(II) ions via an ion exchange technique, and the resulting catalyst showed an increased HMF yield from 8% to 29% at 195 °C for 150 min. Several types of ionic liquids were examined to enhance the HMF formation over H-ZSM-5 at 110 °C [21]. The highest HMF yield of 45% was obtained using 1-butyl-3-methyl imidazolium chloride ([BMIM]Cl) as a solvent when the reaction was prolonged to 8 h and a high catalyst loading was employed. In addition to the low cost of typical organic solvents, the glucose dehydration over H-ZSM-5 can be operated in a wide domain of temperatures in aqueous/organic biphasic solvents, which allowed a high HMF yield at nearly complete conversion of glucose [19,20].

Since the direct synthesis of HMF from glucose consists of two steps (Lewis acid-catalyzed isomerization of glucose to fructose and Brønsted acid-catalyzed dehydration of fructose to HMF) and side-reactions hamper the HMF selectivity in the presence of excess Brønsted and Lewis acidity, carefully manipulating the acid properties of catalysts is required to achieve a high HMF yield. The total acidity and acid site distribution of H-ZSM-5 can be tuned either through dealumination, such as steam treatment [22] and acid leaching [23], or doping of metal ions [24], among which the acid treatment is the simplest one. In general, the acid-treated zeolites obtained were characterized by a noticeable loss of framework Al species and a crystalline microporous structure due to the high-concentration acid solution used [18,25,26]. As a result, the original acid properties were partially altered together with the generation of various new acidic species, e.g., terminal silanol groups, silanol nests, and aluminum oxide (Al_2O_3) clusters.

Herein, we focused on the preparation of H-ZSM-5 catalysts through a mild dealumination using a dilute acid solution, through which the acid properties of the parent zeolite were manipulated without disturbing the framework crystallinity and microporous structure. A commercial H-ZSM-5 with a SiO_2/Al_2O_3 molar ratio of 24 was chosen as the parent zeolite due to a high Al content. Utilization of commercial H-ZSM-5 as a starting material ensures reproducibility of the acid treatment process and the ability of the catalysts obtained to be scaled up. The acid-treated zeolites were applied to the direct dehydration of glucose to HMF in a biphasic water/tetrahydrofuran (THF) solvent. To the best of our knowledge, a high yield with a H-ZSM-5 zeolite catalyst has never been reported.

2. Results and Discussion

2.1. Physiochemical Properties of Catalysts

The XRF result was reported in terms of SiO_2/Al_2O_3 molar ratio, as depicted in Table 1. The SiO_2/Al_2O_3 ratio of the parent zeolite increased slightly after the acid leaching, indicating a mild dealumination. There was no significant difference in the Al content regarding the concentration of nitric acid solution used (0.1–0.3 M). This may be attributed to the recalcitrant nature of the zeolitic framework of H-ZSM-5 zeolite to a low concentration of acid solution [23]. Triantafillidis et al. observed a decrease in the Al_2O_3 content by only 7 wt% after the dealumination of commercial H-ZSM-5 (SiO_2/Al_2O_3 ratio = 27) with 1.5 M HCl at 90 °C for 24 h [18]. The XRD analysis also confirmed that the typical MFI structure of the parent H-ZSM-5 was retained after the dealumination process using different concentrations of acid solution (Figure 1). The modified samples had the same crystallinity as the pristine commercial H-ZSM-5 zeolite (Table 1).

Table 1. Textural properties and SiO_2/Al_2O_3 molar ratio of all catalyst samples.

Sample	**S_{BET} [a] (m^2/g)**	**D_p [b] (nm)**	**V_{micro} [c] (cm^3/g)**	**V_{meso} [d] (cm^3/g)**	**V_{pore} [e] (cm^3/g)**	**SiO_2/Al_2O_3 Ratio [f]**	**Crystallinity [g] (%)**
Parent H-ZSM-5	343	2.76	0.133	0.105	0.238	21.07	100
0.1DeAl.H-ZSM-5	377	2.78	0.128	0.135	0.263	22.09	100
0.2DeAl.H-ZSM-5	318	2.99	0.115	0.123	0.238	22.13	100
0.3DeAl.H-ZSM-5	276	2.80	0.111	0.082	0.193	22.04	100

[a] BET surface area. [b] Diameter of the pore obtained by the BJH method. [c] Volume of the micropore. [d] Volume of the mesopore ($V_{meso} = V_{pore} - V_{micro}$.). [e] Total pore volume. [f] Determined by XRF. [g] Calculated from XRD patterns at 2θ degrees of 14.81°, 23.10°, 23.86°, and 24.37°.

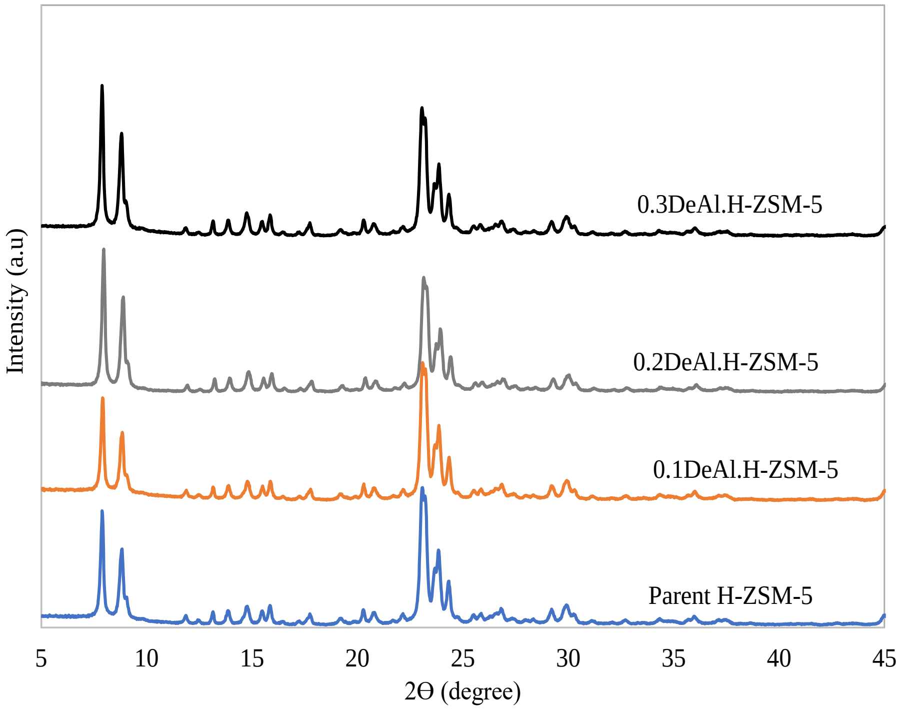

Figure 1. XRD patterns of parent and dealuminated H-ZSM-5 catalysts.

