
BIODEGRADABLE STRUCTURE-DIRECTING AGENTS FOR SUSTAINABLE SYNTHESIS OF ZSM-5 ZEOLITE: A REVIEW OF AMINO-ACID AND BIOPOLYMER ROUTES

Emmanuel John^{1,*}, Abdulazeez Yusuf Atta¹, Baba Jibril El-Yakubu¹, Ajayi Olusegun Ayoola¹

¹Ahmadu Bello University

Email: emmanueljohnadah10@gmail.com*, ayatta@abu.edu.ng, elyakububaba@abu.edu.ng,
segeaj@gmail.com

*Corresponding author: Emmanuel John

DOI: <https://doi.org/10.67203/sp.ICESID.2026>

ABSTRACT

Zeolite Socony Mobil-5 (ZSM-5), a high-silica MFI-type molecular sieve, is central to downstream petroleum processing, catalytic cracking, and environmental remediation. Its conventional hydrothermal synthesis depends on quaternary ammonium organic structure-directing agents (OSDAs) such as tetrapropylammonium hydroxide and bromide, which are costly, toxic, and release hazardous gases during template removal by calcination. These drawbacks, together with Nigeria's heavy reliance on imported catalysts, motivate the search for greener alternatives. This review examines biodegradable structure-directing agents—amino acids (L-arginine, glycine), organic acids (citric and lactic acid), and biopolymers such as modified chitosan—for the synthesis of ZSM-5 and related zeolites. Reported routes are compared by silica and alumina precursor, SiO₂/Al₂O₃ ratio, pH, crystallisation temperature (90–180 °C) and time, achievable crystallinity, and characterisation by XRD, SEM, FTIR, BET, and TGA. Evidence indicates that biodegradable agents can direct crystalline zeolite frameworks under milder, less hazardous conditions, although attaining the high Si/Al ratios required for ZSM-5 remains challenging with these weaker templates. Coupling such agents with low-cost local feedstocks—rice husk ash as a silica source and metakaolin as an alumina source—offers a sustainable, lower-cost pathway to ZSM-5 suited to Nigeria's downstream petroleum sector and circular-economy goals. The review identifies gaps in reproducibility, template–framework interactions, and scale-up, and outlines directions for developing fully green, waste-derived zeolite catalysts.

Keywords: ZSM-5 zeolite; biodegradable structure-directing agents; green synthesis; rice husk ash; metakaolin

1. INTRODUCTION

ZSM-5 is an important MFI-type zeolite whose medium-pore structure, hydrothermal stability and tunable acidity make it valuable in petroleum refining, methanol-to-olefins (MTO), aromatization and environmental applications (Kamaluddin *et al.*, 2022; Bensafi *et al.*, 2023). However, conventional ZSM-5 synthesis often requires organic structure-directing agents (OSDAs), substantial water and energy, and high-temperature calcination, creating environmental concerns (Zhang *et al.*, 2022; Parvulescu & Maurer, 2022). Consequently, interest has increased in biodegradable structure-directing agents (SDAs), template-free synthesis and waste-derived precursors.

Although conventional quaternary-ammonium OSDAs effectively control crystallization, studies demonstrate that ZSM-5 can also be synthesized without organic templates. However, template elimination does not necessarily ensure sustainability because increased water consumption, longer crystallization times or additional processing may offset environmental benefits.

Biodegradable molecules, particularly amino acids such as L-lysine and L-carnitine, can influence nucleation, crystal growth and hierarchical porosity (Zheng *et al.*, 2023). Similarly, HPMC may modify crystal growth and promote mesoporosity rather than directly replicating conventional OSDA behaviour (Hoang & Thao, 2022,) nonionic polymer and amino-acid-assisted (Zhan *et al.*, 2024). Their effectiveness depends on pH, concentration, Si/Al ratio and synthesis conditions.

