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Nanosheet MFI Zeolites for Gas Phase Glycerol Dehydration to Acrolein

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Abstract: To overcome the rapid deactivation of conventional ZSM-5, novel nanosheet MFI zeolites, with different Si/Al molar ratios were well fabricated. It was found that Si/Al molar ratios, do not just affect acid properties, but also determine the morphologies of nanosheet MFI zeolites by changing a-c plane areas of zeolite nanosheets. In reaction of gas phase glycerol dehydration to acrolein, the nanosheet MFI zeolites were much more active and stable than conventional ZSM-5 catalysts, owing to their suitable acidity and unique nanosheet structure. For nanosheet MFI zeolite, with Si/Al = 50 (NMZ-50), the conversion of glycerol is higher than 99% in the initial 12 h, with an acrolein selectivity of 86.6%, better than most previous reports. This superior stability of NMZ-50 can be ascribed to its low coke deposition rate and improved coke tolerance capacity. Additionally, it is interesting to find that Al contents do not just simply affect acid properties, but also determine morphologies of nanosheet MFI zeolites, and thus influence catalytic performance.

Keywords: glycerol dehydration; acrolein; nanosheet; MFI zeolite

1. Introduction

With the depletion of petroleum resources and growing concerns about environmental issues, increasing attention has been paid to the utilization of renewable resources, such as plant biomass [1,2]. As a main co-product in biodiesel production, glycerol is an important renewable resource derived from biomass [3–6]. Despite many applications in cosmetics, pharmaceuticals, and the tobacco industry, after expensive purification processes, glycerol production surplus is still a big problem [7,8]. In this context, upgrading glycerol to value-added chemicals becomes an urgent task, but with a bright future. Acrolein, which can be produced by the dehydration of glycerol, is considered a versatile intermediate for producing acrylic acid or acrylates, detergents, superabsorber polymers, etc. [9,10]. However, acrolein is currently manufactured from propylene, a petrochemical product [11,12]. Therefore, the sustainable production of acrolein from abundant glycerol is a promising technology.

In recent years, a wide range of solid acid catalysts were employed for gas phase dehydration of glycerol to acrolein, such as transition metal oxides, heteropoly acids (HPAs), zeolitic catalysts, and so on [10,13–27]. Among them, zeolites, like HZSM-5 [21], mordenite [28], ITQ-2 [7], etc. received significant attention for their tunable acid properties and unique topologies.

HZSM-5 zeolite (MFI topology) has a three-dimensional 10-membered ring structure, consisting of straight ($5.3 \times 5.6 \text{ \AA}^2$) and sinusoidal ($5.1 \times 5.5 \text{ \AA}^2$) channels with intersections, which has been successfully applied in many petrochemical processes [29]. Meanwhile, recent research shows that

HZSM-5 zeolites achieve high activity in gas phase dehydration of glycerol [28,30–33]. Compared with other catalysts (Beta, mordenite, MCM-22, ITQ-2, etc.), it is more flexible to adjust the acidity and morphology of HZSM-5. Thus, HZSM-5 becomes the most studied zeolites in glycerol dehydration [9,21,34]. However, the single micro-channels in normal HZSM-5 suppress mass transfer, form coke rapidly, and result in fast deactivation by covering acid sites or blocking zeolite channels [21,34–36]. Jia et al. [21] reported that the enhanced performance of nanosized HZSM-5 was ascribed to its short micropores in comparison with bulk one. Meanwhile, zeolites with hierarchically porous structures have also been introduced to glycerol dehydration process. Hierarchically-structured zeolites provide secondary networks of meso- and/or macro- pores and possess advantages associated with each level of porosity [37]. Zhang et al. [34] investigated four types HZSM-5 zeolites with a series of mesopore architectures, which are different from each other in the properties of mesopore size, amount, distribution, and connectivity. Their results show that HZSM-5 with the open and interconnected mesopore architectures is superior to the closed one.

Lately, nanosheet MFI zeolites with only several nanometer thickness along the b-axis dimension have been reported as active and long-lived catalysts in methanol-to-gasoline/-propene. Their large external surface and effective mass transfer contribute to enhanced performance [38–40]. As discussed above, coke formation is the main reason for catalyst deactivation in glycerol to acrolein, so the nanosheet MFI zeolites might be applied to glycerol dehydration as excellent candidates. In this work, we first report on the superior catalytic performance of nanosheet MFI zeolites in gas phase dehydration of glycerol to acrolein. The conventional particle type MFI zeolites were made for comparison. It needs to be emphasized that the effects of Si/Al ratio on morphology, acidity, and catalytic performance of nanosheet MFI zeolites have been attentively explored.

2. Results and Discussion

2.1. Characterization Results

Powder X-ray diffraction patterns in Figure 1 have confirmed that all the synthesized NMZ-X and CMZ-X samples are well-crystallized zeolites with MFI topology. Comparably, only *h0l* reflections at 7.9°, 8.9°, 14.8°, 15.9°, 17.8°, 23.1°, 24.0°, 26.8°, and 30.0° [39] are sharp enough to index for the nanosheet MFI zeolites (Figure 1b). The result indicates that all NMZ-X samples possess coherent domains with wide a-c planes and extremely small framework thickness along b-axis [39,40].

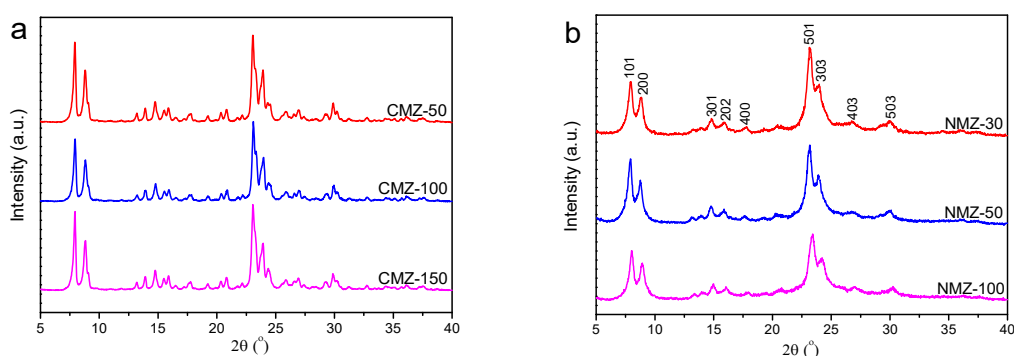


Figure 1. X-ray diffraction (XRD) patterns of (a) CMZ-X and (b) NMZ-X.

