Synthesis of ZSM-5 zeolite by the seed assisted method, and its use for the ethanol dehydration reaction

Brenda N. Cristo[1]; Mariana Arevalo[1]; Juan A. Melo[1]; Juan M. Gonzalez[1]; Jaime Becerra-Chalá[2] and Bernay Cifuentes[1]
[1]Universidad de la Salle, Colombia, *bcristo28@unisalle.edu.co*, *marevalo41@unisalle.edu.co*, *jmelo62@unisalle.edu.co*, *juanmgonzale@unisalle.edu.co*, *bcifuentes@unisalle.edu.co*
[2]Universidad de la Sabana, Colombia, *jaimebch@unisabana.edu.co*

ZSM-5 zeolites were synthesized by a seed-assisted hydrothermal method as an organic structure-directing agent-free alternative to conventional synthesis routes and evaluated as catalysts for ethanol dehydration to ethylene. The synthesis employed tetraethyl orthosilicate as the silicon source, sodium aluminate as the aluminum source, and commercial ZSM-5 seeds with Si:Al ratios of 12.5 and 30. The effects of crystallization time, seed Si:Al ratio, and aluminum content in the synthesis gel were analyzed by SEM, XRD, NH_3-TPD, Py-FTIR, and catalytic testing in a fixed-bed reactor. SEM and XRD results confirmed the formation of the MFI framework, with well-defined ZSM-5 crystals obtained after 72 h of hydrothermal treatment, whereas longer crystallization times promoted minor secondary silica phases. NH_3-TPD showed that the synthesized samples contained mainly weak-to-medium acid sites, with higher desorption intensities for samples prepared with greater aluminum content. Py-FTIR revealed that the Si:Al=30 series was dominated by Lewis-acid contributions, while the Si = 12.5 series, particularly SiAl12.5 0.6Al, showed clearer evidence of accessible Brønsted acid sites. Catalytic tests demonstrated that the seed-assisted ZSM-5 samples were active for ethanol dehydration, although their ethanol conversion was lower than that of the commercial H-ZSM-5 reference. The formation of ethylene confirmed the presence of catalytically relevant acid sites, while the moderate conversion values suggest limitations associated with Brønsted acid-site density, acid strength, and/or diffusional accessibility. These results demonstrate that the seed-assisted route can produce active ZSM-5 catalysts while avoiding organic templates, highlighting its potential as a more sustainable pathway for preparing zeolitic catalysts for bioethanol dehydration to ethylene.

1. INTRODUCTION

Zeolites are crystalline microporous molecular sieves known for their unique three-dimensional frameworks of corner-sharing TO_4 tetrahedra (T = Si, Al, etc.) that create uniform pore systems, tunable acidity (via Si/Al ratio and extra-framework species), and high thermal/hydrothermal stability. Zeolites have found wide applications as adsorbents, ion exchangers, and catalysts in many industrial processes [1]

Among these materials, Zeolite Socony Mobil-5 (ZSM-5) is a typical MFI-type zeolite and is recognized as one of the most important heterogeneous catalysts. The ZSM-5 structure is characterized by a distinctive three-dimensional ten-membered ring intersecting pore structure consisting of 10-membered-ring channels (5.1-5.6 Å). Due to its shape selectivity, intrinsic acidity, high surface area, and thermal stability, ZSM-5 is indispensable in industrial applications such as fluid catalytic cracking (FCC), alkylation, and methanol/ethanol-to-hydrocarbons reactions [2]

The synthesis of ZSM-5 was first achieved via the conventional hydrothermal method patented by Mobil Oil Corporation in 1972. This route typically requires the use of organic structure-directing agents (OSDAs), such as tetrapropylammonium hydroxide (TPAOH) or its salt (TPABr), which guide the formation and stabilize the framework structure. Following synthesis, a high-temperature calcination step is required to remove the organic molecules and open the pore system for catalytic use [3].