The N_2 adsorption–desorption isotherms of parent and dealuminated zeolites are compared in Figure 2. All catalysts display the type I isotherm of a typical microporous material. The presence of a hysteresis loop at $P/P_0 > 0.4$ indicates the mesoporosity of these zeolite samples [19]. The origin of mesopores should be related to interparticle voids located between the zeolite particles and/or inside the particle agglomerates. As shown in Table 1, the parent H-ZSM-5 exhibited a BET surface area and total pore volume of 343 m^2/g and 0.238 cm^3/g, respectively. The acid leaching with 0.1 M nitric acid solution slightly increased the textural properties of the parent zeolite, possibly due to a decreased degree of particle agglomeration. Here, 0.1DeAl.H-ZSM-5 possessed the highest surface area and porosity. Further increasing the acid concentration used in the dealumination resulted in a decreased surface area and total pore volume of the catalysts. This was explained by a partial hydrolysis of the zeolitic framework and a decreased agglomeration of zeolite particles, as discussed below.

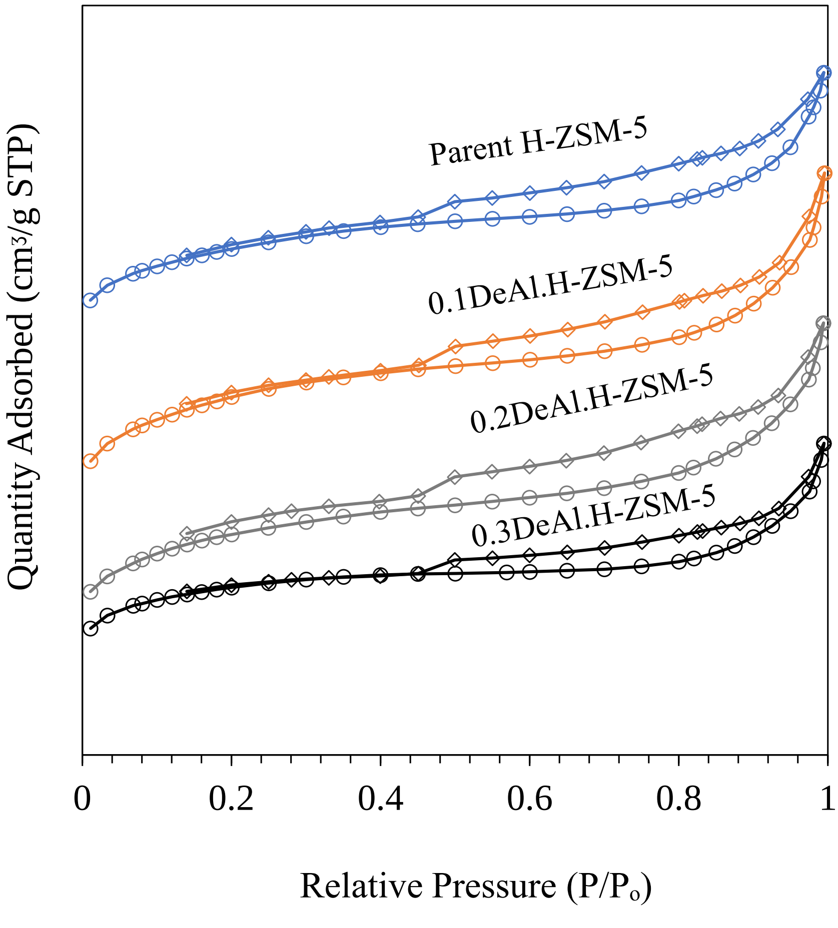

Figure 2. N_2 adsorption–desorption isotherms of parent and dealuminated H-ZSM-5 catalysts. (Symbols: ○ = adsorption data and ◇ = desorption data).

The FE-SEM images of the parent and dealuminated H-ZSM-5 catalysts are presented in Figure 3. The commercial H-ZSM-5 zeolite exhibited a rectangular-shaped nanoparticle agglomerate, similar to the observation of Hoff et al. [27]. Notably, the shape and size of primary zeolite particles were maintained after the acid treatment, but the degree of agglomeration was changed, particularly at a high concentration of the acid solution. The change in the agglomeration nature observed after the dealumination process explained the reduced total pore volume of the catalysts.

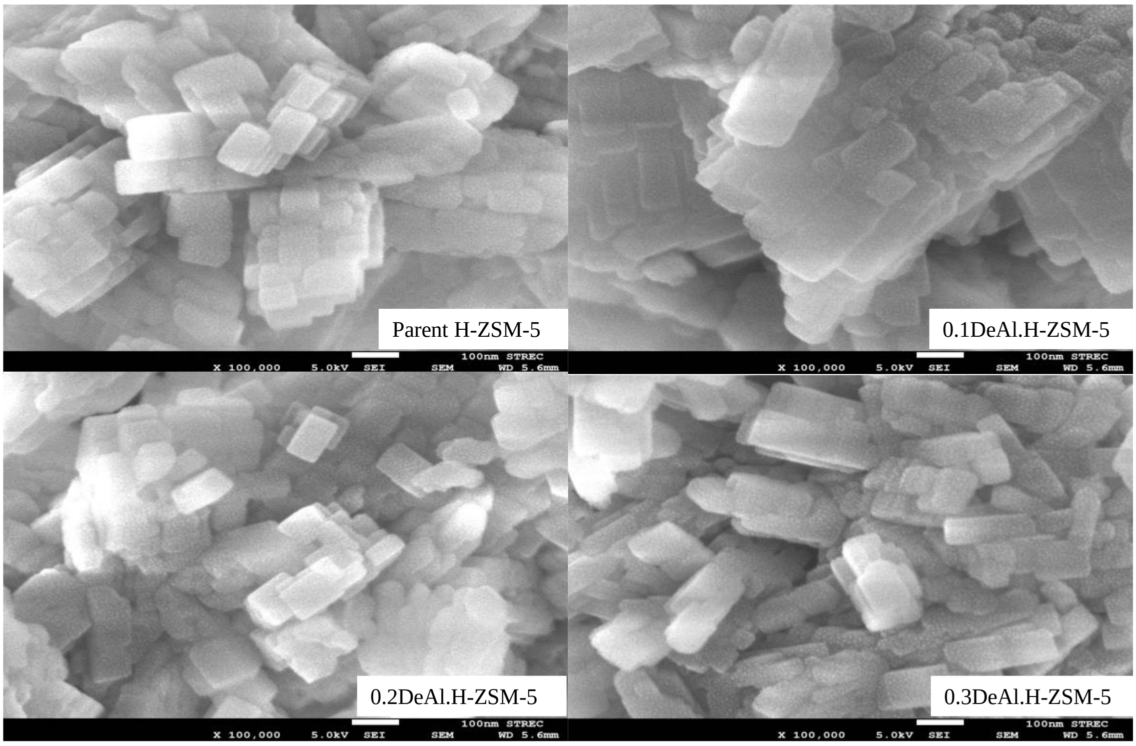

Figure 3. FE-SEM images of parent and dealuminated H-ZSM-5 catalysts at 100,000× magnification.