SEM was employed to characterize zeolite morphologies (Figure 2). For CMZ-X synthesized with TPAOH as the structure directing agent, the zeolites appear in uniform particles of about 400 nm with intergrowth cylindroid (Figure 2a–c). The Si/Al molar ratio of NMZ-X has a great influence on the morphologies of nanosheet MFI zeolites. NMZ-100 (Figure 2f) looks like multi-lamellar stacking of MFI nanosheets with intergrowth in three-dimension, in well agreement with the report by Choi's group [40,41]. The size of NMZ-100 particles is about 1.5 μm assembled by 30–40 nm thickness lamellar

stacking. Meanwhile, NMZ-50 shows similar lamellar staking of MFI nanosheets, but the particle size (500 nm) and lamellar stacking thickness (about 10 nm) are much smaller (Figure 2e). However, NMZ-30 seems like cotton balls and we cannot distinguish the MFI nanosheets from the SEM image (Figure 2d).

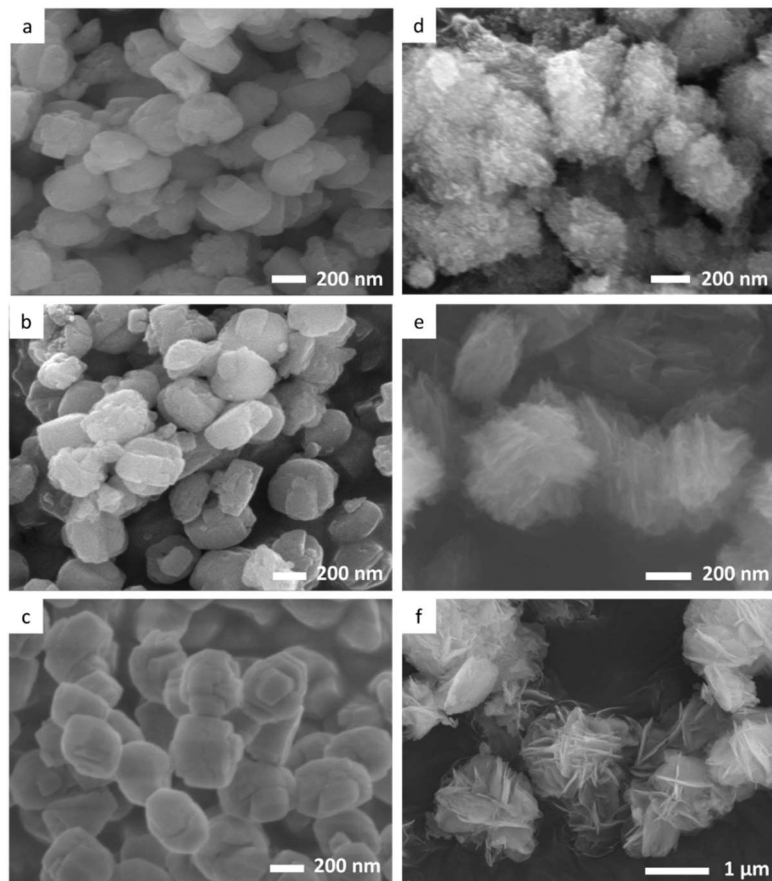


Figure 2. Scanning electron microscope (SEM) images of (a) CMZ-50, (b) CMZ-100, (c) CMZ-150, (d) NMZ-30, (e) NMZ-50, and (f) NMZ-100.

As implied by the XRD patterns, NMZ-30 is well-crystallized and presents characteristics of nanosheet MFI zeolite. Thus, TEM images were taken to recognize the morphology of NMZ-30. As illustrated in Figure 3a,b, NMZ-30 is stacked by MFI nanosheets with much smaller area in a-c planes, which cannot be distinguished by SEM (Figure 2d). By comparing the TEM images of nanosheet MFI zeolites with different Si/Al molar ratios, it can be found that Al content plays a key role in the appearance of NMZ-X. Generally, a Si–O–Al structure is not as stable as a Si–O–Si structure in the MFI framework [42]. It is not easy to grow large area MFI nanosheets with low Si/Al molar ratio, because of the existence of abundant unstable Si–O–Al units. With the increase in Si/Al molar ratio, Al content as well as amount of Si–O–Al unit decreases and width of a-c planes in MFI layer increases quickly from less than 10 nm to several hundred nanometer as marked in Figure 3. Thus, Al content can significantly affect the crystallization processes of MFI nanosheets and determine the final morphology.