However, this traditional methodology presents several drawbacks. OSDAs are expensive and can represent up to 50% of the production cost. Their removal requires high-temperature calcination (typically 400-500°C), which consumes significant energy and generates harmful emissions such as NO_x and CO_2. Moreover, when sodium hydroxide is used as the alkali source, the resulting Na-form ZSM-5 requires multiple ion-exchange steps to produce the active H-form, a time-consuming and energy-intensive procedure [4].

To address these limitations, seed-assisted synthesis has emerged as a promising alternative. This method introduces pre-formed ZSM-5 crystals (seeds) into the initial gel mixture to guide crystallization, reducing the induction period and accelerating crystal growth. The result is a more sustainable and scalable route to MFI materials with catalytic properties comparable to templated zeolites [3], [5]

In this work, ZSM-5 was synthesized via a seed-assisted hydrothermal method using tetraethyl orthosilicate (TEOS) as the silicon source, $NaAlO_2$ as the aluminum source, aqueous NaOH as the mineralizing agent, and commercial ZSM-5 (Si/Al = 12.5 and 30) as seed. The effects of synthesis time, seed Si/Al ratio, and aluminum composition on crystallization and acidity were evaluated.

2. MATERIALS AND METHODS

2.1. Materials

The materials used for the synthesis of H-ZSM-5 samples were tetraethyl orthosilicate (TEOS, 98%, Sigma-Aldrich), sodium aluminate ($NaAlO_2$, 99.95%, Sigma-Aldrich), sodium hydroxide (98%, Merck), and ethanol (99.5%, Panreac). Absolute ethanol (ACS reagent > 99.5%, Sigma-Aldrich) and

argon gas (UAP > 99.99%, Messer) were used during catalytic tests.

2.2. Catalyst synthesis

Commercial NH_4-ZSM-5 (Si/Al = 12.5 or 30) was calcined at 550°C for 4 h (heating rate 1 °C min^{-1}) to obtain H-ZSM-5 seed. TEOS and $NaAlO_2$ were added to an aqueous NaOH solution and stirred for 1 h. Concurrently, H-ZSM-5 was dispersed in 1 mL ethanol under stirring. The seed dispersion was introduced into the synthesis mixture and stirred for an additional 1 h to form a homogeneous gel. To test the effect of temperature, hydrothermal synthesis was performed at 160°C for 24, 48, 72, and 96 h in Teflon-lined stainless-steel autoclaves. The solids were centrifuged (5000 rpm, 10 min), washed to neutral pH, dried at 105 °C overnight, and calcined at 550°C for 4 h. To analyze the effect of Al composition and seed Si:Al ratio, samples were prepared to achieve 300 mol H_2O - X mol Al_2O_3 - 6 mol SiO2 - 2.5 NaOH, as reported in Table 1

Table 1. Compositions used in ZSM-5 samples

		Seed Si:Al molar ratio	
		12.5	30
X (Al moles)	0.30	SiAl12.5 0.3Al	SiAl30 0.3Al
	0.45	SiAl12.5 0.45Al	SiAl30 0.45Al
	0.60	SiAl12.5 0.6Al	SiAl30 0.6Al

2.3. Catalyst characterization

The morphological analysis of the synthesized zeolites was carried out by scanning electron microscopy (SEM) using a dual-beam field-emission system (FIB-FESEM; Scios 2 LoVac, Thermo Fisher Scientific). SEM images were acquired for all samples at magnifications corresponding to 50 µm and 1 µm scale bars. In addition, X-ray diffraction (XRD) patterns were collected for the commercial and synthesized samples using an Aeris X-ray diffraction unit (Panalytical, Malvern, Worcestershire, UK). The measurements were performed over a 2θ range of 5–80° using Cu Kα radiation as the X-ray source. The scanning speed was 5° min^{-1}, and the operating voltage was 40 kV.

