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Alkali treatment time and SiO_2/Al_2O_3 ratio effects on structural modification to produce micro-mesoporous commercial and synthesized ZSM-5 zeolite catalysts

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ABSTRACT

This research investigated the structural modification by a facile alkali treatment of commercial and synthesized ZSM-5 zeolites. The introduction of mesopores to ZSM-5 structure could improve its catalytic performance in cracking and reforming processes. ZSM-5 samples at SiO_2/Al_2O_3 ratios (60, 100, and 140) were synthesized in a fabricated autoclave reactor. ZSM-5 zeolites were alkali-treated at varying times (0.5–3 h). All ZSM-5 samples were examined using XRD, SEM-EDS, surface area and pore analyzer, and particle size analyzer. The results demonstrated that the pore properties of commercial and synthesized ZSM-5 samples depended on alkali treatment time. The increment of alkali treatment time brought about an increased mesopore surface area and volume for both kinds of ZSM-5 samples, accompanied by a more pronounced type IV isotherm. However, increasing the amount of time for alkali treatment (3 h) resulted in a decrease of mesoporosity in the synthesized ZSM-5 samples. The mesopore formation was a result of preferential dissolution of Si from the synthesized ZSM-5 structure, particularly at higher SiO_2/Al_2O_3 ratios. The alkali-treated synthesized ZSM-5 zeolite at a SiO_2/Al_2O_3 ratio of 140 in 0.2 M NaOH aqueous solution for 1 h exhibited a highly produced mesopore surface area and pore volume, plus the preserved MFI structure.

Keywords: modified ZSM-5 zeolite; alkali treatment; micro-mesopore structure; catalyst

1. INTRODUCTION

Zeolites are widely used in the major catalytic reactions in the petroleum refining, as well as petrochemical and pollution control industries (Inada et al., 2005; Primo and Garcia, 2014). For catalytic applications, the enormous range of zeolite structures with varying pore size and pore geometries provides numerous forms of shape selectivity (Vennestrøm et al., 2011). However, it appears that the presence of micropores in zeolite catalysts may limit the catalytic efficiency of the zeolite in many cases, i.e. pore blockage by coke deposit occurring during the reaction, and bulky reactant molecule diffusion limitations (Han et al., 2019). In recent years, it has been demonstrated that the

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inclusion of an auxiliary mesopore system improves the diffusion rate of molecules in zeolites, resulting in an increased catalytic activity and a longer lifetime for the catalyst (Hua et al., 2011; Schmidt et al., 2013; Kim et al., 2017). It has been reported that mesoporous zeolites can be synthesized directly utilizing carbon, organosilane surfactants, and cationic polymers (Mochizuki et al., 2012). Nevertheless, the high cost of highly prepared templates makes commercialization challenging.

Recent research has shown that desilication by alkali treatment is an efficient alternative for producing mesopores in zeolite, while preserving structural integrity and effectively producing two hierarchical pores (Sun et al., 2021; Mishra et al., 2022; Wang et al., 2023). Hierarchical porous zeolites have emerged as a significant class of materials, owing to their enhanced performance in various catalyzed reactions when compared to their microporous counterparts (Caicedo-Realpe and Pérez-Ramírez, 2010). In addition, sodium hydroxide (NaOH) treatment is the most common alkali etching method used to create hierarchical zeolite (Ji et al., 2017). Many researchers applied an alkali treatment with NaOH solution for ZSM-5 zeolite structural modification. Groen et al. (2004) reported that the optimal alkali treatment conditions for HZSM-5 zeolite were a 25 to 50 Si/Al molar ratio in 0.2 M NaOH solution for 30 min at 65°C. Ding et al. (2017) experimented with alkali treatment for the preparation of hierarchical porous HZSM-5 zeolites. The results demonstrated that the micropore structure and crystallinity of HZSM-5 were retained when treated with a weak NaOH concentration (≤ 0.3 M). Shahid et al. (2017) used a 0.2 M NaOH solution at 80°C for 2 h preparing hierarchical zeolites. Li et al. (2019) employed 0.2 M NaOH solution to prepare alkali-treated NaZSM-5 at 80°C for 4 h. Mesa et al. (2021) prepared the hierarchical hierarchical ZSM-5 zeolite by alkali treatment, and reported that the increased treatment time and alkali concentration greatly affected the mesopore volume. It was due to the increased silicon extraction from the zeolitic structure and the need for greater time to relate the defects created in a mesopore network. Furthermore, Gao et al. (2010) prepared the mesopore ZSM-5 zeolite via alkali treatment of the parent ZSM-5 zeolite for catalytic cracking of butene. The highest yield of ethene and propene was gained when the treated NaOH solution concentration was 0.1–0.2 M. Zhao et al. (2011) employed a 0.2 M aqueous NaOH solution for 5 h at 90°C for the alkali treatment of ZSM-5 zeolites, used as a catalyst in heavy oil cracking. Safari et al. (2020) also studied the catalyst activity of mesoporous HZSM-5 treated with 0.2 M NaOH solution at 80°C for 2 h in heavy oil cracking.

In this work, the structural modification was aimed at the commercial (purchased) ZSM-5 zeolite and the synthesized ZSM-5 zeolite, prepared hydrothermally in a fabricated stainless steel autoclave reactor. A facile alkali treatment was employed to create micro-mesoporous commercial and synthesized ZSM-5 zeolite catalysts, with varying alkali treatment times and SiO_2/Al_2O_3 molar ratios.