The solid-state ^{27}Al NMR spectra of parent H-ZSM-5 and 0.1DeAl.H-ZSM-5 are compared in Figure 4A. The chemical shifts at 54 ppm, 37 ppm, and 0 ppm are ascribed to Al species with tetrahedral (Al^{IV}), pentahedral (Al^{V}), and octahedral (Al^{VI}) coordinations in the H-ZSM-5 zeolite, respectively [26,28]. Both Al^{V} and Al^{VI} species can be present as coordinatively unsaturated Al atoms attached in the zeolitic framework and/or extra-framework Al (EFAl) species [26]. The broad signal around −30 ppm was assigned to non-framework Al species in the form of three-coordinate cationic Al^{3+} in the distorted environment [28] and/or charge-neutral Al_2O_3 clusters [18,26]. The distribution (area%) of Al species found for the zeolite samples before and after the dealumination is summarized in Supplementary Materials (SM) Table S1. The acid treatment removed some Al^{VI} species, while the relative fraction of the Al^{V} atoms notably increased, which is consistent with the previous report by You et al. [26]. As mentioned above, the framework of H-ZSM-5 was insignificantly perturbed using 0.1 M HNO_3 solution. The change in the Al environment on the mild dealumination should be attributed to partial removal of EFAl species via hydrolysis and the ion exchange process [25]. Kooyman et al. demonstrated that the dealumination process was a facile method to control the types of Al species, and, thus, the acid properties of H-ZSM-5 catalysts [23].

As shown in Figure 4B, the ^{29}Si NMR spectra of the parent and modified H-ZSM-5 zeolites were deconvoluted into four components, resonating at −85 ppm, −95 ppm, −105 ppm, and −111 ppm, which corresponded to the Si atoms in different coordinations with Al atoms, namely Si(3Al), Si(2Al), Si(1Al), and Si(0Al) species, respectively [25,26,29,30]. Meanwhile, these chemical shifts can be assigned to $Si(OSi)_{4-n}(OR)_n$, where n is 0, 1, 2, or 3, and R is a proton [26,30]. The relative fractions of different Si species are summarized in Table S2 (SM). The dealumination with 0.1 M acid solution mainly increased the fraction of the band at −85 ppm, while other Si coordinations were not significantly changed. The result can be explained by an increase in the number of silanol groups (≡Si–OH) due to a partial hydrolysis of aluminosilicate framework during the acid treatment [31]. This was confirmed by the FTIR spectra of these samples thermally treated at 500 °C (Figure S1: SM). The bands at 3610 cm^{-1} and 3740 cm^{-1} corresponded to bridging hydroxyl groups and silanol groups, respectively [32], while the band at 3680 cm^{-1} was assigned to the hydroxyl groups attached to Al debris and/or the partially hydrolyzed framework Al [33]. Obviously, the content of silanol groups increased by the mild dealumination process, and the band of bridging hydroxyl groups became sharp. The overall results obtained from the NMR and FTIR analysis indicate that using a dilute acid solution removed some EFAl species from the parent H-ZSM-5 and slightly hydrolyzed the zeolitic framework.

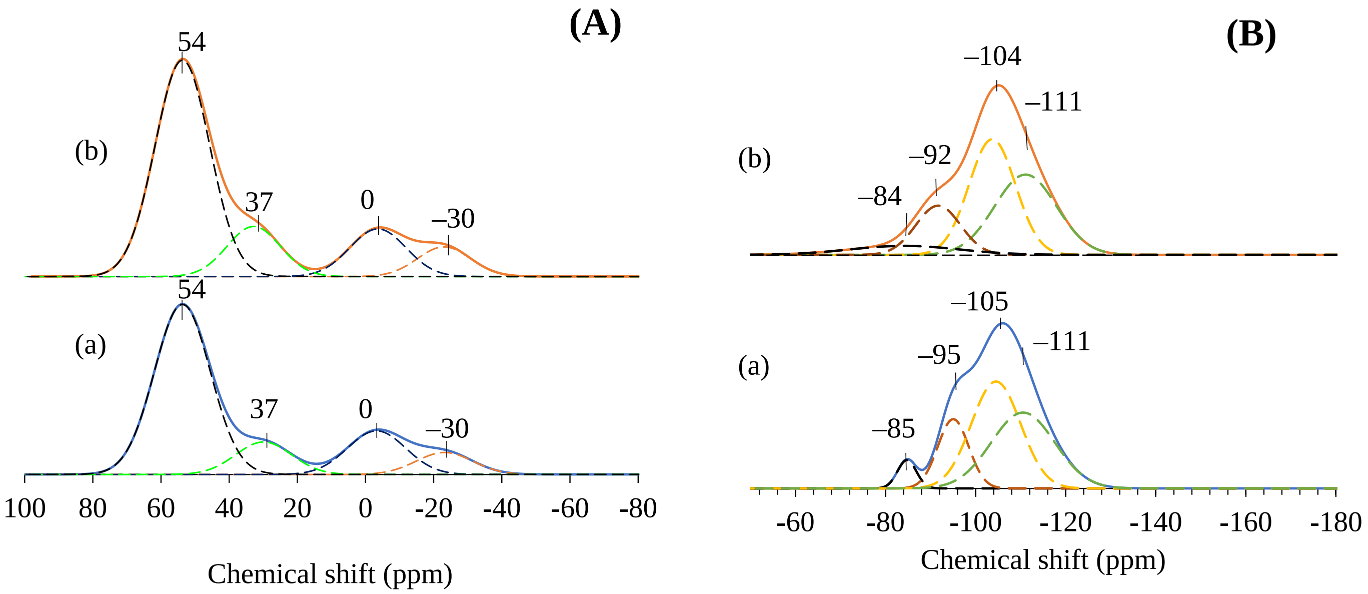

Figure 4. (**A**) ^{27}Al and (**B**) ^{29}Si MAS NMR spectra of (**a**) parent H-ZSM-5 and (**b**) 0.1DeAl.H-ZSM-5.

The total acidity and acid site distribution of the parent and modified H-ZSM-5 zeolites were characterized by the NH_3-TPD analysis. The weak, moderate, and strong acid sites corresponded to the NH_3 desorption peaks located in the temperature region of 50–200 °C, 200–350 °C, and 350–500 °C, respectively, as depicted in Figure 5A. By treating the parent H-ZSM-5 with various HNO_3 solutions, the area under the TPD profiles, and, thus, the total acidity, was increased. The distribution of acid sites with different strengths is shown in Table 2. The acid treatment with 0.1 M acid solution enhanced particularly strong acidity. Since the TPD technique cannot differentiate the type of acid sites, the Py-FTIR analysis was carried out to quantify the Brønsted and Lewis acidity (Figure 5B). The bands at 1545 cm^{-1} and 1455 cm^{-1} were related to the pyridine molecules adsorbed onto the Brønsted and Lewis acid sites, respectively, whereas the superimposition derived from the vibration of the pyridine that interacted with both acid types was located at 1490 cm^{-1} [32]. After the dealumination with 0.1 M HNO_3, the numbers of the Brønsted and Lewis acid sites showed a 1.5-fold and 5.5-fold increase, respectively. As suggested by the solid-state NMR analysis, this was explained by a partial hydrolysis of non-framework Al_2O_3 clusters as well as the zeolitic framework, resulting in a diverse coordination of Al atoms. Further increasing the acid solution concentration increased the number of weak and moderate acid sites, while the strong acidity was slightly decreased. The Py-FTIR analysis indicates that 0.2DeAl.HZSM-5 and 0.3DeAl.HZSM-5 had a lower number of Lewis acid sites than 0.1DeAl.HZSM-5. However, the Brønsted acidity continuously increased with the concentration of the HNO_3 solution. The removal of some cationic EFAl species via the ion exchange process replaced the Lewis acid sites with acidic protons, rendering the Brønsted acidity increased [32].