2.4. Acidity

The acidity of the H-SSZ-13 samples was measured by ammonia temperature-programmed desorption (NH_3-TPD) and Py-FTIR.

2.4.1. NH_3-TPD

NH_3-TPD measurements were carried out using a ChemBET Pulsar unit (Quantachrome Instruments, Boynton Beach, FL, USA) equipped with a thermal conductivity detector (TCD). Prior to analysis, 0.10 ± 0.01 g of sample was activated under flowing N_2 for 4 h at 550 °C, using a heating ramp of 1 °C min^{-1}, after an initial degassing step in N_2 at 120 °C for 1 h with a flow rate of 50 mL min^{-1}. The sample was then cooled to 80 °C for NH_3 adsorption by passing 5 vol% NH_3/N_2 at 50 mL min^{-1} for 60 min. After saturation, the catalyst was purged with N_2 at 50 mL min^{-1} for 1 h to remove physisorbed NH_3. The TPD profiles were subsequently recorded from 50 to 1000 °C under N_2 flow at 50 mL min^{-1}, using a heating rate of 10 °C min^{-1}.

2.4.2. Py-FTIR

The acidity of the zeolite samples was also evaluated by pyridine adsorption followed by Fourier-transform infrared spectroscopy (Py-FTIR). Prior to analysis, the samples were dried at 150 °C for 10 h and subsequently at 300 °C for 12 h, using a heating ramp of 2 °C min^{-1}.

Samples were placed in a glass cell equipped with ZnSe windows for pyridine adsorption/desorption experiments and FTIR spectral acquisition. Initially, the samples were degassed under vacuum at 4.6×10^{-7} hPa and heated at 350 °C for 12 h to remove moisture from the analyzed material. The FTIR spectra of the degassed samples were recorded as references.

Pyridine adsorption was carried out at 150 °C using twelve pulses of 60 s each until saturation of the pellets with pyridine vapor. The samples were then maintained at the same temperature for 15 min. Afterward, the cell was cooled to room temperature, and physically adsorbed pyridine was removed for 15 min. FTIR spectra were collected with a resolution of 4 cm^{-1} and 128 scans. Finally, pyridine desorption was performed at ambient temperature, 150, 250 and 350°C.

2.5. Catalytic activity

Catalytic activity for ethanol dehydration was evaluated at atmospheric pressure and temperatures ranging 150-550°C using an automated reaction system based on procedures reported by Quiroga et al. [6]. The reactor consisted of a 16 mm ID 30 cm long bench top tubular quartz tube, with a frit at mid-length to hold the catalyst bed and housed in a temperature-controlled furnace. Each run used 50 mg catalyst diluted with quartz. Argon (175.6 mL min^{-1}) served as carrier gas, and ethanol was fed at 0.0315 mL min^{-1}. Products were quantified online using an Agilent 8890 GC equipped with FID and TCD detectors and HP-PLOT/Q, molecular sieve 5A, and Porapak Q columns.

3. RESULTS AND DISCUSSION

3.1. Morphological analysis

SEM micrographs in Figure 1 show clear morphological evolution with synthesis time. At 24 h, crystals exhibit low uniformity and small particles indicative of early nucleation. At 72 h, well-defined homogeneous crystals are observed. At 96 h, crystals are well developed but show surface irregularities possibly associated with minor secondary phases.

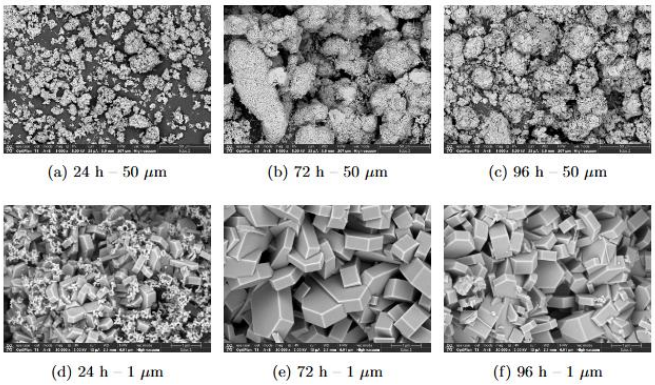

Figure 1. SEM micrographs of ZSM-5 synthesized under different crystallization times. (a–c) Images at 50 μm scale for 24, 72, and 96 h, respectively; (d–f) corresponding images at 1 μm scale for the same synthesis times.