2. MATERIALS AND METHODS

2.1 Materials

Aluminium nitrate nonahydrate ($Al(NO_3)_3{\cdot}9H_2O$, PanReac AppliChem, Germany and Spain) and sodium silicate solution (Na_2SiO_3, PanReac AppliChem, Germany and Spain) were used as a source of alumina and silica, respectively. Tetrapropyl ammonium bromide or TPABr ($C_{12}H_{28}BrN$, 98%, Acros Organics, Belgium) was employed as a direct-structuring template. Commercial ZSM-5 zeolite ($SiO_2/Al_2O_3=60$) in fine powder form was purchased from Hongze Hua Yuan (Tianjin, China).

2.2 Preparation of synthesized ZSM-5 zeolite

ZSM-5 zeolite with three SiO_2/Al_2O_3 ratios of 60, 100, and 140 was crystallized in a fabricated stainless steel autoclave reactor, under hydrothermal condition (210°C, 5.5 h). Following the hydrothermal synthesis step, a solid crystal product was properly washed to remove excessive chloride ion, and afterwards dried at 110°C for 2 h. Finally, the solid crystal product was calcined at 540°C for 3 h in a muffle furnace to obtain the synthesized ZSM-5 zeolite samples S60, S100, and S140 (Rueangjitt et al., 1998; Uppala et al., 2010).

2.3 Alkali treatment of commercial and synthesized ZSM-5 zeolites

A facile alkali treatment of commercial and synthesized ZSM-5 zeolite samples was carried out using 120 mL of a 0.2 M NaOH aqueous solution. The NaOH aqueous solution was heated to 75°C in a rounded-bottom flask equipped with a reflux condenser, and then 3 g of ZSM-5 zeolite sample was added. The solid-liquid mixture was stirred at 75°C for 0.5, 1, 2, and 3 h. The hot slurry was quickly cooled in an ice bath. After, the solid product was filtered and delicately washed with distilled water using a Buchner funnel vacuum pump, until a neutral pH of filtrate was obtained. The solid product was dried at 110°C for 2 h in an air oven (Zhao et al., 2011). The samples of alkali-treated commercial ZSM-5 zeolite were identified as C60-xh, and the samples of alkali-treated synthesized ZSM-5 zeolite with SiO_2/Al_2O_3 molar ratios of 60, 100, and 140 were identified as S60-xh, S100-xh, and S140-xh, respectively (x is alkali treatment time). All of the samples and alkali treatment conditions are listed in Table 1.

2.4 Characterization

The X-ray diffraction (XRD) patterns of the samples were identified by Rigaku SmartLab X-ray diffractometer (Rigaku, Japan), with Cu $K\alpha$ radiation at 40 kV and 30 mA source, at a scanning rate of 10°/min, over the 2θ range between 5° and 50°. The prominent XRD peak of ZSM-5 zeolite ($2\theta=22.5–25°$) was used to measure the percent relative crystallinity.

The N_2 adsorption-desorption isotherms were determined using Autosorb-1 MP (Quantachrome, USA). The specific surface area was evaluated using Brunauer-Emmett-Teller (BET) method. The average pore size and volume were measured using Barrett-Joyner-Halenda (BJH) technique, and the micropore surface area and volume were calculated using t-plot method.

The surface morphology and elemental analysis were determined using JSM-IT300 scanning electron microscope (JEOL, Japan), equipped with energy dispersive X-ray spectrometer (EDS) with an acceleration voltage of 15 kV. The samples were sputtered with a thin film of gold.

The particle size distribution (PSD) curves were determined by Malvern Mastersizers laser particle size analyzer (Malvern Instruments, UK).

Table 1. ZSM-5 zeolite samples and alkali treatment conditions

Sample		Alkali treatment condition
Commercial ZSM-5 zeolite SiO_2/Al_2O_3 = 60	C60	-
	C60-0.5h	NaOH 0.2 M, 75°C, 0.5 h
	C60-1h	NaOH 0.2 M, 75°C, 1 h
	C60-2h	NaOH 0.2 M, 75°C, 2 h
	C60-3h	NaOH 0.2 M, 75°C, 3 h
Synthesized ZSM-5 zeolite SiO_2/Al_2O_3 = 60	S60	-
	S60-0.5h	NaOH 0.2 M, 75°C, 0.5 h
	S60-1h	NaOH 0.2 M, 75°C, 1 h
	S60-2h	NaOH 0.2 M, 75°C, 2 h
	S60-3h	NaOH 0.2 M, 75°C, 3 h
Synthesized ZSM-5 zeolite SiO_2/Al_2O_3 = 100	S100	-
	S100-0.5h	NaOH 0.2 M, 75°C, 0.5 h
	S100-1h	NaOH 0.2 M, 75°C, 1 h
	S100-2h	NaOH 0.2 M, 75°C, 2 h
	S100-3h	NaOH 0.2 M, 75°C, 3 h
Synthesized ZSM-5 zeolite SiO_2/Al_2O_3 = 140	S140	-
	S140-0.5h	NaOH 0.2 M, 75°C, 0.5 h
	S140-1h	NaOH 0.2 M, 75°C, 1 h
	S140-2h	NaOH 0.2 M, 75°C, 2 h
	S140-3h	NaOH 0.2 M, 75°C, 3 h