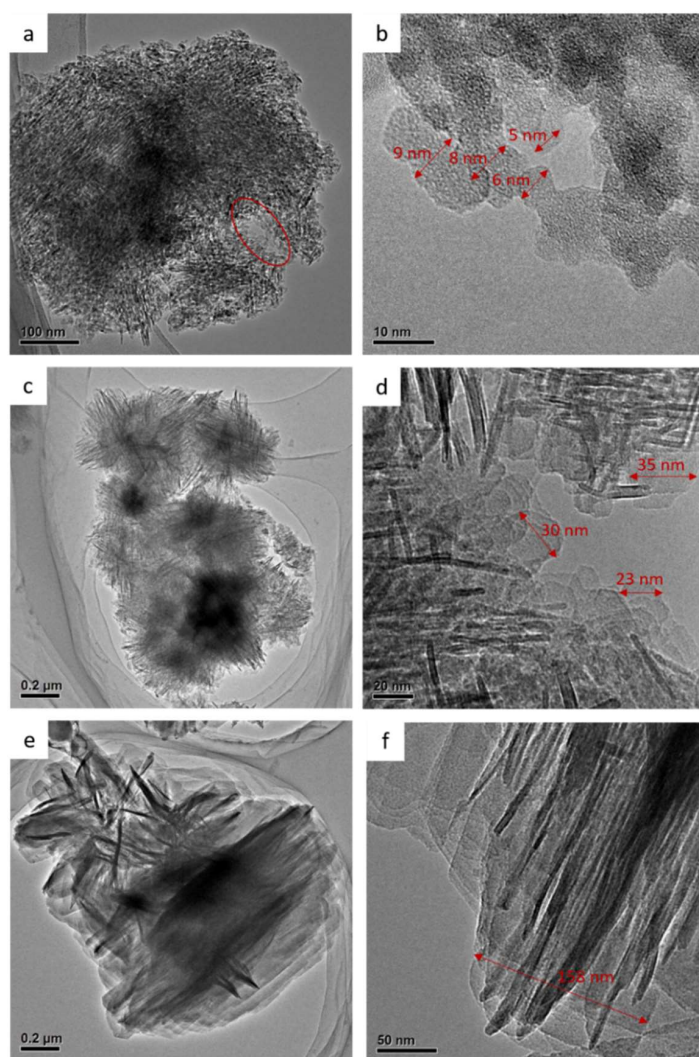


Figure 3. Transmission electron microscope (TEM) images of (a,b) NMZ-30, (c,d) NMZ-50, and (e,f) NMZ-100 at different magnifications.

The morphologies of NMZ-X samples affect the N₂ adsorption-desorption isotherms (Figure S1a). The textural properties of all samples are listed in Table 1. According to IUPAC classification, all the NMZ-X samples show typical IV isotherm, demonstrating their mesoporous properties [18]. Although the BET surface area of NMZ-30 is very close to that of NMZ-50, their pore size distributions are not identical. For Figure S1b, the mesopore size distribution of NMZ-30 is broader than NMZ-50 and NMZ-100. The difference is related to the a-c plane area of the MFI nanosheet, which results in different assembly manners in NMZ-X.

Table 1. Chemical composition and textural properties of different samples.

Sample	Si/Al ^a	Surface Area (m ² g ^{−1})			Pore Volume (cm ³ g ^{−1})	
		Total	Micro ^b	External ^c	Total	Meso ^d
NMZ-30	28	543	271	272	0.67	0.63
NMZ-50	46	563	267	296	0.71	0.66
NMZ-100	94	432	241	191	0.53	0.45
CMZ-50	48	355	262	93	0.21	0.10
CMZ-100	96	363	275	88	0.22	0.12
CMZ-150	143	370	279	91	0.21	0.11

^a Determined by ICP-AES. ^b By t-plot method. ^c External = Total – Micro. ^d Using BJH method.

The NH_3 -TPD measurements were conducted to probe the accessible acid sites over zeolite samples (Figure 4). All samples present two desorption peaks in different temperature regions. The low-temperature peak is generally assigned to chemisorption of ammonia on weak acid sites, and the high-temperature one is ascribed to strong acid sites. The acid sites amount and acid strength distribution are very close for NMZ-X and CMZ-X, with similar Si/Al molar ratios. Meanwhile, the quantitative results of acid properties are presented in Table S1. Among them, NMZ-30 possesses the most acids sites owing to its high Al content.

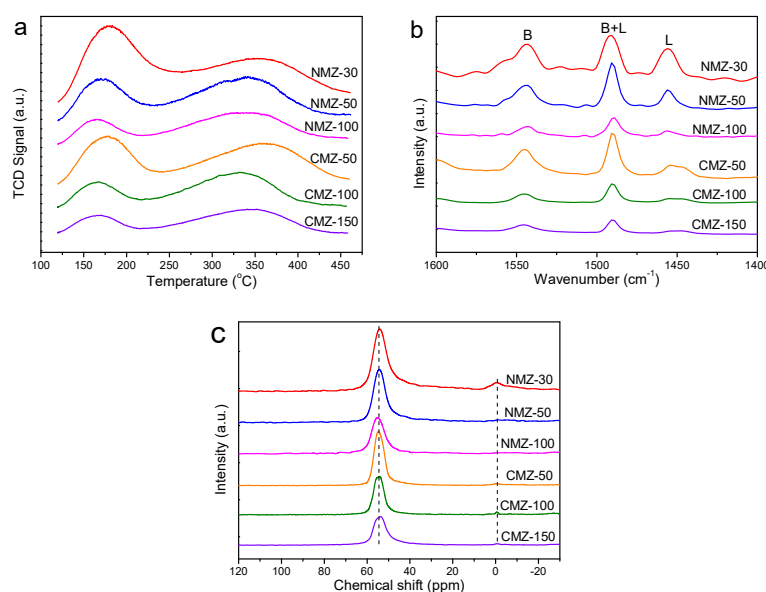


Figure 4. (a) NH_3 -TPD profiles, (b) FT-IR spectra of adsorbed pyridine collected at 150 $^{\circ}\text{C}$ and (c) ^{27}Al MAS NMR spectra of NMZ-X and CMZ-X.

The acid type has a great influence on reaction activity and product distribution in gas phase dehydration of glycerol, as reported by Wang et al. [17]. The Py-IR spectra, given in Figure 4b, and the data presented in Table S1, illustrate that NMZ-30 shows the lowest B/L ratio. This result can be confirmed by ^{27}Al MAS NMR spectra in Figure 4c. Clearly, the vast majority of Al species in all samples are tetracoordinated (AlIV, the broad signal around 56 ppm). AlIV species are the source of Brønsted acid [42]. However, the peak at 0 ppm of NMZ-30, octahedral Al species associated with Lewis acid sites, is much larger than the other samples, coincidental with Py-IR results.

The used catalysts were obtained after glycerol conversion decreased to about 80%, and then characterized by TGA in flowing air. The TGA and DTA curves, as recorded in the coke oxidation processes, are displayed in Figure 5. For NMZ-X, two strong exothermic peaks centered at 360 $^{\circ}\text{C}$ and 510 $^{\circ}\text{C}$ originate from the removal of different kinds of carbon deposits. The large former peak comes from hydrogen-rich carbonaceous residues [43]. As disclosed by Bauer et. al. [43], coke becomes more hydrogen deficient because of hydrogen transfer reactions with longer reaction time. So the latter one can be ascribed to some condensed cokes resulting from a long time on a stream, which are difficult to be eliminated. Comparatively, only one broad peak can be observed in the DTA curves of CMZ-X. Rapid deactivation might lead to the generation of abundant hydrogen-rich cokes on CMZ-X samples for the short reaction time, but the peak centers were slightly higher than 360 $^{\circ}\text{C}$. The reason for this phenomenon was that some cokes in CMZ-50 were located in the micropores, which were a bit difficult to elimination [22]. The cokes in different depth of the zeolite channels were sequentially burning at different temperature, resulting in one broad peak. The coke contents of spent catalysts are inversely proportional to the Si/Al ratios (Figure 5a), because more acid sites in zeolites with lower Si/Al molar ratio facilitate the formation of more cokes. Moreover, NMZ-X possess much better tolerance capacity for coke formation.