XRD patterns in figure 2 indicate that the 72 h sample closely matches commercial ZSM-5, whereas the 96 h sample shows an additional reflection at 2θ ≈ 27°, consistent with extra-framework keatite-type silica.

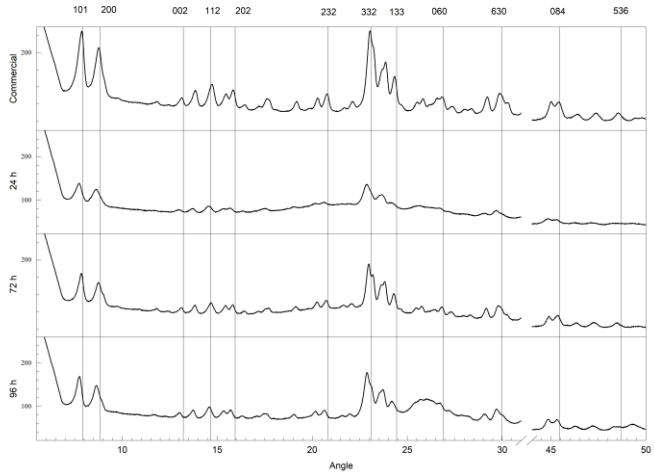

Figure 2. XRD spectra for commercial and synthesized ZSM-5 samples

3.2. Acidity

The acidity of the seed-assisted synthesized ZSM-5 samples was evaluated by NH_3-TPD and pyridine-adsorbed FTIR spectroscopy in order to correlate the acid properties with the catalytic behavior in ethanol dehydration. The NH_3-TPD profiles of the samples synthesized using seeds with Si:Al ratios of 30 and 12.5 are shown in Figures 3 and 4, respectively. In all cases, the profiles exhibit desorption signals mainly between 100 and 300 °C, which are commonly associated with weak to medium acid sites. A less intense contribution at higher temperatures, particularly between approximately 350 and 500 °C, can also be observed for some samples, indicating the presence of stronger acid sites.

For the samples prepared using seeds with Si = 30, the synthesized materials showed higher NH_3 desorption intensity than the commercial H-ZSM-5 reference in the low- and medium-temperature regions. Among these samples, SiAl30 0.45Al and SiAl30 0.6Al presented the most intense desorption profiles, suggesting that increasing the aluminum content in the synthesis gel favored the generation of additional acid sites. However, the relatively broad desorption bands indicate a heterogeneous acid-site distribution, which may be related to differences in aluminum incorporation, extra-framework aluminum species, or incomplete development of the zeolitic framework during seed-assisted crystallization.