3. RESULTS AND DISCUSSION

3.1 Crystalline characteristics

The XRD patterns and relative crystallinity of untreated and alkali-treated ZSM-5 zeolite samples are presented in Figure 1 and Table 2, respectively. The XRD patterns of all samples, including untreated and alkali-treated commercial and synthesized ZSM-5 zeolite, mainly consisted of typical peaks of the MFI structure, referred to XRD pattern data of standard ZSM-5 zeolite (Treacy and Higgins, 2001). After alkali treatment with NaOH aqueous solution, the results showed that the intrinsic lattice structure of both commercial and synthetic types of alkali-treated ZSM-5 zeolite samples remained unchanged without any new phase formation. Moreover, it was noticed that the diffraction peak intensity of the alkali-treated samples decreased when compared to the untreated samples, especially with longer alkali treatment time. This was confirmed by the percent relative crystallinity of alkali-treated samples that gradually decreased with increasing alkali treatment time. For the commercial ZSM-5 zeolite, the percent relative crystallinity drastically decreased from 100% to 64–69% after alkali treatment, and the increasing alkali treatment time had little effect on relative crystallinity. Concerning synthesized ZSM-5 zeolite experimentally treated at 0.5 h, the percent relative crystallinity decreased to 95.99%, 82.45%, and 71.33% for S60-0.5h, S100-0.5h, and S140-0.5h, respectively, due to the SiO_2/Al_2O_3 ratio being higher. At 3 h of alkali treatment time, of C60-3h, S60-3h, S100-3h and S140-3h, each of their relative crystallinities decreased to 71.65%, 85.72%, 88.26%, and 76.20%, respectively. These results of alkali-treated synthesized ZSM-5 zeolite revealed that alkali treatment time had a significant effect on relative crystallinity compared to alkali-treated commercial ZSM-5 zeolite. The decrease of both peak intensity and percent relative crystallinity indicated a noticeable loss of crystallinity. Decreasing of both peak intensity and relative crystallinity resulted from the dissolving of silica species in an alkali solution and their consequent leaching from the zeolitic framework, leading to partial damage to the zeolite framework (Li et al., 2019).

3.2 Porosity properties

Figure 2 illustrates the N_2 adsorption-desorption isotherms of untreated and alkali-treated ZSM-5 zeolite samples. The untreated commercial ZSM-5 zeolite sample (C60) gave a type I isotherm, which was characteristic of microporous materials with a high nitrogen adsorption at relatively low pressure. The isotherm of the alkali-treated commercial ZSM-5 zeolite samples showed an improved uptake at higher pressure and a significantly larger hysteresis loop with type IV isotherm when the alkali treatment time was increased, indicating that large-size mesopores were formed (Khoshbin and Karimzadeh, 2017). For the synthesized ZSM-5 zeolite samples, all untreated samples (S60, S100, and S140) exhibited similar isotherms with high N_2 uptake at low partial pressure and a small hysteresis loop approximately 0.4–0.9 of the P/P_0 value. These results suggest that the untreated synthesized ZSM-5 zeolite had a high microporosity, as well as a small amount of mesoporosity. After increasing alkali treatment time, the samples showed that type IV isotherms with a hysteresis loop at P/P_0 >0.45 were more pronounced due to capillary condensation within the pores, indicating that more mesopores were formed. The result obtained by Zhao et al. (2011) was similar. This proved that a microporous and mesoporous structure was created.