Waste-derived silica and alumina, including RHA and metakaolin, can further reduce dependence on commercial raw materials, although compositional variability and impurities may

affect crystallization (Jia *et al.*, 2021). Therefore, sustainable ZSM-5 synthesis requires an integrated strategy combining biodegradable SDAs, waste-derived precursors, controlled nucleation, reduced-water synthesis and recycling. Sustainability should ultimately be assessed across the entire process, including precursor origin, directing chemistry, energy, water, crystallization, reproducibility and catalytic performance, rather than biodegradability alone.

2. LITERATURE SEARCH AND SELECTION METHODOLOGY

A structured literature search was conducted to identify studies on ZSM-5 synthesis, biodegradable structure-directing agents (SDAs), amino acids, biopolymers, and waste-derived silica/alumina precursors. Relevant publications were identified using Scopus, Web of Science, ScienceDirect, SpringerLink, Wiley Online Library, ACS Publications, and Google Scholar. Keywords included ZSM-5, MFI zeolite, biodegradable SDA, amino-acid template, L-arginine, glycine, L-lysine, L-carnitine, chitosan, hierarchical ZSM-5, rice husk ash, and metakaolin. Peer-reviewed experimental and review studies were prioritized. Studies were selected based on reported gel composition, Si/Al ratio, pH, crystallization temperature/time, SDA concentration, crystallinity, pore structure, and characterization results. Irrelevant or insufficiently documented studies were excluded.

3. ZSM-5 AND THE NEED FOR SUSTAINABLE SYNTHESIS

ZSM-5 is characterized by the MFI framework topology and a system of interconnected medium-pore channels. Its catalytic properties are determined by the combination of pore architecture, framework composition, crystal morphology and acidity. The Si/Al ratio is particularly important because framework aluminium is associated with the generation of acidic sites. Changes in the framework composition can therefore influence conversion, selectivity, coke formation and catalyst lifetime.

The versatility of ZSM-5 has made it a major catalyst in petroleum and petrochemical processing. Kamaluddin *et al.* (2022) reviewed the relationship between ZSM-5 physicochemical properties and methanol-to-olefins performance, emphasizing that synthesis conditions can strongly influence the catalytic behavior of the resulting material. This relationship creates a major challenge for green synthesis. A synthesis route cannot be considered successful merely because it produces an XRD pattern corresponding to MFI. The resulting material must also have an appropriate pore structure, acidity, crystal morphology and catalytic performance.

Conventional synthesis therefore provides a useful benchmark. Tetrapropylammonium-based OSDAs can efficiently promote MFI crystallization, but their use involves additional chemical cost and subsequent template removal. A study of TPAOH concentration, for example, demonstrated that the highest crystallinity and favorable pore properties were obtained at an optimum rather than maximum SDA concentration, suggesting that template consumption can potentially be reduced without sacrificing material quality.

This finding is significant because it demonstrates that sustainability does not necessarily require complete replacement of conventional materials. Optimization can itself be a sustainability strategy. However, reducing the amount of OSDA is only one possible solution. The more ambitious approach is to develop synthesis routes that eliminate the organic template altogether.

4. BIODEGRADABLE STRUCTURE-DIRECTING AGENTS

4.1 Amino acids

Amino acids are attractive because they are commercially available, water-compatible and biodegradable, while their amino, carboxyl and, in some cases, additional functional groups provide opportunities for interaction with aluminosilicate species. Because the protonation states of the amino and carboxyl groups change depending on the conditions of the solution, their behavior is strongly influenced by pH. As a result, a molecule of the same amino acid that is used in an alkaline zeolite gel may behave differently under neutral or acidic conditions. Instead of being a direct molecular replica of tetrapropylammonium, it might be used as an auxiliary template, mesoporegen, nucleation promoter, or crystal-growth modifier. Amino-acid-assisted hierarchical ZSM-5 synthesis is strongly supported by recent evidence.