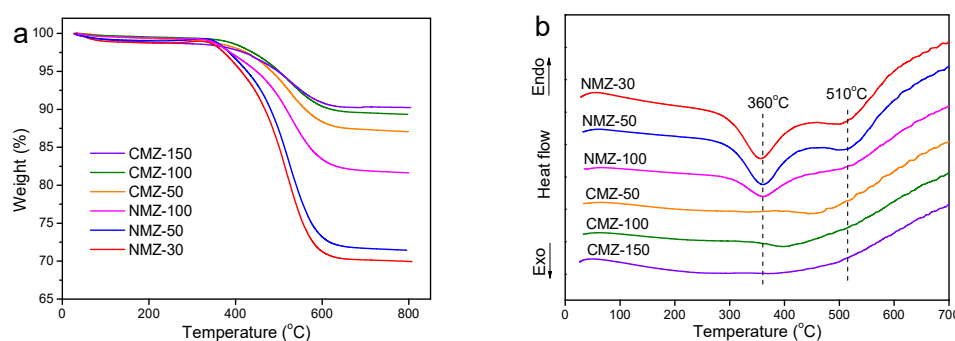


Figure 5. (a) Thermogravimetric analysis (TGA) and (b) differential thermal analysis (DTA) curves of different used catalysts.

2.2. Effects of Nanosheet Structure on the Catalytic Performance for Glycerol Dehydration

The roles of porosity and acidity for catalysts in gas phase dehydration of glycerol reaction have been discussed in many previous literature [7,9,19–21,34,44,45]. It is generally believed that the reaction activity and acrolein selectivity are essentially controlled by the acid type and strength. As confirmed by NH_3 -TPD (Figure 4a), NMZ-X, and CMZ-X, with similar Si/Al ratios show minor difference in the acid amount and acid strength distribution. ^{27}Al MAS NMR spectra (Figure 4c) illustrate that Al coordination states are almost the same in NMZ-50, NMZ-100, CMZ-50 and CMZ-100. Along with Py-IR results (Figure 4b), it can be concluded that the acid sites of these four samples present similar nature in acid type. Thus, the advantage of nanosheet MFI zeolites can be demonstrated by the comparison of catalytic performance of NMZ-X and CMZ-X with similar Si/Al ratios (50 and 100).

In light of previous literature [9,28,34], the evaluation experiments were conducted in gas phase at 320 °C, with an aqueous solution containing 20 wt.% glycerol, and no carrier gas was used. Figure 6 illustrates the changes of glycerol conversion and acrolein selectivity with time on stream, and the data are also presented in Table 2 in detail. Apparently, NMZ-X presented much better performance than their CMZ-X counterparts. For conventional HZSM-5, CMZ-100 exhibited high initial activity, but underwent a dramatic deactivation. Glycerol conversion almost linearly decreased to 83% after 10 h on stream over CMZ-100. Despite similar Si/Al ratio as CMZ-100, NMZ-100 reached a much longer lifetime. Of all the examined catalysts, NMZ-50 achieved the best performance. The glycerol conversion in the initial 12 h kept at high values of higher than 99% and still maintained at about 85% after 36 h reaction. The stability of the zeolites discussed in this section follows the order of $\text{NMZ-50} > \text{NMZ-100} \gg \text{CMZ-100} > \text{CMZ-50}$. Obviously, the nanosheet MFI zeolites exhibit much better catalytic stability than the conventional ones.

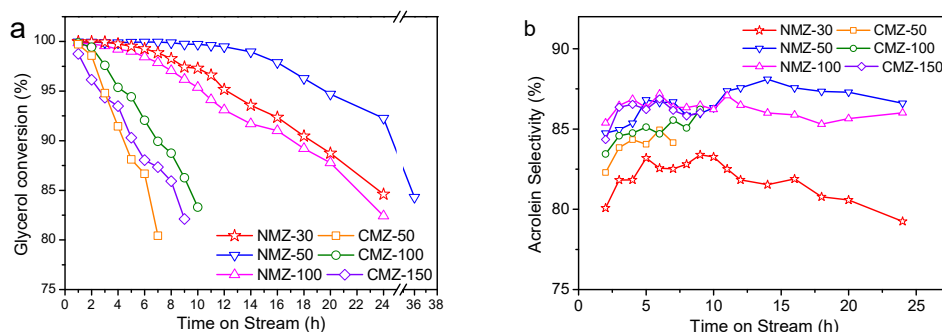


Figure 6. (a) Glycerol conversion and (b) acrolein selectivity as a function of reaction time over different catalysts. Reaction conditions: atmospheric pressure, 320 °C, WHSV (weight hourly space velocity) = 2.1 h^{-1} , 0.25 g catalyst.

Table 2. Catalytic performance for glycerol dehydration^a.

Sample	TOS (h)	Conversion (%)	Product Selectivity (%)		
			Acrolein	Acetol	Others ^b
NMZ-30	4	99.7	81.8	7.9	10.3
	8	98.3	82.8	8.4	8.8
NMZ-50	4	99.8	85.4	4.9	9.7
	8	99.7	85.9	5.3	8.8
NMZ-100	4	99.2	86.8	4.7	8.5
	8	97.1	86.3	5.2	8.5
CMZ-50	4	91.3	84.3	5.1	10.6
	8	<80.0	-	-	-
CMZ-100	4	95.4	84.7	4.8	10.5
	8	89.9	85.1	5.0	9.9
CMZ-150	4	93.5	86.5	4.7	8.8
	8	87.3	85.8	4.4	9.8

^a Reaction conditions: atmospheric pressure, 320 °C, WHSV = 2.1 h⁻¹, 0.25 g catalyst; ^b Selectivity of Others = 1 – Selectivity of Acrolein – Selectivity of Acetol.