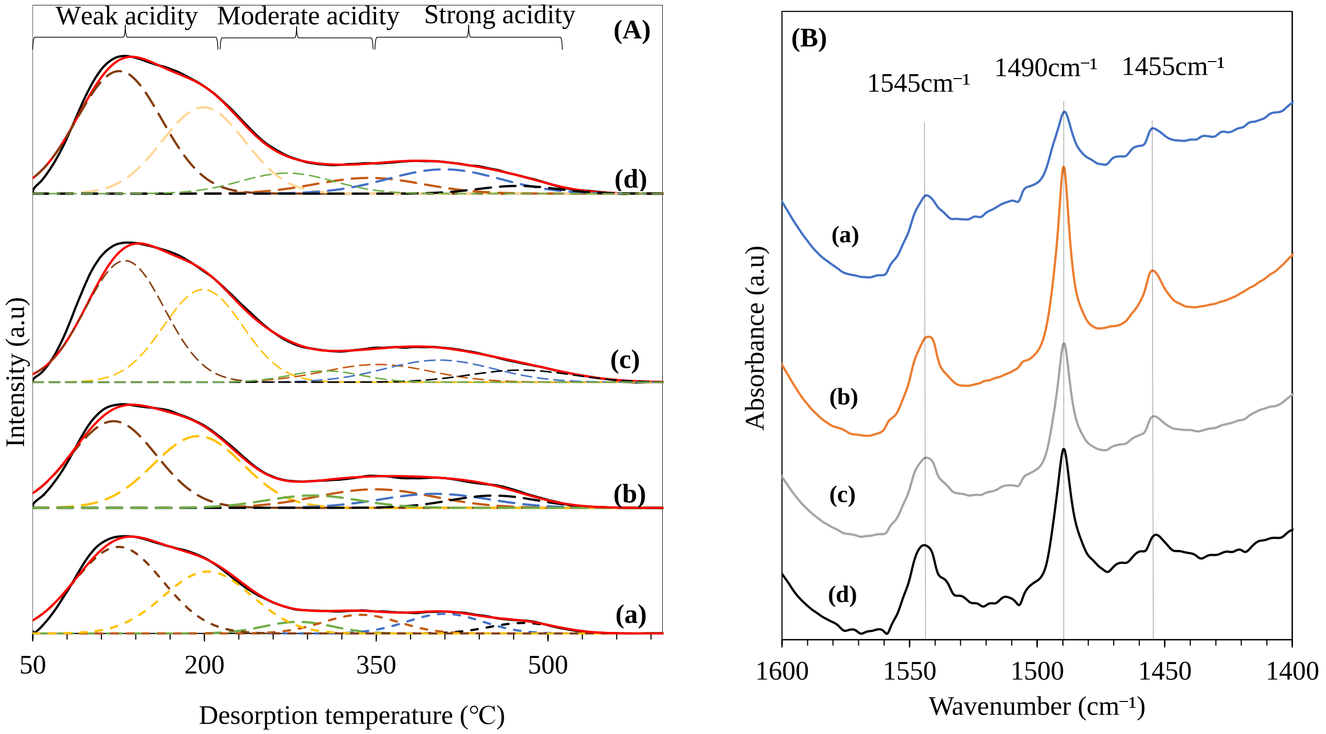

Figure 5. (**A**) NH_3-TPD profiles and (**B**) Py-FTIR spectra of (**a**) parent H-ZSM-5, (**b**) 0.1DeAl.H-ZSM-5, (**c**) 0.2DeAl.H-ZSM-5, and (**d**) 0.3DeAl.H-ZSM-5.

Table 2. Distribution and type of acid sites of parent and dealuminated H-ZSM-5 catalysts.

Catalysts	Acid Sites Distribution (mmol/g) [a]				Type of Acid Sites (mmol/g) [b]		
	Weak	**Moderate**	**Strong**	**Total**	**L**	**B**	**B/L Ratio**
H-ZSM-5	0.735	0.233	0.166	1.134	0.020	0.176	7.35
0.1DeAl.HZSM-5	0.711	0.255	0.224	1.189	0.109	0.261	2.39
0.2DeAl.HZSM-5	1.008	0.291	0.210	1.509	0.051	0.264	5.20
0.3DeAl.HZSM-5	0.976	0.257	0.199	1.432	0.069	0.374	5.39

[a] Determined by NH_3-TPD analysis (weak: 50–200 °C, moderate: 200–350 °C, strong: 350–500 °C). [b] Determined by Py-FTIR analysis (L—Lewis acidity, B—Brønsted acidity).

As evidenced by the XRD and XRF analysis, the crystallinity and elemental composition of the modified zeolites obtained were not significantly altered at relatively high concentrations of the acid solution. However, the degree of particle agglomeration and the interparticle void volume of the acid-treated catalysts were significantly decreased. Losch et al. [34] demonstrated that a H-ZSM-5 zeolite with highly dispersed crystallites had superior acid properties to the agglomerated ones. The total acidity of the modified zeolite remained high even at a 0.3 M acid solution. Our study pointed out the advantage of mild dealumination, by which the acid properties were improved without a detrimental effect on the structural and textural properties of commercial H-ZSM-5.

2.2. Glucose Dehydration to HMF

The plausible reaction pathways for glucose dehydration to HMF and other byproducts are presented in Figure 6. The Lewis acid sites facilitate glucose isomerization to fructose via a 1,2-intramolecular hydride shift [35]. Then, the formed fructose is dehydrated over Brønsted acid centers, removing three molecules of water to form HMF. It was demonstrated that a high Brønsted acidity deteriorated the HMF yield by promoting the HMF rehydration to levulinic acid (LA) and formic acid (FA) [20]. In this work, furfural was also observed as a byproduct. It is a xylose dehydration product from the retro-aldol condensation of fructose intermediates, which is catalyzed by Brønsted acid sites [36]. Humins, either soluble or insoluble polymers, are inevitably formed through condensation among glucose, fructose, and furans, as well as other reactive intermediates, such as 2,5-dioxo-6-hexanal (DHH) [37]. The previous works pointed out that the generation of humins can be retarded, thus, increasing the HMF selectivity, by optimizing not only the total number of acid sites but also the molar ratio of Brønsted/Lewis (B/L) acidity [37,38].

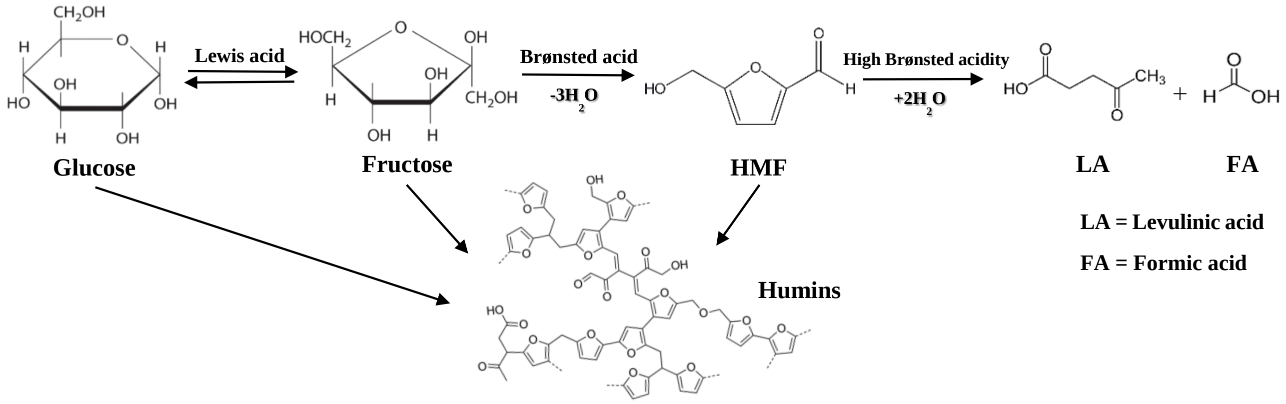

Figure 6. Reaction pathways for formation of HMF and other byproducts in acid-catalyzed glucose dehydration.