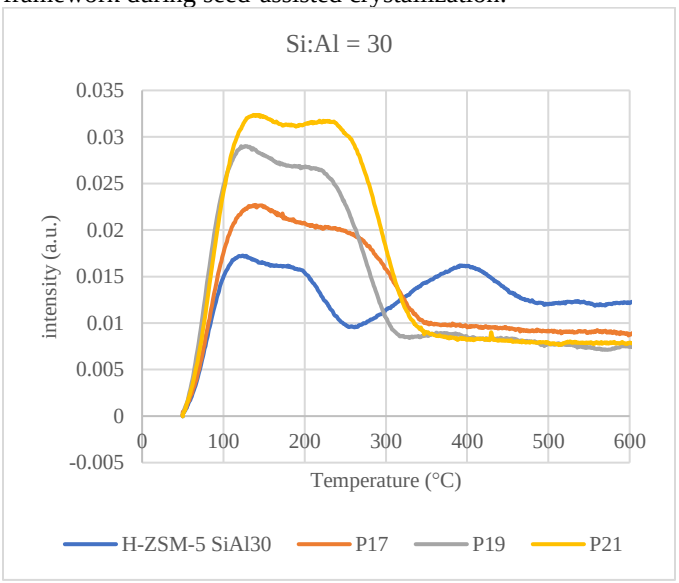

Figure 3. NH3-TPD results for ZSM-5 samples Si:Al = 30

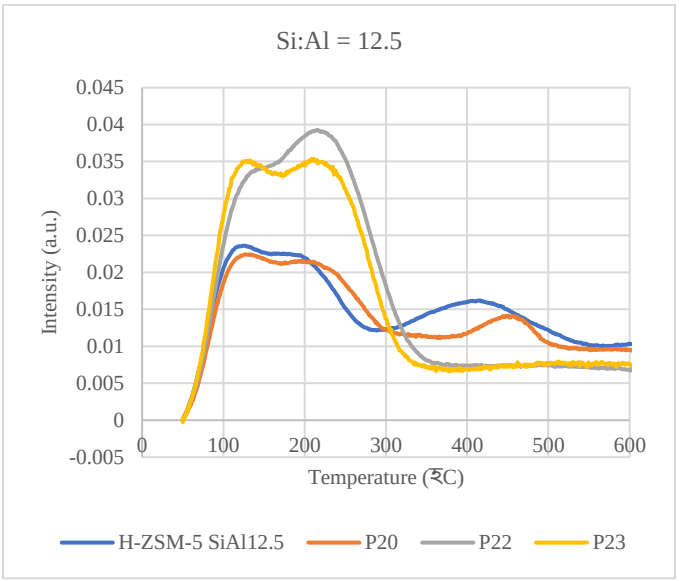

Figure 4. NH3-TPD results for ZSM-5 samples Si:Al = 12.5

A similar trend was observed for the samples prepared using seeds with Si = 12.5. These materials also exhibited relevant NH_3 desorption between 100 and 300 °C, with SiAl12.5 0.6Al showing the highest overall intensity. This result suggests that

the higher aluminum content promoted a larger concentration of acid sites. Nevertheless, the predominance of low- and medium-temperature desorption signals indicates that a significant fraction of the acid sites corresponds to weak or medium-strength sites rather than strong Brønsted acid sites. This feature is important for ethanol dehydration because Brønsted acid sites are responsible for the formation of ethylene, whereas insufficient acid strength or low accessibility can limit ethanol conversion.

The Py-FTIR spectra provide additional information about the nature of the acid sites (Figures 5 and 6). The bands observed near 1445 cm^{-1} are assigned to pyridine coordinated to Lewis acid sites, whereas the band around 1540–1545 cm^{-1} is associated with pyridinium ions formed on Brønsted acid sites. The band near 1490 cm^{-1} corresponds to the contribution of pyridine interacting with both Lewis and Brønsted acid sites. Therefore, the extended spectral range up to 1560 cm^{-1} allows a more complete evaluation of the acid-site distribution in the synthesized ZSM-5 samples.