The catalytic performance of NMZ-50 and CMZ-50 was further evaluated at different WHSV. As shown in Figure 7a, there was no big difference in their initial activity (the first point) for NMZ-50 and CMZ-50 at WHSV of 6 and 12 h⁻¹. When WHSV increased to 60 h⁻¹, the initial conversion of NMZ-50 and CMZ-50 reached 100% and 85%, respectively. At all WHSV conditions, NMZ-50 showed much better stability than CMZ-50.

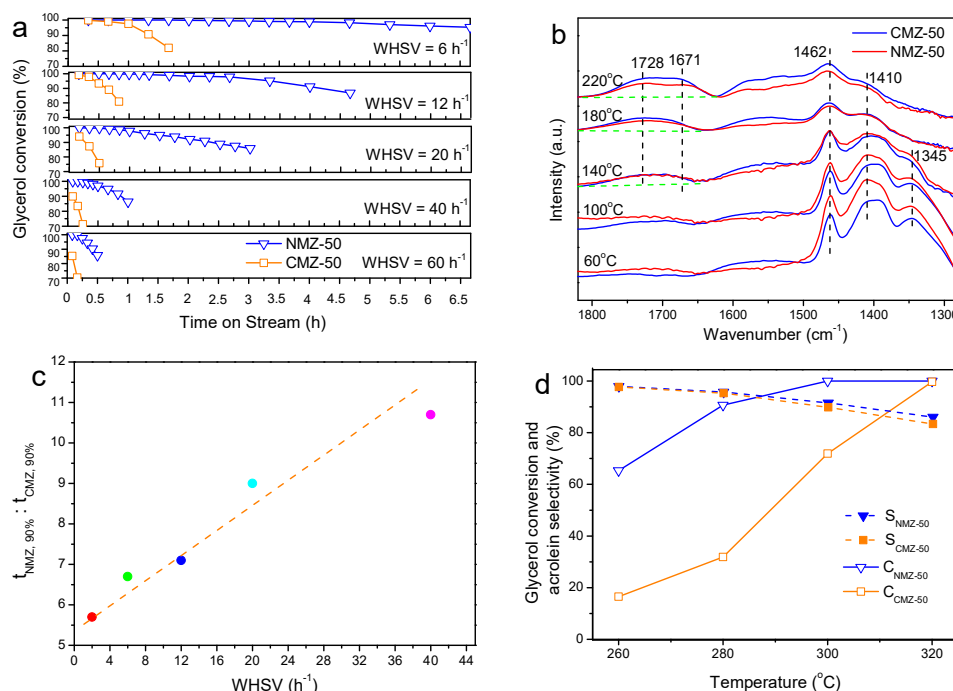


Figure 7. (a) Glycerol conversion on NMZ-50 and CMZ-50 at different WHSV at 320 °C; (b) In situ FT-IR spectra after adsorbing glycerol at different temperature; (c) Relationship between $t_{\text{NMZ},90\%}:t_{\text{CMZ},90\%}$ and WHSV; (d) Correlation between glycerol conversion and temperature at the initial reaction period of 0–1 h at WHSV of 2.1 h⁻¹, other reaction conditions: atmospheric pressure, 0.25 g catalyst, S: selectivity to acrolein, C: conversion of glycerol.

To gain information in glycerol dehydration process and deeply understand the superior stability of NMZ-X, in situ FT-IR experiments of adsorbed glycerol were conducted. Figure 7b displays the IR spectra of adsorbed species on CMZ-50 and NMZ-50, under high vacuum, at different temperatures.

As the catalyst wafer and added glycerol kept the same weights, the peak area is proportional to the amount of adsorbed species. Table S2 summarizes the main bands observed in the region of 1800–1300 cm^{-1} after glycerol adsorption. The adsorbed glycerol is characterized by typical bands at 1462 cm^{-1} (δCH_2), 1410 cm^{-1} (δOH), and 1345 cm^{-1} (δCH) [46]. At low temperatures (60 and 100 $^\circ\text{C}$), more glycerol was adsorbed on NMZ-50 than CMZ-50. When the temperature was increased to 140 $^\circ\text{C}$, the amount of adsorbed glycerol became very close on two samples. Meanwhile, the band of adsorbed acrolein (1728 cm^{-1} $\nu\text{C=O}$ and 1671 cm^{-1} $\nu\text{C=C}$) appeared, but the existence of acetol could not be excluded for its characteristic peak of $\nu\text{C=O}$ at 1728 cm^{-1} [47,48]. With further rising temperature, the peak area at 1650–1800 cm^{-1} region became larger on CMZ-50 than NMZ-50. Although FT-IR is just a semi-quantitative technique, small peak area may infer that products could diffuse easily on NMZ-50. The better diffusivity of products can be reasonably explained by the significantly shortened micropores in nanosheet structure and plentiful mesopores, as indicated by pore volume of NMZ-50 and CMZ-50 in Table 1. Rapid diffusion can suppress consecutive reactions of products to form the coke precursor and slow down coke formation rate, which is supported by the low coke deposition rate of NMZ-50 obtained according to TGA results (Table 3). Contrarily, poor diffusion on CMZ-50 leads to an accumulation of stuck products and quick formation of coke. The generated cokes block zeolite channels, cover acid sites and result in deactivation of CMZ-50, which can be confirmed by BET result that only 16.0% micro surface area remained (Table 3).

Table 3. Coke content and coke deposition rate of different catalysts.

Sample	TOS ^a (h)	Coke Content ^b (%)	Coke Deposition Rate ^c ($\text{g}_{\text{coke}} \text{g}_{\text{cat}}^{-1} \text{h}^{-1}$)	Surface Area ^d ($\text{m}^2 \text{g}^{-1}$)/Percentage Remained (%)		
				Total	Micro	External
NMZ-50	36	27.5	1.05×10^{-2}	296/52.6	99/37.1	197/66.6
CMZ-50	7	11.7	1.89×10^{-2}	66/18.5	42/16.0	24/25.8

^a TOS: Time on stream; ^b Coke contents were calculated from TGA profiles of used catalysts (the catalysts were collected after glycerol conversion decreased to about 80%); ^c Coke deposition rate was calculated with the following formula: Coke deposition rate = $1/(1 - \text{Coke content}) \times \text{Coke content}/\text{TOS}$; ^d Surface areas of deactivated NMZ-50 and CMZ-50.