2.2.1. Effect of Mild Dealumination of H-ZSM-5

The dehydration of glucose without any catalyst was examined to understand the influence of heterogeneous catalysts with bifunctionality on the HMF synthesis. As shown in Table 3, the HMF yield was poor (17.1%), while the yield of fructose remained high (13.2%) at 38.0% glucose conversion. When H-ZSM-5 was introduced into the reaction, the glucose conversion and HMF yield were increased dramatically to 97.8% and 59.6%, respectively. The combined Lewis and Brønsted acid centers of the parent zeolite actively promoted the isomerization and dehydration steps, respectively. Moreover, the bifunctional nature of the catalyst suppressed the formation of pentose intermediate, as deduced from a low furfural yield (less than 1%). No traces of fructose or LA were detected. Meanwhile, a high amount of humins and other byproducts (soluble oligomers) was observed, as deduced from the dark brown color of the spent catalyst and the reaction mixture. A high amount of the polymerized products in the reaction suggests that the acid properties of the commercial H-ZSM-5 needed optimization for more efficient synthesis of HMF.

Table 3. Glucose dehydration [a] over HZSM-5 and dealuminated H-ZSM-5 catalysts.

Catalyst	Glucose Conversion (%)	Yield (%)				
		Fructose	LA	HMF	Furfural	Others [b]
No catalyst	38.0	13.2	1.5	17.1	0.2	5.1
H-ZSM-5	97.8	0.0	0.0	59.6	0.6	35.6
0.1DeAl.HZSM-5	99.0 ± 1.3	0.4 ± 0.0	0.9 ± 1.1	64.7 ± 0.1	0.8 ± 0.3	30.0 ± 3.5
0.2DeAl.HZSM-5	96.4 ± 2.6	1.2 ± 0.6	6.5 ± 5.6	60.4 ± 0.6	0.8 ± 0.1	25.1 ± 1.4
0.3DeAl.HZSM-5	95.6 ± 2.0	1.5 ± 0.6	2.2 ± 0.1	61.7 ± 0.6	0.8 ± 0.1	27.1 ± 3.3

[a] Reaction conditions: catalyst loading, 500 mg; glucose concentration, 3.6 wt%; reaction temperature, 170 °C; reaction time, 60 min. [b] Mainly humins.

When 0.1DeAl.H-ZSM-5 was utilized as a catalyst, the yield of HMF notably increased to 64.7% at near-completion of the glucose conversion. As shown in Table 2, this result was attributed to an increased number of total acid sites, with especially strong acidity from 0.166 mmol/g to 0.224 mmol/g for the parent and dealuminated zeolite catalysts, respectively. Khumho et al. [39] investigated the catalytic conversion of glucose into

HMF over niobium oxides supported on carbon/silica nanocomposite. They found that the catalyst with the highest number of strong acid sites gave the highest yield of HMF. Furthermore, the mild dealumination process reduced the yield of humins by 5.6%. This result should be related to a decreased B/L molar ratio of zeolite from 7.35 to 2.39 after the dealumination (Table 2). Yousatit et al. [40] demonstrated that the catalyst with a higher proportion of Lewis acid sites was more suitable than the one with a high Brønsted acidity in the selective synthesis of HMF from glucose. This is related to the fact that the isomerization of glucose to fructose is the rate-determining step [41], and Brønsted acid sites are responsible for the aldol addition and condensation of HMF to humins [42]. Notably, the suitable B/L ratio of the bifunctional catalysts used in the direct conversion of glucose was significantly different among studies in the literature [42–44]. This could be attributed to the difference in the physicochemical properties of catalysts, such as specific surface area, pore size, hydrophobicity, as well as the difference in the reaction conditions studied.

The glucose conversion slightly dropped to 96.4% and 95.6% in the presence of the 0.2DeAl.H-ZSM-5 and 0.3DeAl.H-ZSM-5 catalysts, respectively. Although the HMF yield was still maintained at higher than 60%, there was a significant change in the distribution of the other products. The outcome of this result was associated with the acid properties of the dealuminated catalysts. Here, 0.2DeAl.H-ZSM-5 and 0.3DeAl.H-ZSM-5 exhibited an increased number of weak-to-moderate acid sites, while the strong acidity was reduced (Table 2). This should lower their catalytic activity in the glucose isomerization and fructose dehydration. Furthermore, both catalysts with a decreased Lewis acidity (a high B/L ratio) were not suitable for the glucose isomerization to fructose as the rate-determining step [41]. Besides, the 0.2DeAl.H-ZSM-5 and 0.3DeAl.H-ZSM-5 catalysts gave higher LA yield than the parent H-ZSM-5 and 0.1DeAl.H-ZSM-5. This result could be explained by an increased content of weakly acidic silanol groups in the zeolites treated with relatively high concentrations of acid solution, which increased the catalyst hydrophilicity and affinity for water required for rehydration of HMF to obtain LA.

2.2.2. Effect of Reaction Conditions on HMF Synthesis

Owing to the superior catalytic performance to the commercial H-ZSM-5 and other acid-treated zeolite catalysts, the reaction conditions for the acid-catalyzed dehydration of glucose were optimized over 0.1DeAl.H-ZSM-5 in order to obtain the highest HMF yield. As illustrated in Figure 7A, the glucose conversion and HMF yield were low, at 62.5% and 31.2%, respectively, when the reaction was conducted at 150 °C. The yield of fructose remaining at this temperature was 15%. This indicates that the energy available in the system was insufficient for the dehydration of glucose to HMF. An increase in the reaction temperature to 170 °C drove the glucose conversion nearly to completion (>99%) at which point the HMF yield reached 64.7% since the isomerization and dehydration steps are endothermic processes [41,45]. Meanwhile, other byproducts generated at low temperatures were reduced above 160 °C, except for humins. It was demonstrated that the formation of humins through the condensation of glucose and/or fructose has a comparable activation energy (114–127 kJ/mol) to the fructose dehydration to HMF [46]. Therefore, both catalytic routes are accelerated proportionally at elevated temperatures. Further increasing the temperature above 170 °C enhanced the formation of polymerized products by consuming HMF, since there was no glucose and fructose available in the reaction system. Hence, the reaction temperature of 170 °C was selected as the optimum one for screening other reaction parameters.