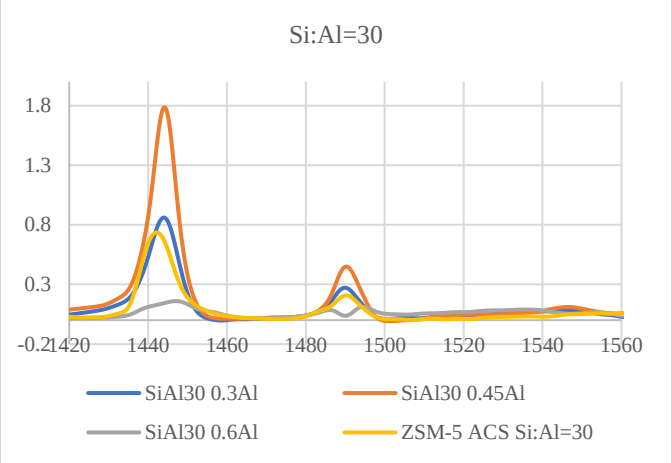

Figure 5. Py-FTIR results for ZSM-5 samples Si:Al = 30

For the Si = 30 series, the Py-FTIR spectra show intense bands near 1445 cm^{-1} and 1490 cm^{-1}, while the Brønsted-acid band near 1540–1545 cm^{-1} is weak or barely distinguishable. Among these samples, SiAl30 0.45Al displays the highest intensity in the Lewis-acid region, followed by SiAl30 0.3Al and SiAl30 0.6Al. This behavior suggests that the incorporation of aluminum under these synthesis conditions favored the formation of pyridine-accessible Lewis acid sites, probably related to extra-framework aluminum species or coordinatively unsaturated aluminum centers, rather than a proportional increase in accessible framework Brønsted acid sites.

For the Si = 12.5 series, a different behavior is observed. The SiAl12.5 0.6Al sample shows the most intense bands in the Py-FTIR spectra, including a strong contribution near 1445 cm^{-1}, a pronounced band near 1490 cm^{-1}, and a clearer signal in the 1540–1545 cm^{-1} region. This indicates that increasing the aluminum content in the synthesis gel promoted the formation of both Lewis and Brønsted acid sites, with SiAl12.5 0.6Al presenting the highest concentration of pyridine-accessible acid sites among the synthesized samples. The commercial ZSM-5 reference with Si = 12.5 also shows acid-site contributions in this region, although with lower intensity than SiAl12.5 0.6Al.

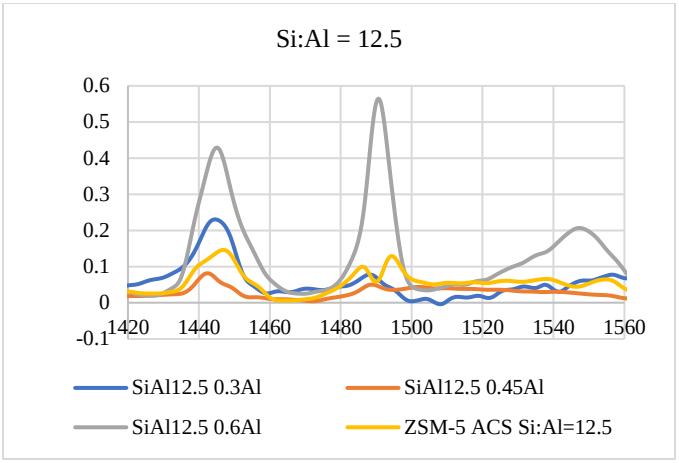

Figure 6. Py-FTIR results for ZSM-5 samples Si:Al = 30

The Py-FTIR results are consistent with the NH_3-TPD profiles, which showed higher ammonia desorption intensity for samples with greater aluminum content, particularly in the Si = 12.5 series. However, the comparison between both techniques also indicates that total acidity and acid-site nature do not evolve identically. NH_3-TPD reflects the overall acid-site population accessible to ammonia, whereas Py-FTIR differentiates Lewis and Brønsted acid sites using pyridine as a probe molecule. This distinction is important because ethanol dehydration to ethylene is mainly promoted by Brønsted acid sites, while Lewis acid sites may contribute less directly to the desired dehydration pathway.

The acidity characterization indicates that the seed-assisted synthesis produced ZSM-5 materials with measurable acidity. The Si = 30 samples were dominated by Lewis-acid contributions, whereas the Si = 12.5 samples, especially SiAl12.5 0.6Al, showed stronger evidence of accessible Brønsted acid sites. This difference helps explain the catalytic results: samples with higher Brønsted acidity tended to favor ethylene formation, while limited ethanol conversion suggests that the number, strength, and accessibility of active Brønsted sites remain lower than in the commercial H-ZSM-5 reference.