Additionally, a lifetime ratio of NMZ-50 and CMZ-50 was represented as $t_{\text{NMZ},90\%}:t_{\text{CMZ},90\%}$ (a ratio of reaction time at 90% glycerol conversion for NMZ-50 and CMZ-50). The relationship between $t_{\text{NMZ},90\%}:t_{\text{CMZ},90\%}$ and WHSV is shown in Figure 7c. At WHSV of 2.1, 6, 12, 20 and 40 h^{-1} , $t_{\text{NMZ},90\%}:t_{\text{CMZ},90\%}$ is respectively 5.7, 6.7, 7.1, 9.0, and 10.7, which is significantly larger than coke deposition rate ratio (CMZ-50: NMZ-50 = 1.8). As shown in Table 1, the mesopore volume of NMZ-50 is 6.6 times larger than that of CMZ-50. A larger mesopore volume of NMZ-50 possess larger coke capacity, and better coke tolerance ability. Thus, the superior stability can be ascribed to the greatly shortened b-axis and large mesopore volume of NMZ-50, which not only slow down coke formation rate, but also significantly improved coke tolerance ability.

However, high temperature-facilitated glycerol conversion and acid sites could be sufficient on both catalysts at 320 $^\circ\text{C}$. Furthermore, at high temperatures, it is difficult to tell that the slight lower glycerol conversion on CMZ-50 (Figure 7a) originated from the lower initial reaction rate or faster deactivation with high WHSV. Because low temperature suppresses both glycerol conversion and consecutive reaction of products [12], to rationally compare the activity of NMZ-50 and CMZ-50, reactions were then performed at 260, 280, and 300 $^\circ\text{C}$. The disparity of reactivity was much more significant at low temperatures (Figure 7d). At 260 $^\circ\text{C}$, the conversion of NMZ-50 was about four times that of CMZ-50. As disclosed above, the differences between CMZ-50 and NMZ-50 lie in the external surface area and mesopore volume resulting from different morphologies. Because mesoporous structure shortens transport path and acid sites on external surface area can be easily approached [34], large external surface area and abundant mesopore volume of NMZ-50 can facilitate transportation of glycerol molecules to acid sites for dehydration. For CMZ-50, although the acidity is similar, its microporous structure and low external surface area impede transportation of glycerol molecules,

leading to low activity. Thus, the nanosheet structure of NMZ-50 can be confirmed as the key factor for high activity. One interesting phenomenon observed in Figure 7b is that acrolein selectivity decreases with increasing temperature for both catalysts and disparity between two catalysts is negligible at all temperature investigated here. The reasons for high acrolein selectivity at low temperature may attribute to the preference for acrolein production or inhibiting C–C bond cleavage caused by low temperature [8]. There is no further discussion on this point because it is not the major concern of this article.

Besides the advantage of stability, CMZ-50 also exhibited an improved acrolein selectivity compared to CMZ-50, and the acrolein selectivity was nearly unchanged even after the catalyst deactivation begun, as shown in Figure 6b. The average acrolein selectivity of NMZ-50 and CMZ-50 were 86.6%, and 83.9%, respectively. The high selectivity of both catalysts can be ascribed to large amounts of Brønsted acid sites, wherein the secondary hydroxyl group of glycerol molecules can be selectively eliminated, followed by consecutive dehydration to form acrolein [9,34,44]. High WHSV reactions also show the same trend (Figure 7a). The slight lower acrolein selectivity on CMZ-50 might be related to more secondary reactions of acrolein in its longer micropores to generate other products or coke species, in agreement with above discussions about stability.

In summary, the above results unambiguously confirm the great advantages of nanosheet MFI zeolites over conventional ZSM-5 for glycerol dehydration. NMZ-50 shows a long lifetime of 36 h (glycerol conversion > 85%), which is among the best performance for this reaction [7,8,16,21,22,29,34]. The shortened micropore and large mesopore volume provided by nanosheet structure can respectively slow down the coke deposition rate and improve the coke tolerance capacity, leading to superior performance of NMZ-X in glycerol dehydration.

2.3. Effects of Si/Al Ratios

The acidity of the catalyst plays a vital role in gas-phase dehydration of glycerol. As well-known, the acidic property of MFI zeolites can be adjusted by Si/Al ratio. For CMZ-X, there are no big differences in morphologies, BET surface areas, and pore size distributions. By taking the characterization results of ^{27}Al MAS NMR, NH_3 -TPD, and Py-IR into comprehensive consideration, the main difference of CMZ-X is the amount of acid sites (Table S1). Comparatively, the most appropriate Si/Al ratio was 100 for the conventional ZSM-5 in this study.

However, the situation is completely different for NMZ-X. As discussed above, Al contents determine the morphologies of nanosheet MFI zeolites. With increasing Si/Al ratios from 30 to 100, the width in a-c plane grows from lower than 10 nm to a few hundred nanometers. The area of a-c plane has a great influence on the stacking process of MFI nanosheets, resulting in inconsistent morphology and texture property. To investigate the initial activity of NMZ-X, glycerol dehydration experiments at 260 °C were conducted with $\text{WHSV} = 2.1 \text{ h}^{-1}$. As shown in Figure 8, the activity of NMZ-X follows the order of $\text{NMZ-30} > \text{NMZ-50} > \text{NMZ-100}$. As summarized in Table 1, the BET surface areas of NMZ-30, NMZ-50, and NMZ-100 are 543, 563, and 432 $\text{m}^2 \text{ g}^{-1}$, respectively. For a detailed comparison of NMZ-30 and NMZ-50, their micropore areas are nearly the same and mesopore area of NMZ-50 are only about 3.6% larger than NMZ-30, indicating their similar mass transfer capacity. Meanwhile, the acid amount depends on the Al content of zeolite. Lower Si/Al ratio results in more acid sites (Table S1). Thus, the high activity can be ascribed to plenty of acid site in NMZ-30. However, the stability sequence is defined as $\text{NMZ-50} > \text{NMZ-30} > \text{NMZ-100}$ (Figure 6a), not consistent with the activity order. Obviously, more acid site leads to more rapid coke formation (Table 3 and Table S3). Thus, the short lifetime of NMZ-30 may result from its fast coke formation rate. Regarding NMZ-100, relatively poor performance may be explained by the combined effects of thick lamellar stacking, low surface area, and insufficient acid sites.