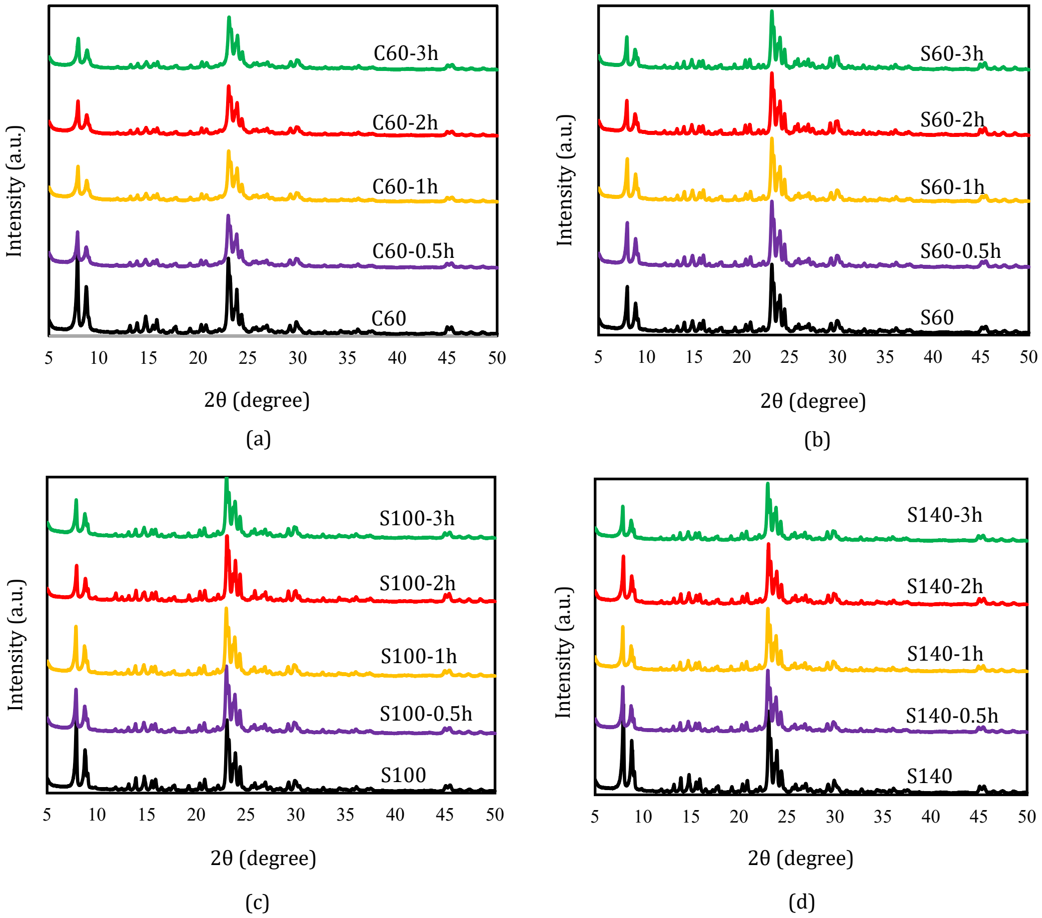


Figure 1. XRD patterns of (a) commercial ZSM-5 zeolite with SiO_2/Al_2O_3 of 60, and synthesized ZSM-5 zeolites with SiO_2/Al_2O_3 of (b) 60, (c) 100, and (d) 140, at different alkali treatment times

Table 2. Relative crystallinity and Si/Al ratio of untreated and alkali-treated ZSM-5 zeolite samples at different alkali treatment times

Sample	Relative crystallinity (%)	Si/Al ratio
C60	100.00	30.16
C60-0.5h	77.13	16.19
C60-1h	74.41	15.80
C60-2h	72.92	16.29
C60-3h	71.65	14.17
S60	100.00	21.88
S60-0.5h	95.99	13.92
S60-1h	91.99	10.78
S60-2h	91.48	9.17
S60-3h	85.72	7.64
S100	100.00	29.67
S100-0.5h	94.78	19.04
S100-1h	92.99	12.37
S100-2h	91.31	11.31
S100-3h	88.26	10.03
S140	100.00	41.93
S140-0.5h	82.45	19.10
S140-1h	82.08	19.41
S140-2h	79.66	15.31
S140-3h	76.20	14.75

Figure 3 shows the BJH pore diameter distribution curves of the commercial and synthesized ZSM-5 zeolite samples at different alkali treatment times. Variation of the treatment time of 0.5, 1, 2, and 3 h led to a similar behavior, and a longer treatment time showed broadening of pore size distribution. The alkali-treated samples exhibited mesopore distribution curves centered at approximately 2.5 nm and increased the proportion of pores by approximately 3–10 nm. It indicates that more mesopores were created in ZSM-5 zeolite crystal structure, by destroying micropores in alkali solution, when treatment time increased for both commercial and synthesized samples.

Table 3 summarizes the porosity properties of untreated and alkali-treated commercial and synthesized ZSM-5 zeolite samples acquired via the varying alkali treatment times. The untreated commercial ZSM-5 zeolite (C60) showed a high surface area (S_{micro}) and volume (V_{micro}) of micropores, which was characteristic of microporous ZSM-5 zeolite. The S_{micro} and V_{micro} values of alkali-treated commercial ZSM-5 zeolite samples sharply decreased compared to the untreated commercial sample. They also decreased at increasing treatment times, whereas the S_{meso} and V_{meso} values dramatically increased. Therefore, the alkali treatment of commercial ZSM-5 zeolite with NaOH aqueous solution caused a remarkable decrease in the S_{micro} and V_{micro} values.Additionally, microporosity consistently decreased while the values of mesopore volume-to-total pore volume (V_{meso}/V_{total}) gradually increased. It is possible that the mesopores became the micropores (Wang et al., 2023). For the synthesized ZSM-5 zeolite samples, the S_{meso}/S_{total} and V_{meso}/V_{total} values of the alkali-treated samples were significantly greater than those of the untreated samples with increasing alkali treatment times. The highest total volume (V_{total}) was obtained from the alkali-treated synthesized samples after NaOH solution treatment for 2 h. The highest surface areas of mesopore (S_{meso}) were 156, 264, and 274 m^2/g for S60-2h, S100-2h, and S140-2h, respectively, with pore volumes of mesopore (V_{meso}) at 0.257, 0.378, and 0.411 cm^3/g, respectively. These results indicate that longer retention time affects the creation of mesopore in ZSM-5 zeolite crystal. On the other hand, when treatment time was increased to 3 h, the S_{meso} and V_{meso} values decreased. Extended treatment duration results in the reduction of mesoporosity due to the excessive dissolution of silicon (Groen et al., 2007), as well as the collapse of pores. In addition, the SiO_2/Al_2O_3 ratio also affected the formation of mesopores in the synthesized ZSM-5 zeolite. Under the same alkali treatment condition (0.2 M NaOH solution), the higher the SiO_2/Al_2O_3 ratio, the greater the disappearance of silicon atoms were, because silicon was preferentially removed from the higher SiO_2/Al_2O_3 ratio of the synthesized ZSM-5 zeolite crystal structure. The S140-1h sample exhibited the greatest S_{meso} and V_{meso} values, of 299 m^2/g and 0.451cm^3/g, respectively. The synthesized ZSM-5 zeolite treated with alkali at SiO_2/Al_2O_3 140 in 0.2 M NaOH concentration for 1 h was the optimal alkali treatment because it exhibited the highest mesoporosity with obvious intercrystal microporosity. The optimal treatment time and SiO_2/Al_2O_3 ratio of the synthesized ZSM-5 zeolite are beneficial for effective mesopore formation.