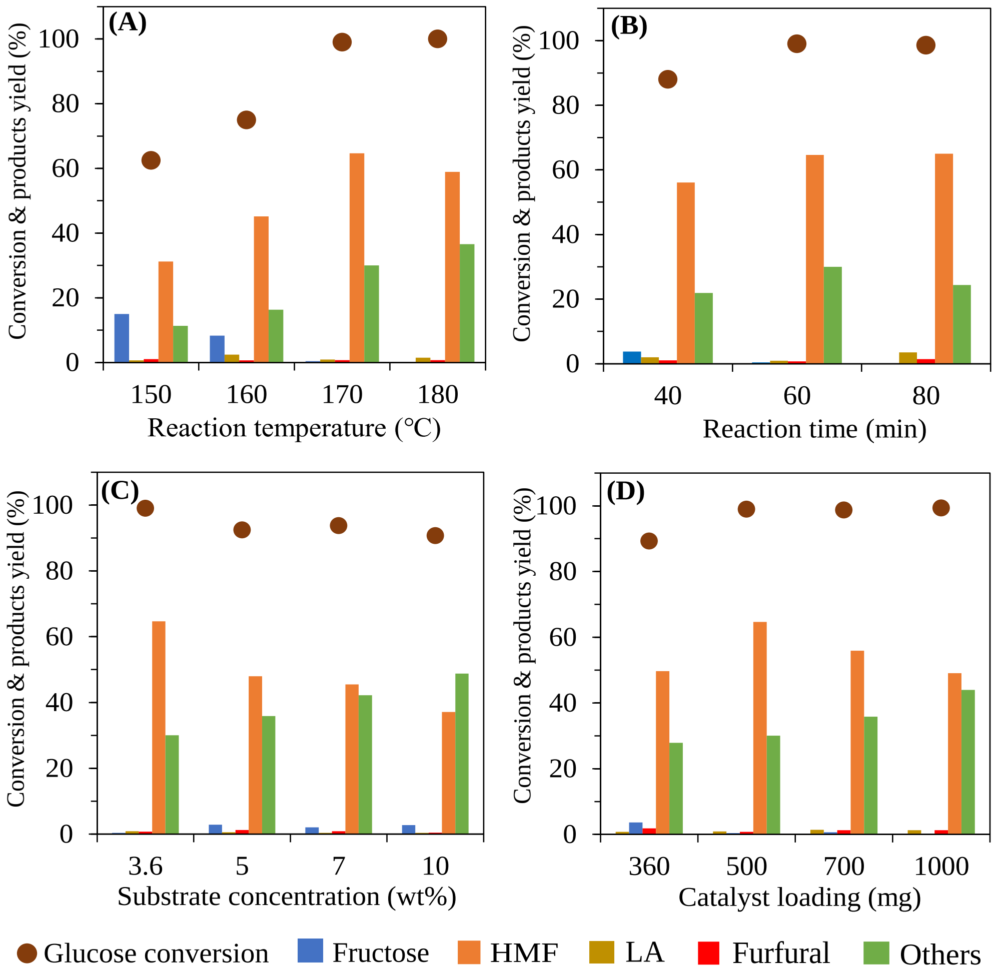

Figure 7. Effects of (**A**) reaction temperature, (**B**) reaction time, (**C**) substrate concentration, and (**D**) catalyst loading in the conversion of glucose to HMF over 0.1DeAl.H-ZSM-5 (central reaction conditions: catalyst loading, 500 mg; glucose concentration, 3.6 wt%; reaction temperature, 170 °C; reaction time, 60 min.

Since the direct conversion of glucose to HMF is a consecutive reaction process accompanied by various side reactions, the reaction time is an important parameter to control the products selectivity and enhance the HMF yield. Herein, the effect of reaction time was studied in the range of 40–80 min (Figure 7B). At 40 min, an HMF yield of 56.1% was obtained at 88.0% glucose conversion, along with a fructose and LA yield of 3.8% and 2.0%, respectively. As the reaction time was prolonged to 60 min, the conversion of glucose jumped to >99% and the yield of HMF was achieved at 64.7%. There was no significant change in the glucose conversion and HMF yield at 80 min, but the distribution of byproducts was altered. Atanda et al. [47] reported that the transformation of HMF to humins at a certain temperature was a function of time. Recently, an acid concentration dependence kinetic study demonstrated that the polymerization and condensation of HMF proceeded at different reaction rates to the rehydration of HMF to LA [38]. In a strong acid-catalyzed system without any glucose and fructose, the rate of HMF conversion into LA was larger than that of HMF-derived humin formation. Considering the HMF yield and ease of products separation, the reaction time of 60 min was a suitable period for the HMF synthesis in this study.

Basically, the concentration of substrate not only controls the yield of formed products but also determines the desired product throughput and economic feasibility of the process. In this work, the glucose concentration in the aqueous phase was varied from 3.6–10 wt% (Figure 7C). It was found that 3.6 wt% of glucose was the suitable substrate concentration by which both the glucose conversion and the HMF yield reached the highest values of >99% and 64.7%, respectively. Around 6–9% of glucose remained in the reaction once the weight of the substrate was increased above the suitable concentration. The HMF yield dropped, while the humin formation was enhanced, proportional to the glucose concentration. An increased availability of HMF and other reactive intermediates formed at a high concentration of substrates induced the polycondensation routes to the unwanted oligomers. This result also implied the cause of catalyst deactivation due to various organic compounds depositing on the surface of the zeolite catalyst. Therefore, a glucose concentration of 3.6 wt% was suitable for the HMF synthesis in this study.

Optimizing the catalyst loading level is a facile approach to increase the number of acid sites responsible for the glucose dehydration, and, thus, to selectively control the HMF formation. When the amount of 0.1DeAl.H-ZSM-5 catalyst in the reaction was extended from 360 mg to 500 mg, the glucose conversion and HMF yield were increased from 89.3% and 49.7% to >99% and 64.7%, respectively. However, using higher levels of catalyst loading deteriorated the HMF yield concomitantly with an enhanced humins yield. The observed trend was similar to the recent study by Ramesh and co-workers [48]. Zhang et al. [49] found that the surplus catalyst provided an excess number of active sites responsible for the HMF hydrolysis and polycondensation to form humins. Based on the result obtained, we concluded that the loading level of 500 mg was suitable for the direct conversion of glucose into HMF over 0.1DeAl.H-ZSM-5.

2.2.3. Reusability Study of 0.1DeAl.H-ZSM-5

The reusability of heterogeneous catalysts generally reflects their catalytic stability and potential application to industrial chemical processes. In the direct conversion of glucose to HMF, the acidic catalysts developed so far have suffered from serious deactivation due to the presence of various reactive intermediates and oligomers that competitively adsorbed on the catalyst surface. To verify the reusability of 0.1DeAl.H-ZSM-5 as a suitable catalyst, the spent catalyst recovered from the reaction mixture was thoroughly washed with hot water (~80 °C), and then toluene (twice each). Subsequently, the washed sample was dried at 80 °C overnight, followed by calcination at 500 °C for 4 h to ensure the removal of all organic deposits. Once the regenerated catalyst was reused in the reaction under the optimized conditions, the glucose conversion and HMF yield dropped remarkably from >99% to 60.4% and from 64.7% to 32.0%, respectively (Figure 8). On the one hand, this result might be associated with the existence of humins that remained adsorbed on the strong acid sites of the catalyst. On the other hand, some strong acid sites in the form of EFAl species were removed from the fresh catalyst during the first run. Other organic solvents with different polarities (THF, ethanol, and isopropanol) were tried in the washing step based on the hypothesis that an increased polarity of solvent could facilitate the removal of oxygenated organic deposits. However, using toluene with the lowest polarity index gave better result. It is worth noting that the performance of catalysts reused in the second and third cycles was not significantly different to the first reuse. This implied that the change in the characteristics of the 0.1DeAl.H-ZSM-5 catalyst occurred only in the first contact with the reaction mixture, and then this catalyst could be reused in the HMF synthesis without a noticeable loss of activity. It should also be addressed that the yield of HMF obtained over the reused catalyst was twofold higher than the reaction without any catalyst.