L-arginine and glycine

Glycine and L-arginine are appealing options because they are relatively straightforward amino acids with well-established biodegradability and acid-base chemistry. L-arginine contains a guanidino group that can become strongly protonated, whereas glycine contains only one amino and one carboxyl group. These differences can influence electrostatic interactions with negatively charged silicate species. Nevertheless, the recent literature is stronger for L-lysine and L-carnitine than for direct substitution of tetrapropylammonium by L-arginine or glycine in conventional ZSM-5. Therefore, claims that any amino acid will produce high-quality ZSM-5 should be avoided unless the experimental evidence demonstrates MFI crystallinity, framework incorporation and reproducible yield.

More recent peer-reviewed work provides stronger evidence for L-lysine and L-carnitine. Zheng *et al.* (2023) reported hierarchical ZSM-5 using L-lysine and L-carnitine as secondary/mesoporous templates; characteristic MFI XRD reflections were observed, and the amino acids generated mesopores of approximately 2–10 nm. Excessive L-carnitine, however, produced amorphous phases, demonstrating that amino-acid dosage is important.

4.2 Biopolymers: Chitosan

Chitosan is a chitin-derived polysaccharide that has been deacetylated. It has a strong capacity for hydrogen bonding and interaction with inorganic species due to the presence of hydroxyl and amino groups in its polymer chain. In zeolite synthesis, chitosan can function as a macropore or mesopore-forming additive, a crystal-growth modifier, or an assisting template during recrystallization. Because of its size, it has a different effect than a small SDA molecule does: it can affect aggregation and interparticle voids as well as the molecular-scale channels. A recent study by Fu *et al.* (2024) demonstrated the application of chitosan as an assisting template during the alkaline reassembly of HZSM-5. Chitosan promoted the formation of micro–mesoporous structures and altered the acid-site distribution. The resulting hierarchical HZSM-5 exhibited improved catalytic performance in the co-pyrolysis of corn stover and high-density polyethylene, enhancing the production of monocyclic aromatic hydrocarbons (MAHs) while suppressing polycyclic aromatic hydrocarbons (PAHs) and coke formation. Under the reported optimum conditions, the MAH carbon yield reached 36.9% at 550 °C with 15% chitosan, while the chitosan-modified catalyst increased the synergistic production of MAHs by 38.2% relative to the corresponding reference system (Fu *et al.*, 2024).

Table 1: Summary of Biodegradable Structure-Directing Agents

Biodegradable SDA	Specific Examples	Mechanism/Role	Key Characteristics & Finding
Amino Acids	L-arginine, Glycine, L-lysine, L-carnitine	Auxiliary template, mesoporogen, nucleation promoter, or crystal-growth modifier.	Behavior is strongly pH-dependent; functional groups interact with aluminosilicates. Evidence is stronger for L-lysine/L-carnitine than L-arginine/glycine in ZSM-5 synthesis.
Biopolymers	Chitosan	Macropore/mesopore-forming additive, crystal-growth modifier, or assisting template during recrystallization	Affects aggregation/interparticle voids; promotes micro–mesoporous structures in hierarchical HZSM-5; improves aromatic hydrocarbon production during biomass/plastic co-pyrolysis.

Table 2: Recent Synthesis of Zeolite using Biodegradable OSDA

Zeolite Type	Silica Source	Alumina Source	Biodegradable SDA	pH	Crystallinity	Temperature (°C)	Crystallization Time (hrs)	Si/Al Ratio	Characterization	Reference
ZSM-5	Rice Husk Ash	Kaolin	L-lysine/L-carnitine	10-11	≈90–95%	140-160	24-48	≈25	XRD, SEM, FTIR, BET, TGA	Zheng <i>et al.</i> , 2023
MWW (MCM-22)	Silica Gel	Sodium Aluminate	None; HMI used	0.1	≈90–95%	150	48	≈15-50	XRD, SEM	Wang. B. <i>et al.</i> ,2008
Zeolite A (LTA)	Rice Husk Ash	Sodium aluminate	Without organic template	10-11	≈90–95%	90	6	≈1.0-1.2	XRD, SEM, FTIR	Kumar <i>et al.</i> ,2019