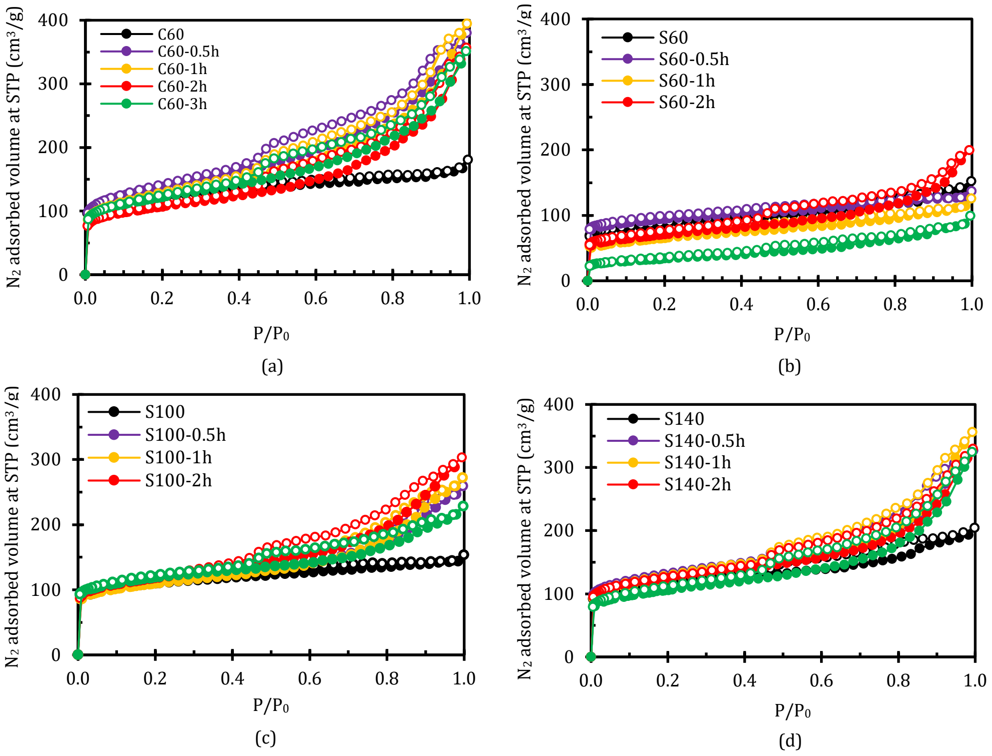


Figure 2. N_2 adsorption-desorption isotherms of (a) commercial ZSM-5 zeolite with SiO_2/Al_2O_3 of 60, and synthesized ZSM-5 zeolites with SiO_2/Al_2O_3 of (b) 60, (c) 100, and (d) 140, at different alkali treatment times