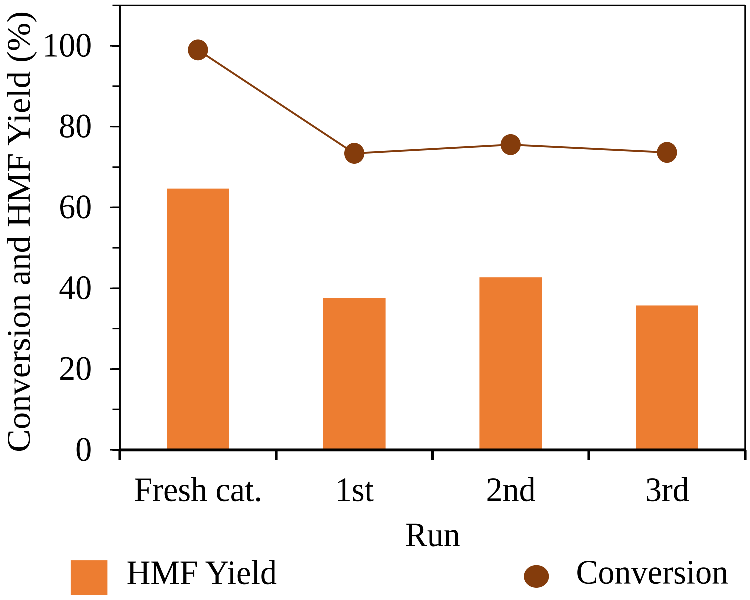

Figure 8. Reusability study of 0.1DeAl.H-ZSM-5 in the glucose dehydration to HMF. Reaction conditions: catalyst loading, 500 mg; glucose concentration, 3.6 wt%; reaction temperature, 170 °C; reaction time, 60 min (except for the 1st–3rd reuse, reaction time was 90 min).

2.3. Performance Comparison between 0.1DeAl.H-ZSM-5 and Other Heterogeneous Catalysts

The catalytic performance of 0.1DeAl.H-ZSM-5 was compared with other zeolite-based catalysts in the direct dehydration of glucose into HMF, as shown in Table S3 (SM). According to our results and the literature reported so far, H-ZSM-5 is a good zeolitic catalyst for HMF synthesis from glucose, especially in a biphasic solvent system [19,20,50]. Compared to large-pore zeolites, the MFI zeolite might benefit from its smaller microporous channels that limit the condensation degree of reactive intermediates to oligomers. Several attempts have been made to adjust the total acidity and the B/L ratio of zeolite catalysts through different techniques, such as modified synthesis procedures [51], metal doping [52,53], and high-temperature calcination [43]. However, there have been some difficulties in controlling the distribution, type, and strength of newly generated acid sites. The reaction ended up with an HMF yield of <60% in most of the cases. Furthermore, these techniques are related to hazardous chemicals or high energy consumption. Herein, the proposed mild dealumination is a simple but efficient procedure to alter the acid properties of commercial H-ZSM-5. Using dilute HNO_3 solution in the dealumination process increased the number of Lewis acid sites in the resulting acid-treated H-ZSM-5 with the preserved microporous MFI framework. Consequently, the glucose–fructose isomerization as the rate-limiting step was facilitated, and, meanwhile, the polymerization of reactive intermediates and HMF to humins was retarded.

3. Experimental

3.1. Material and Chemical Reagents

D(+)-Glucose anhydrous was supplied by Kemaus, Australia. THF (99.5%), nitric acid (65%), and ammonium chloride (NH_4Cl, 99.8%) were provided by QRëC, New Zealand, while sodium chloride (99%) was purchased from J.T Baker, USA. D-Fructose (extra pure) was a product of LOBA Chemie, India. Levulinic acid, HMF, and furfural standards were all purchased from Sigma-Aldrich (St. Louis, MI, USA), USA. Commercial proton-form H-ZSM-5 with a SiO_2/Al_2O_3 molar ratio of 24 was obtained from TOSOH Corporation Limited, Japan. Prior to use, the commercial H-ZSM-5 was calcined at 550 °C for 6 h.

3.2. Mild Dealumination of H-ZSM-5

The dealuminated H-ZSM-5 catalysts were prepared by acid leaching of commercial H-ZSM-5 using nitric acid solutions with concentrations of 0.1, 0.2, and 0.3 M. In a typical procedure, 3 g of commercial H-ZSM-5 was accurately weighed in a one-necked round-bottom flask, and then 120 mL of nitric acid solution was introduced under vigorous stirring. The resulting mixture was heated using an oil bath connected with a thermocouple, and then refluxed at 80 °C for 2 h. After that, the mixture was allowed to cool down, followed by filtration, and was then washed thoroughly until a neutral pH was reached. The solid obtained was dried at 80 °C overnight, ground into powder, and calcined at 550 °C for 6 h at a heating rate of 5 °C/min. The dealuminated zeolites were denoted as *x*DeAl.H-ZSM-5, where *x* represents the concentration of the nitric acid solution.

3.3. Catalyst Characterization

The crystallinity of zeolite samples was examined by powder X-ray diffraction (XRD). The XRD patterns were recorded over a 2θ range of 5°–80° using a Bruker D8 ADVANCE X-ray diffractometer with Cu Kα radiation (λ = 1.541 Å) operating at 40 KV and 30 mA. Wavelength dispersive X-ray fluorescence spectroscopy (Rigaku, ZSX Primus III+) was used to examine the elemental composition of zeolites before and after the dealumination.

A Micromeritics ASAP 2020 porosity and surface area analyzer was employed to determine the textural properties of the catalysts. Before the analysis, the calcined samples were degassed for 1 h at 300 °C under vacuum. The measurement of nitrogen (N_2) physisorption was carried out at −196 °C, using a vacuum setpoint of 50 µmHg. The specific surface area (S_{BET}) was calculated from the adsorption branch in the relative pressure (P/P_0) ranging from 0.05 to 0.25, using the Brunauer–Emmett–Teller (BET) equation. The total pore volume (V_{pore}) was obtained from the adsorption data at a P/P_0 of 0.99. The Barret–Joyner–Halenda (BJH) plot of the adsorption data was used to calculate the pore size ($\mathrm{D_p}$). The micropore surface area of the catalysts was evaluated by the *t*-plot method from the adsorption data.

Field emission scanning electron microscopy (FE-SEM) was applied to the morphological study of pristine and modified H-ZSM-5 samples. The FE-SEM images were recorded on a JEOL JSM-7610F instrument operating at 5.0 kV. Before the image capturing, the sample was spread on a carbon tape, and then sputter-coated with gold.