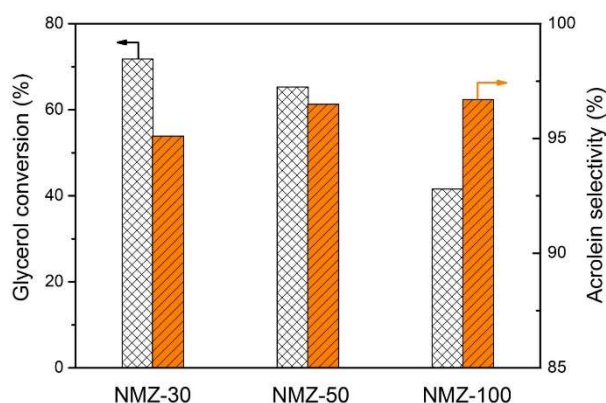
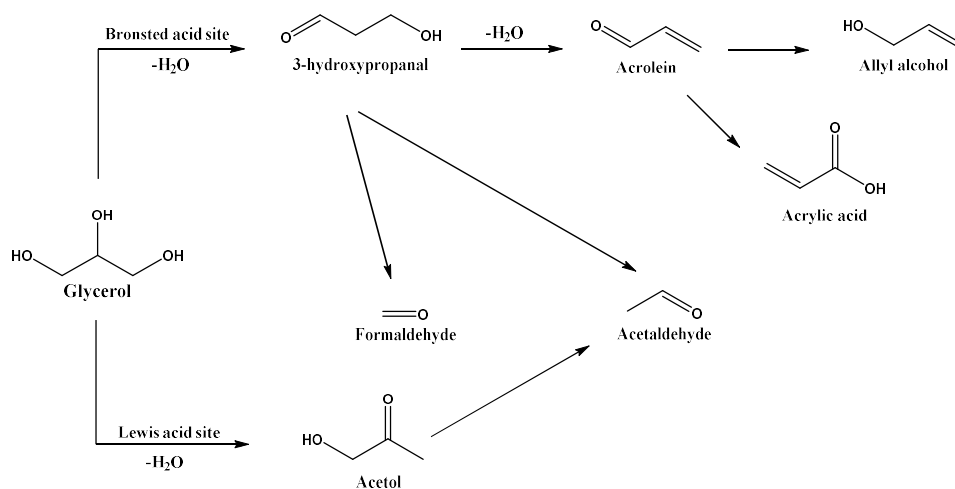


Figure 8. Catalytic performance of NMZ-X at 260 °C with WHSV = 2.1 h⁻¹.

Regarding product selectivity, NMZ-30 obtains the lowest acrolein selectivity in all NMZ-X samples (Figures 6b and 8). As reported earlier [9], the rupture of secondary C–O bonds is easier than the terminal C–O bonds when glycerol molecules coordinate with Brønsted acid sites, while Lewis acid sites facilitate the cleavage of terminal C–O bonds to produce acetol. As the B/L ratio of NMZ-30 is lower than the other zeolites (Table S1), the poor selectivity to acrolein of NMZ-30 might be explained by its higher proportion of Lewis acid sites, coincident with the improved selectivity to acetol (Table 2). Besides acrolein and acetol, formaldehyde, acetaldehyde, acrylic acid, and allyl alcohol were also detected. Based on above results and former reports [9,23,27], the formation pathways of all detected products were shown in Scheme 1.



Scheme 1. Proposed reaction pathways for gas phase dehydration of glycerol to acrolein on HZSM-5 catalyst.

2.4. Catalyst Reutilization

The catalytic performance of fresh and regenerated catalysts was investigated to explore the reusability of NMZ-50, as shown in Figure 9 (WHSV = 2.6 h⁻¹, 0.2 g NMZ-50). The used NMZ-50 was regenerated at 550 °C for 24 h in a 5 vol.% O₂/N₂ flow. The regenerated NMZ-50 showed almost the same glycerol conversion as a fresh one, but the selectivity to acrolein decreased slightly. As reported previously for ZSM-5 zeolite, a portion of framework aluminum may turn into extra-framework aluminum during the reaction and regeneration processes [49]. The generation of extra-framework aluminum leads to less Brønsted acid and more Lewis acid sites. Accordingly, the selectivity to acrolein decreased slightly.

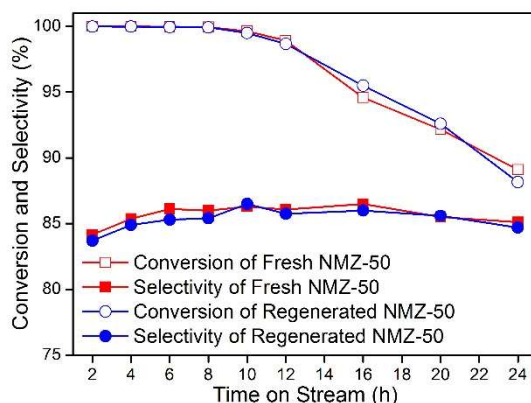


Figure 9. Glycerol conversion and acrolein selectivity of fresh and regenerated NMZ-50. Reaction conditions: atmospheric pressure, 320 °C, WHSV = 2.63 h^{−1}, 0.2 g catalyst.

3. Experimental

3.1. Catalyst Preparation

The nanosheet MFI zeolites were synthesized, following the method reported by Choi et al. [40,41], using [C₁₈H₃₇-N⁺(CH₃)₂-(CH₂)₆-N⁺(CH₃)₂-C₆H₁₃]Br₂ (simplified as C₁₈₋₆₋₆Br₂) as a bifunctional template. The conventional MFI zeolites (particle type ZSM-5) with different Si/Al molar ratios of 50, 100, and 150 (in synthesis gel) were hydrothermally synthesized by using tetrapropylammonium hydroxide (TPAOH) as the structure directing agent [50]. After a series of procedures, H-form zeolites were obtained finally. For simplicity, the prepared nanosheet MFI, and conventional HZSM-5 zeolites were designated as NMZ-X, and CMZ-X (X refers to Si/Al molar ratio in synthesis gel), respectively. Synthesis details can be found in the Supplementary materials.