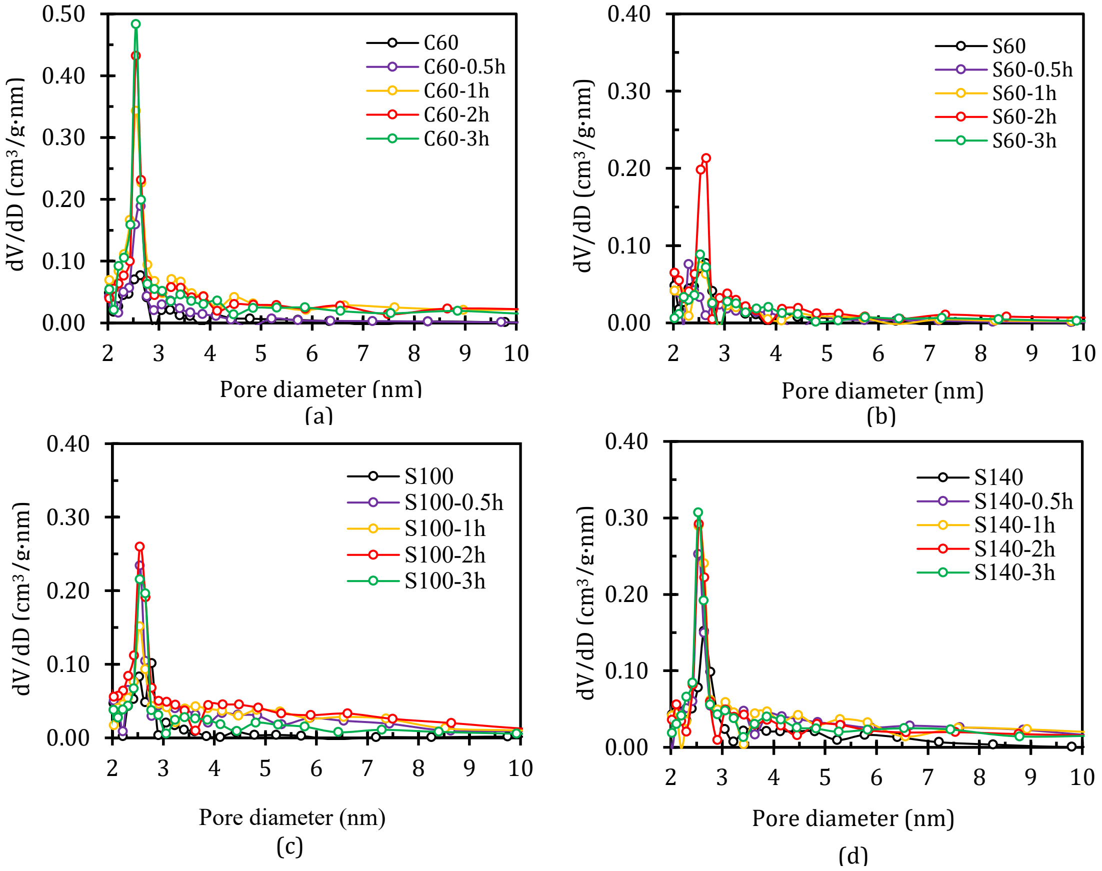


Figure 3. Pore size distribution curves of (a) commercial ZSM-5 zeolite with SiO_2/Al_2O_3 of 60, and synthesized ZSM-5 zeolites with SiO_2/Al_2O_3 of (b) 60, (c) 100, and (d) 140, at different alkali treatment times

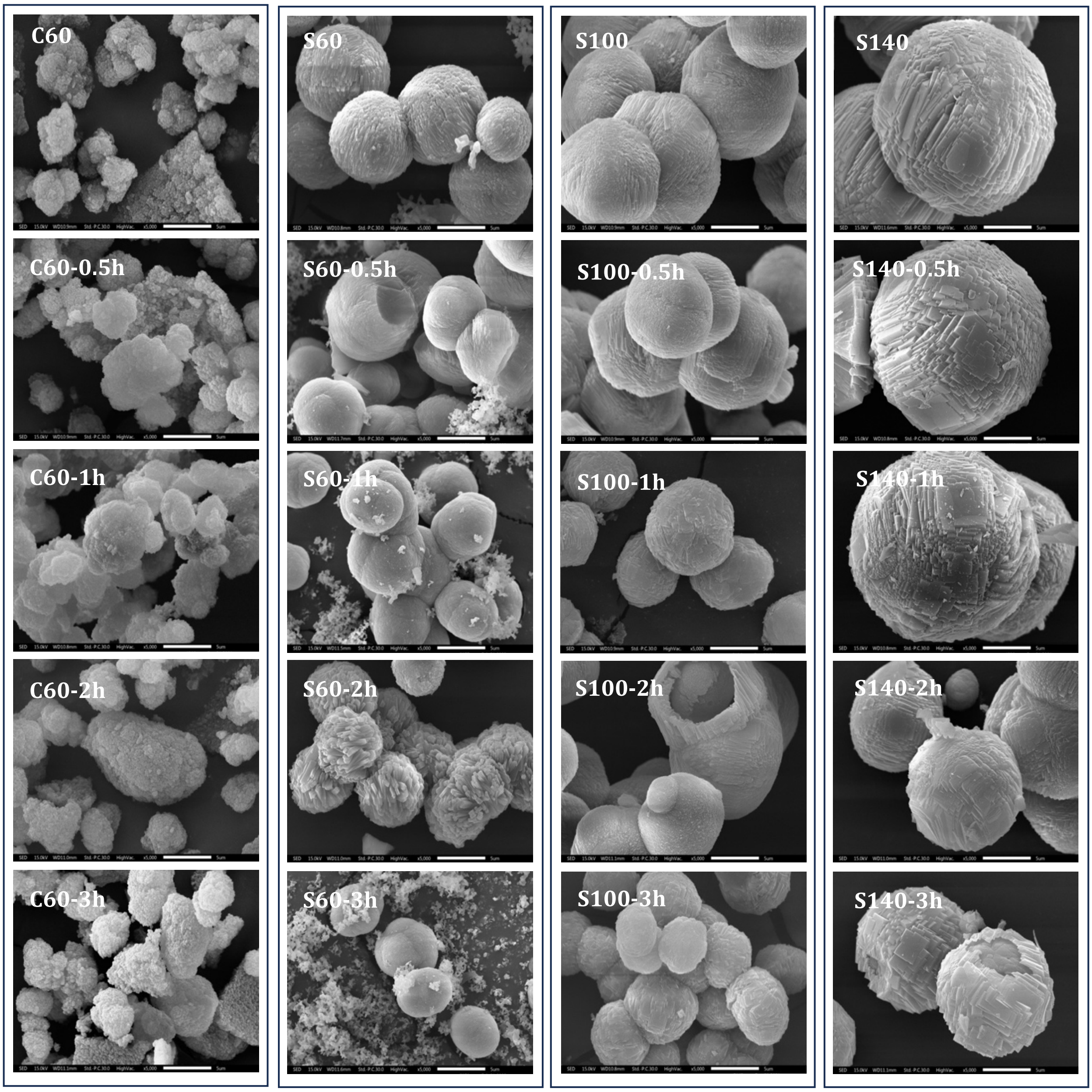
Table 3. Porosity properties of untreated and alkali-treated ZSM-5 zeolite samples at different alkali treatment times