3.3. Catalytic activity

The catalytic performance of the synthesized H-ZSM-5 samples was evaluated in the ethanol dehydration reaction, and the results are summarized in Figure 7. Ethanol conversion and ethylene selectivity varied significantly depending on the seed Si:Al ratio and the aluminum content used during synthesis. The commercial H-ZSM-5 reference with Si:Al = 30 showed the highest catalytic activity, reaching almost complete ethanol conversion and high ethylene selectivity. This behavior is

consistent with the presence of well-developed and accessible Brønsted acid sites in the commercial material.

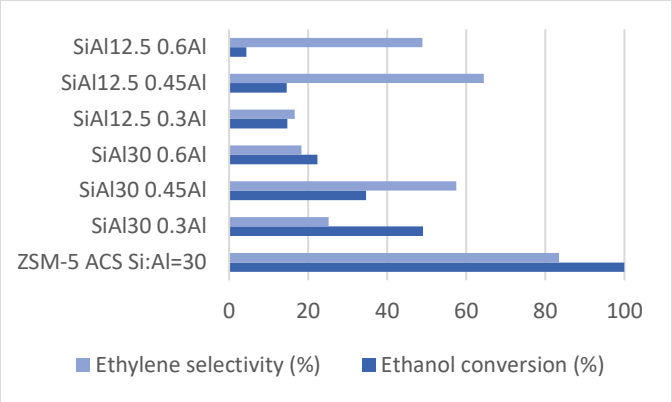

Figure 7. Catalytic test for seed assisted synthesized ZSM-5 (Compared at maximum conversion temperature, 400°C).

The seed-assisted synthesized catalysts showed lower ethanol conversion than the commercial reference, indicating that although the MFI structure was formed, the concentration, strength, or accessibility of the active acid sites was not yet equivalent to that of the commercial H-ZSM-5. Among the synthesized materials prepared using seeds with Si:Al = 30, the SiAl30 0.3Al sample showed the highest ethanol conversion, whereas SiAl30 0.45Al and SiAl30 0.6Al displayed lower conversion values despite showing relevant acidity by NH_3-TPD and Py-FTIR. This suggests that the total acid concentration alone does not fully determine catalytic performance; the nature of the sites, their accessibility, and possible diffusion limitations within the zeolite crystals also influence the reaction.

For the samples synthesized using seeds with Si:Al=12.5, ethylene selectivity increased with aluminum content, with SiAl12.5 0.45Al and SiAl12.5 0.6Al showing higher selectivity toward ethylene than SiAl12.5 0.3Al. However, ethanol conversion remained relatively low for this series. This behavior suggests that the available acid sites can promote the dehydration pathway once ethanol is activated, but the overall number of accessible strong Brønsted acid sites may still be insufficient to achieve high ethanol conversion.

The comparison between acidity and catalytic performance indicates that the most intense NH_3-TPD or Py-FTIR signals do not necessarily correspond to the highest ethanol conversion. This can be attributed to the fact that NH_3 is a small probe molecule capable of accessing acid sites that may not be equally accessible to ethanol under reaction conditions. In addition, Py-FTIR showed a strong contribution of Lewis acid sites, whereas ethanol dehydration to ethylene requires accessible Brønsted acid sites. Therefore, the moderate conversion values observed for the synthesized catalysts are likely related to an imbalance between total acidity and effective Brønsted acidity.

Despite these limitations, the formation of ethylene confirms that the seed-assisted synthesized ZSM-5 samples possess catalytically active acid sites. The results demonstrate that the OSDA-free synthesis route can produce active ZSM-5 catalysts for ethanol dehydration, but further optimization is required to increase framework aluminum incorporation, improve Brønsted acid-site density, and enhance the accessibility of active sites.