The chemical environments of aluminum (Al) and silicon (Si) in the zeolite catalysts were respectively investigated by solid-state ^{27}Al and ^{29}Si magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy. The NMR spectra were recorded on a BRUKER/AVANCE III HD/Ascend 400 WB Fourier transform NMR spectrometer at room temperature, using an excitation pulse length of 5 µs and 4000 µs, pulse delay of 3 s and 5 s, an acquisition time of 0.0390485s, and number of scans of 1000 (^{27}Al NMR) and 1500 (^{29}Si NMR), respectively. The chemical shifts in the ^{27}Al and ^{29}Si MAS NMR spectra are represented in parts per million (ppm) using aluminum chloride hexahydrate ($AlCl_3 \cdot 6H_2O$) and sodium trimethylsilylpropanesulfonate (DSS) as reference standards, respectively. The samples were hydrated with saturated ammonium chloride (NH_4Cl) solution for 3 d before the analysis.

Temperature-programmed desorption of ammonia (NH_3-TPD) was conducted by using a Micromeritics AutoChemII 2920 chemisorption analyzer to determine the effect of dealumination on the number and distribution of acid sites. The calcined zeolite (~80 mg) was pretreated under helium (He) gas flow (50 mL/min) at 550 °C for 30 min using a ramp rate of 10 °C/min. After cooling down to 50 °C, the sample was equilibrated with an NH_3 gas flow (10 vol% NH_3 in He) for 30 min, followed by flushing with He for 30 min to remove the physisorbed NH_3. The desorption of NH_3 was measured with a thermal conductivity detector at the temperature range of 50 °C to 800 °C (a heating rate of 10 °C/min). The quantitative determination of the NH_3 desorbed was performed by deconvoluting the TPD profiles with OriginPro software.

The number of Brønsted and Lewis acid sites present in the parent and dealuminated H-ZSM-5 catalysts was examined by *in situ* Fourier transform infrared spectroscopy for pyridine adsorption (Py-FTIR). The fresh zeolite powder was shaped into a self-supported wafer (2 cm diameter), and then loaded into a quartz cell. The pretreatment was carried out at 500 °C for 60 min under evacuation to remove impurities. The cell was then cooled down to 50 °C, followed by introducing pyridine vapor at 500 Pa for 30 min, and then degassing from 100 °C to 500 °C for 15 min at each temperature. The analysis was performed on a Thermo-Fisher Scientific NICOLET iS10 FTIR spectrometer, recording the spectra for 96 scans over a wavenumber range of 400–4000 cm^{-1}.

3.4. Glucose Dehydration to HMF

A typical catalytic dehydration of glucose was carried out in a biphasic system with a 2:1 volume ratio of THF: H_2O (saturated with NaCl) using a 60 mL Teflon-lined stainless steel autoclave reactor. An aqueous solution containing glucose anhydrous and NaCl was made by dissolving 7.2 g of glucose and 40 g of NaCl in 200 mL of deionized water under vigorous stirring. Then, 10 mL of the obtained solution was mixed with THF (20 mL) and freshly calcined catalyst (0.5 g) in the autoclave reactor, after which it was pressurized with 10 bar of N_2 gas. The reaction temperature was controlled using a silicone oil bath equipped with a proportional–integral–derivative thermocouple and a hot plate stirrer. Once the target temperature was reached, the starting reaction time was recorded. After 60 min, the reactor was quenched in an ice bath, followed by liquid product recovery by using a centrifuge.

The aqueous and organic products were filtered with a 0.2 μL PTFE syringe filter and analyzed by high-performance liquid chromatography (HPLC) using an Agilent 1100 Series HPLC system equipped with a Bio-Rad HPX87-H column operated at 60 °C in the presence of 5 mM H_2SO_4 as a mobile phase (flow rate of 0.5 mL/min). Typically, 1 mL of solution containing the analyte (800 μL) and internal standard (200 μL) was prepared as an analysis sample. A diode array detector was used to examine the products' composition in the organic phase at a UV wavelength of 240 nm, while the products in the aqueous phase were analyzed with a refractive index detector. The glucose conversion and product yields were calculated as follows:

$$\text{Conversion } (\%) = \frac{(\text{Initial concentration of glucose} - \text{concentration of glucose after reaction}) \times 100}{\text{Initial concentration of glucose}}$$

$$\text{Yield } (\%) = \frac{\text{Concentration of desired product} \times 100}{\text{Initial concentration of glucose}}$$

$$\%\ \text{Other byproducts} = \text{Conversion} - (\%)\ \text{Total products yield } (\%)$$

4. Conclusions

In summary, a series of acid-treated zeolites were successfully prepared from commercial H-ZSM-5 via a mild dealumination process using dilute HNO_3 solution. The resulting DeAl.H-ZSM-5 catalysts exhibited the preserved crystallinity and morphology. Although the acid treatment slightly affected the Al content of zeolite, the ^{27}Al and ^{29}Si NMR analysis revealed that the chemical environment of Al and Si atoms was locally altered. The mild dealumination removed some EFAl oxide species from the parent H-ZSM-5, and partially hydrolyzed the zeolitic framework, resulting in an increased fraction of coordinatively unsaturated framework Al species. Consequently, the total acidity was enhanced; indeed, the number of Lewis acid sites in 0.1DeAl.H-ZSM-5 was fivefold higher than that in the pristine H-ZSM-5. Here, 0.1DeAl.H-ZSM-5 was the suitable catalyst, giving an HMF yield of 64.7% at near-completion of the glucose conversion. A relatively high number of strong acid sites and a decreased B/L ratio of 0.1DeAl.H-ZSM-5 were crucial for reducing the formation of byproducts, and, thus, increasing the selectivity to HMF. Due to a good reusability and simple preparation procedure, the mildly dealuminated H-ZSM-5 catalysts shows potential for the industrial production of HMF from glucose.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal13060982/s1, Table S1. Fractions of Al species in the parent and dealuminated H-ZSM-5 catalysts. Table S2. Fractions of Si species in the parent and dealuminated H-ZSM-5 catalysts. Table S3. Glucose conversion and HMF yield obtained over different zeolite-based acid catalysts. Figure S1. FTIR spectra of the parent H-ZSM-5 and 0.1DeAl.H-ZSM-5 in the O–H stretching region.

Author Contributions: Conceptualization, O.O. and C.N.; methodology, O.O. and S.Y.; validation, S.Y. and C.N.; formal analysis, O.O. and C.N.; investigation, O.O. and S.Y.; resources, C.N.; writing—original draft preparation, O.O.; writing—review and editing, U.R. and C.N.; supervision, U.R. and C.N.; funding acquisition, C.N. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Thailand Science Research and Innovation (TSRI), Chulalongkorn University, grant number CUFRB65_bcg(4)_072_23_02.

Data Availability Statement: The data presented in this study are available in the article and the Supplementary Materials.

Acknowledgments: The authors are grateful to the financial support from the ASEAN/NON-ASEAN Scholarship Board (O.O.), the Center of Excellence in Catalysis for Bioenergy and Renewable Chemicals (CBRC), and the Program in Petrochemistry and Polymer Science, Chulalongkorn University, and the International Research Network (contract no. IRN61W0003), Thailand Science Research and Innovation (TSRI). The technical support from the Center of Excellence on Petrochemical and Materials Technology (PETROMAT), Chulalongkorn University, is also acknowledged.

Conflicts of Interest: The authors declare no conflict of interest.

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