Sample	D_{avg}, nm	S_{total},[a] m²/g	S_{micro},[b] m²/g	S_{meso}, m²/g	$\frac{S_{meso}}{S_{total}}$	V_{total},[c] cm³/g	V_{micro},[b] cm³/g	V_{meso}, cm³/g	$\frac{V_{meso}}{V_{total}}$
C60	2.59	441	307	134	0.304	0.228	0.159	0.069	0.303
C60-0.5h	4.74	496	171	325	0.655	0.588	0.096	0.492	0.837
C60-1h	5.43	450	123	327	0.727	0.610	0.070	0.540	0.885
C60-2h	5.72	386	84	302	0.782	0.552	0.051	0.501	0.908
C60-3h	6.58	516	73	443	0.859	0.639	0.047	0.592	0.926
S60	2.98	317	195	122	0.385	0.235	0.103	0.132	0.562
S60-0.5h	2.44	347	233	114	0.329	0.219	0.124	0.095	0.434
S60-1h	3.32	234	114	120	0.513	0.195	0.073	0.122	0.626
S60-2h	4.86	254	98	156	0.614	0.309	0.052	0.257	0.832
S60-3h	5.13	119	43	76	0.638	0.154	0.023	0.131	0.851
S100	2.21	403	278	125	0.310	0.238	0.146	0.092	0.387
S100-0.5h	4.19	401	157	244	0.608	0.421	0.087	0.334	0.793
S100-1h	4.01	401	176	225	0.561	0.402	0.097	0.305	0.759
S100-2h	4.39	427	163	264	0.618	0.469	0.091	0.378	0.806
S100-3h	3.27	432	240	192	0.444	0.353	0.128	0.225	0.637
S140	2.96	429	255	174	0.406	0.316	0.136	0.180	0.570
S140-0.5h	4.32	510	208	302	0.592	0.561	0.114	0.447	0.797
S140-1h	4.95	445	146	299	0.672	0.551	0.100	0.451	0.819
S140-2h	4.50	453	179	274	0.605	0.510	0.099	0.411	0.806
S140-3h	4.30	379	115	264	0.697	0.502	0.084	0.418	0.833

Note: [a] BET method; [b] t-plot method; [c] volume adsorbed at $P/P_0 = 0.99$

3.3 Surface morphology

The surface morphology of commercial and synthesized ZSM-5 zeolite samples at different alkali treatment times were presented by SEM images, as shown in Figure 4. There was no significant difference in crystallite shape between untreated (C60) and alkali-treated commercial ZSM-5 zeolites (C60-0.5h, C60-1h, C60-2h, and C60-3h), despite the fact that treatment time was increased to 3 h. For the untreated synthesized ZSM-5 zeolites, the samples consisted of large spherical crystallites and a smooth surface (S60, S100, and S140), and the spherical crystal size tended to be larger at higher SiO_2/Al_2O_3 ratios. After treatment for 1 h in a NaOH aqueous solution, the edges of particles were corroded. The synthesized ZSM-5 zeolite particles exhibited more defects and their surface gradually became rougher when the alkali treatment duration was extended to 2 h. During the alkali treatment with a prolonged retention time, the surface was found to contain grooves and voids, and the crystal particle size was smaller, particularly at a higher SiO_2/Al_2O_3 ratio. This suggests that silicon (Si) was preferentially removed from the crystal structure with the higher-ratio SiO_2/Al_2O_3 synthesized ZSM-5 zeolites.