3.2. Characterization

The actual atomic compositions of all zeolite samples were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Thermo iCAP6300). SEM and TEM images were obtained by field emission scanning electron microscope (FESEM, JSM 7001-F) and transmission electron microscope (TEM, JEM-2001F). The powder X-ray diffraction (XRD) patterns of NMZ-X and CMZ-X were recorded on a Rigaku MiniFlex II X-ray diffractometer with Cu Kα radiation (154.06 pm, 30 kV and 15 mA) at a scanning speed of 4° min^{−1}. N₂ adsorption-desorption isotherms were measured at −195.8 °C on a TriStar3020 II gas adsorption analyzer. The specific surface area and meso- and micro-pore volume were calculated using Brunauer-Emmett-Teller (BET), Barrett-Joyner-Halenda (BJH, desorption branch), and t-plot methods. The spectra of ²⁷Al magic angle spinning nuclear magnetic resonance (²⁷Al MAS NMR) were recorded on a Bruker Avance III 600 MHz Wide Bore spectrometer with Al(NO₃)₃ as a reference.

The acid site density of the synthesized zeolites was measured by temperature-programmed desorption of ammonia (NH₃-TPD) carried out in a Micromeritics Autochem II 2920 chemisorption analyzer equipped with a thermal-conductivity detector (TCD). Before adsorption, approximately 0.1 g sample was heated at 550 °C for 2 h in a pure helium flow (30 mL min^{−1}) and then cooled to 120 °C. Followed by this pre-treatment, the sample was saturated with NH₃ in NH₃/He mixture (1:9 volume ratio) for 30 min. Thereafter, the physisorbed NH₃ was removed by flushing the sample tube with pure helium (30 mL min^{−1}) at 120 °C for 2 h. The sample was subsequently heated from 120 °C to 500 °C with a rate of 10 °C min^{−1} to get the NH₃-TPD profile.

Fourier transform infrared spectra of adsorbed pyridine (Py-IR) were measured on a Bruker Tensor 27 FT-IR spectrometer. Firstly, the zeolite sample was pressed into a self-supported wafer and placed in a vacuum cell. Prior to the measurement, the sample cell was evacuated to 10^{−2} Pa at 350 °C

for 2 h. Then pyridine vapor was introduced into the sample cell at room temperature for 1 h and the spectra were recorded after evacuation at 150 °C for 1 h. The concentration of Brønsted and Lewis acid sites were calculated by using the procedures reported by Madeira and co-workers [51].

In situ FT-IR experiments of glycerol adsorption were performed on the same spectrometer mentioned above. Specifically, a self-supported catalyst wafer (15.0 ± 0.2 mg) was firstly evacuated to 10^{-2} Pa at 350 °C for 2 h, then the spectra were collected at elected temperature in the course of cooling down and used as background. After cooling to room temperature, 5 μ L of 20% glycerol aqueous solution were dropped to the center of the wafer and then IR spectra of catalyst and adsorbed species were recorded under high vacuum at preset temperature. The spectra of adsorbed species can be acquired by subtracting the background spectra.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed on a Rigaku Thermo plus Evo TG 8120 instrument to determine the content and properties of deposited coke. About 10 mg of used catalyst was placed in α -Al₂O₃ crucible and heated from room temperature to 800 °C in flowing air (30 mL min⁻¹). The weight loss between 300 to 700 °C was regarded as the coke content.

3.3. Catalytic Reaction

The gas phase dehydration of glycerol was performed in a stainless steel fixed bed reactor (inner diameter, I.D. = 8 mm) under atmospheric pressure at 320 °C. Before the reaction, the catalyst (0.25 g) was in situ activated at a reaction temperature in N₂ for 2 h. A 20 wt.% glycerol aqueous solution was fed into the reactor by a pump, and the weight hourly space velocity (WHSV) of glycerol was controlled at 2.1 h⁻¹. The reaction products were condensed by a cold trap and collected hourly for analysis on a Shimadzu GC-2010 Plus gas chromatograph equipped with a flame ionization detector (FID) and a HP-PONA capillary column (I.D. = 0.20 mm, length = 50 m), and the samples were injected by an auto-sampler. The external standard method was adopted for direct quantitative determination of unreacted glycerol and two main products (i.e., acrolein and acetol) in the collected liquid.

All of reactions were stopped when the conversion of glycerol decreased to about 80%. Then, the reactor was purged by flowing N₂ until the system cooled down to room temperature. The conversion of glycerol and selectivity to identified products have been calculated as bellow:

$$\text{Glycerol conversion} = \frac{\text{moles of reacted glycerol}}{\text{moles of glycerol in the feed}} \times 100\%$$

$$\text{Product selectivity} = \frac{\text{moles of carbon in a defined product}}{\text{moles of carbon in reacted glycerol}} \times 100\%$$

4. Conclusions

Nanosheet MFI zeolites are much more active and stable than their conventional counterparts and have been demonstrated to be superior candidates for gas phase dehydration of glycerol to acrolein. NMZ-50 achieved excellent performance, exhibiting above 99% conversion in initial 12 h and about 85% even after 36 h reaction time. Meanwhile, it gave nearly constant high acrolein selectivity of about 87%. However, glycerol conversion underwent nearly linear decrease to 84% in less than 10 h over the best conventional ZSM-5 zeolite (CMZ-100). The used NMZ-50 catalyst was facilely regenerated by burning coke, and no obvious decline in catalytic performance was observed between the regenerated and fresh sample.

Notably, this work indicate that morphology of NMZ-X can be adjusted by changing Al content and Si/Al molar ratio determines the catalytic performance of NMZ-X in two ways: morphology and acidity. The shortened micropores and large mesopore volume provided by the nanosheet structure of NMZ-X facilitate transportation of glycerol, slow down the coke deposition rate of coke and dramatically improve the coke tolerance capacity, resulting in superior activity and stability.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/9/2/121/s1>, Figure S1. (a) N₂ adsorption-desorption isotherms at −195.8 °C and (b) pore size distribution, Table S1. Overall acidic properties of different zeolite catalysts, Table S2. Summary of the infrared band assignments, Table S3. Coke content of used catalysts and corresponding coke deposition rate.

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