4. CONCLUSIONS

ZSM-5 zeolites were successfully synthesized by a seed-assisted hydrothermal method without the use of organic structure-directing agents. SEM and XRD characterization confirmed the formation of the MFI framework, with the best crystal development obtained after 72 h of crystallization. Longer synthesis times led to the appearance of minor secondary phases, indicating that crystallization time must be carefully controlled to obtain phase-pure ZSM-5.

NH_3-TPD analysis confirmed that the synthesized materials contained acid sites, mainly in the weak-to-medium strength range. Increasing the aluminum content in the synthesis gel generally increased the NH_3 desorption intensity, particularly for the Si:Al = 12.5 series. Py-FTIR analysis showed bands associated with pyridine adsorbed on Lewis acid sites and with total acidity, while the characteristic Brønsted-acid band was not clearly observed in the analyzed spectral region. These results indicate that the synthesized samples presented measurable acidity, but with an important contribution of Lewis acid sites and a limited concentration of accessible Brønsted acid sites.

Catalytic tests in ethanol dehydration showed that the commercial H-ZSM-5 reference achieved the highest ethanol conversion and ethylene selectivity. The seed-assisted synthesized catalysts were active toward ethylene formation, confirming the presence of catalytically relevant acid sites. However, their ethanol conversion was lower than that of the commercial reference. This behavior was attributed to the lower concentration and/or accessibility of strong Brønsted acid sites, as well as possible diffusional limitations associated with the synthesized materials.

The results demonstrate that seed-assisted synthesis is a promising OSDA-free route for producing ZSM-5 catalysts for ethanol dehydration. Nevertheless, further optimization of the synthesis parameters is required to improve aluminum incorporation into the zeolite framework, increase accessible Brønsted acidity, and enhance catalytic performance toward ethylene production from ethanol.

ACKNOWLEDGMENT

The authors acknowledge the financial support provided by the Colombian Ministry of Science technology and innovation (Minciencias) through contract 441-2023 and Universidad de La Salle through the project FING-24209.

REFERENCES

[1] W. Yan, Y. Li, F. S. Xiao, Z. Liu, and J. Yu, "The Future of Zeolites," *Chemistry of Materials*, vol. 36, no. 15, pp. 7103–7105, Aug. 2024, doi: 10.1021/acs.chemmater.4c01675.

[2] T. Bai *et al.*, "Directly synthesis of H-form ZSM-5 zeolites with n-butylamine in the presence of seed and ethanol," *Microporous and Mesoporous Materials*, vol. 370, Apr. 2024, doi: 10.1016/j.micromeso.2024.113057.

[3] B. Bensafi, N. Chouat, and F. Djafri, "The universal zeolite ZSM-5: Structure and synthesis strategies. A review," Dec. 01, 2023, *Elsevier B.V.* doi: 10.1016/j.ccr.2023.215397.

[4] A. Javdani, J. Ahmadpour, and F. Yaripour, "Modified seed-induced synthesis of ZSM-5 aggregates and their catalytic performance in methanol to propylene conversion: Co-effect of ball milling and alkaline treatment of seed," *Advanced Powder Technology*, vol. 34, no. 10, Oct. 2023, doi: 10.1016/j.apt.2023.104184.

[5] Y. H. Chen, D. M. Han, and Q. Zhang, "Seed-induced synthesis of hierarchical architectures of ZSM-5 nanocrystalline aggregates by the solid state crystallization," *Advanced Powder Technology*, vol. 33, no. 8, Aug. 2022, doi: 10.1016/j.apt.2022.103666.

[6] E. Quiroga *et al.*, "Industrial crude bioethanol dehydration to ethylene: Doping ZSM-5 to enhance selectivity and stability," *J. Environ. Chem. Eng.*, vol. 12, no. 1, Feb. 2024, doi: 10.1016/j.jece.2023.111803.