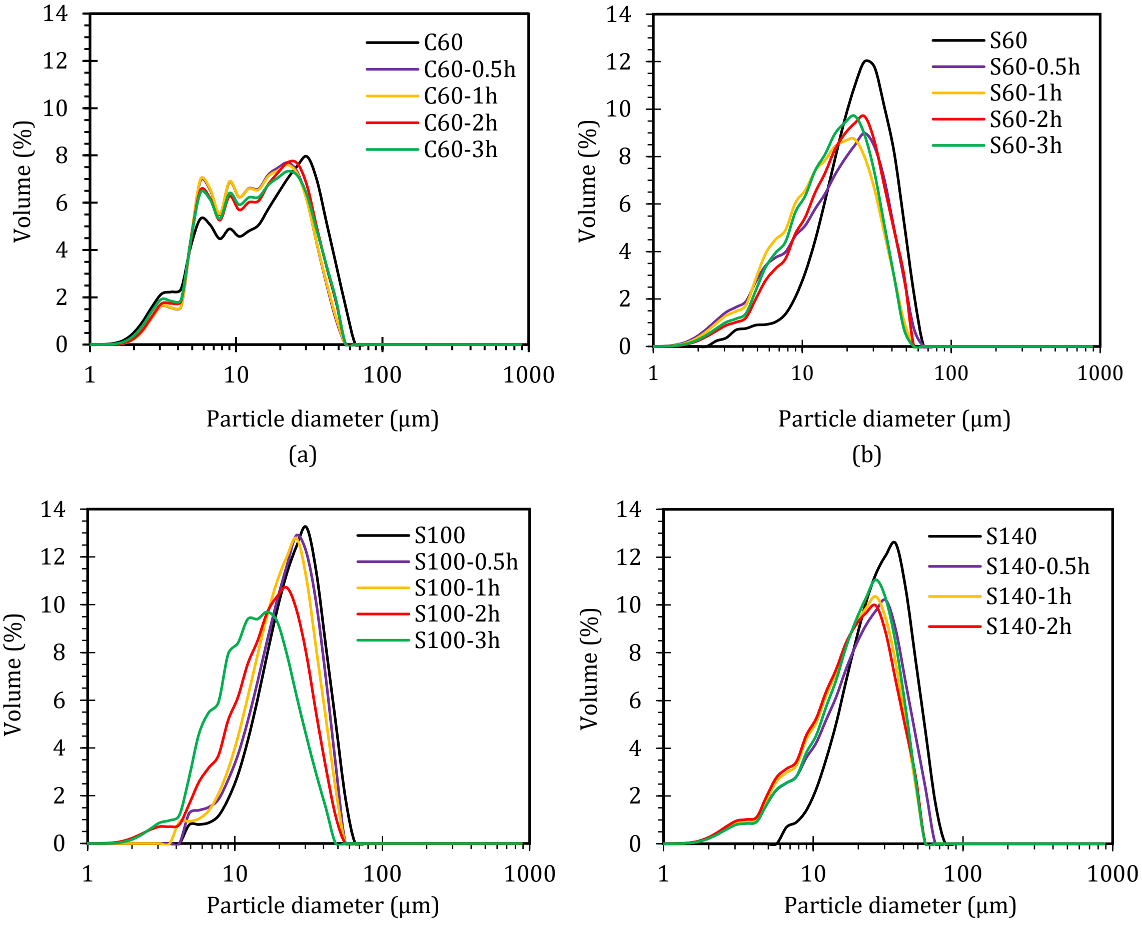


(a) (b) (c) (d)

Figure 4. SEM images of (a) commercial ZSM-5 zeolite with SiO_2/Al_2O_3 of 60, and synthesized ZSM-5 zeolites with SiO_2/Al_2O_3 of (b) 60, (c) 100, and (d) 140, at different alkali treatment times

3.4 Particle size distribution

Figure 5 and Table 4 show the results of particle size distribution curves and average particle diameter of commercial and synthesized ZSM-5 zeolites at different treatment times. For the commercial ZSM-5 zeolite, it was observed that the particle size distribution curves of the untreated and alkali-treated samples seemed not to be that different. However, when the C60 untreated sample was treated with NaOH aqueous solution, the average particle diameter of C60-0.5h, C60-1h, C60-2h, and C60-3h treated samples slightly decreased, compared to the untreated ones. For the synthesized ZSM-5 zeolite, the untreated samples showed that the average particle diameter was 21.49, 24.19, and 24.69 μm for the S60, S100, and S140 untreated samples, respectively. For the condition of alkali treatment time of 3 h, their average particle diameter tended to decrease and reduced to 16.05, 14.13, and 19.78 μm for S60-3h, S100-3h, and S140-3h, respectively. Additionally, it was found that a longer period of alkali treatment resulted in a smaller particle size, for both alkali-treated commercial and synthesized ZSM-5 zeolites. This result implies that NaOH aqueous solution can partly dissolve silica species from ZSM-5 zeolite particles.



(a) (b) (c) (d)

Figure 5. Particle size distribution curves of (a) commercial ZSM-5 zeolite with SiO_2/Al_2O_3 of 60, and synthesized ZSM-5 zeolites with SiO_2/Al_2O_3 of (b) 60, (c) 100, and (d) 140, at different alkali treatment times

4. CONCLUSION

The combination of micropores and mesopores in commercial and synthesized ZSM-5 zeolites were produced via desilication using NaOH aqueous solution with an appropriate alkali treatment time. The results from XRD patterns, SEM images, and PSD curves demonstrated that the increasing alkali treatment time led to a noticeable loss of crystallinity and the destruction of the zeolitic structure. Furthermore, the pore size distribution revealed that the incremental number of mesopores were obtained with longer treatment times, whereas the number of micropores decreased. For commercial ZSM-5 zeolite, the alkali treatment condition for 3 h gave the optimum condition with the highest S_{meso} and V_{meso} values. For synthesized ZSM-5 zeolite, the crystal structure and mesoporous porosity strongly depended on alkali treatment time and SiO_2/Al_2O_3 ratio. The alkali-treated synthesized ZSM-5 zeolite with a SiO_2/Al_2O_3 ratio of 140 in 0.2 M NaOH aqueous solution for 1 h had the highest S_{meso} and V_{meso} values, with a preserved microporosity and MFI structure. The optimal porosity and the existence of micropore-mesopore ZSM-5 zeolite structure dominantly related to the enhanced catalytic performance in terms of physical mass transport and shape selectivity.

Table 4. Average particle diameter of untreated and alkali-treated ZSM-5 zeolite samples at different alkali treatment times

Sample	**Average particle diameter (μm)**
C60	17.63
C60-0.5h	15.35
C60-1h	14.74
C60-2h	15.29
C60-3h	15.23
S60	21.49
S60-0.5h	18.15
S60-1h	15.82
S60-2h	16.56
S60-3h	16.05
S100	24.19
S100-0.5h	21.99
S100-1h	20.09
S100-2h	17.46
S100-3h	14.13
S140	24.60
S140-0.5h	21.34
S140-1h	18.96
S140-2h	18.61
S140-3h	19.78

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