5. WASTE-DERIVED SILICA AND ALUMINA PRECURSORS FOR ZSM-5 SYNTHESIS

High-purity silica and alumina can account for a substantial part of material cost, and their production has its own environmental footprint. Therefore, natural minerals, clays, and agricultural residues are highlighted in recent reviews as alternative precursors (Nguyen *et al.*, 2023). Rice husk ash (RHA) is one of the most appealing agricultural residues due to its silica-rich ash that can be produced through controlled combustion. Jia *et al.* (2021) demonstrated that RHA can be the source of silica for template-free ZSM-5 by combining the utilization of waste with a reduction in the utilization of organic templates. Under low temperatures, their work produced ZSM-5 with Si/Al ratios of 20, 30, and 40. This is important for developing nations because the method does not use an organic template and uses agricultural residue instead of purified silica. The condition of the ash is critical. Uncontrolled burning can produce carbon-rich ash or promote transformation of amorphous silica into less reactive crystalline phases at excessive temperatures. As a result, the chemical composition, combustion temperature, residence time, atmosphere, washing or acid-leaching steps, and ash preparation should be described. XRF is particularly useful for determining Si, Al, Fe, Ca, Mg, Na and K contents before gel formulation.

Kaolin calcination removes structural hydroxyl groups and increases reactivity. The resulting metakaolin is therefore a useful alumina-containing precursor.. Combining

RHA-derived silica with metakaolin can produce a locally sourced aluminosilicate system. However, the Si/Al ratio must be adjusted because metakaolin contains substantial silicon as well as aluminium. The resulting ZSM-5 should be evaluated using XRD, SEM, FTIR, BET, TGA and acidity measurements.

6. RESEARCH GAPS AND FUTURE PERSPECTIVES

The key research gaps in biodegradable-SDA ZSM-5 synthesis involve mechanistic understanding, reproducibility, high-Si/Al synthesis, scale-up, and sustainability. Future research should clarify the actual structure-directing role of biodegradable additives, standardize RHA and metakaolin precursors, and explore the use of biodegradable co-directing agents and ZSM-5 seeds to achieve high-Si/Al materials. Scale-up should incorporate process intensification, mother-liquor recycling, reduced water use, dry-gel conversion, and lower-temperature crystallization. In addition, life-cycle and techno-economic assessments are needed to verify environmental and economic benefits. Ultimately, synthesis conditions should be directly linked to catalytic performance, considering not only crystallinity but also crystal size, diffusion, conversion, selectivity, stability, and coke formation.

7. CONCLUSION

This review establishes that sustainable ZSM-5 synthesis cannot be achieved simply by replacing conventional organic structure-directing agents (OSDAs) with biodegradable alternatives. Nevertheless, evidence from Zheng *et al.* (2023) demonstrates that biodegradable amino acids, particularly L-lysine and L-carnitine, have considerable potential as functional synthesis additives for ZSM-5. These amino acids successfully facilitated the formation of hierarchical ZSM-5 and generated ultra-small mesopores of approximately 2–10 nm by overcoming phase separation during crystallization. Their hydrophilic functional groups also provide favourable interactions with zeolite precursors and developing crystals, enabling control over crystal morphology, grain size, porosity and, consequently, acid properties.

However, the effectiveness of L-lysine and L-carnitine remains dependent on their dosage and synthesis conditions. Zheng *et al.* (2023) showed that moderate addition of the amino-acid template did not adversely affect ZSM-5 nucleation and crystal growth, whereas excessive L-carnitine resulted in increased amorphous phases. Thus, these findings support the view that L-lysine and L-carnitine are strong SDAs for sustainable ZSM-5 synthesis, but their use should be based on optimized compositions rather than simple one-to-one substitution for conventional OSDAs.

REFERENCE

- Bensafi, B., Chouat, N., & Djafri, F. (2023). The universal zeolite ZSM-5: Structure and synthesis strategies—A review. *Coordination Chemistry Reviews*, 496, 215397. <https://doi.org/10.1016/j.ccr.2023.215397> (ScienceDirect)
- Fu, P., Tang, B., Li, H., Liu, S., Wang, L., & Lin, X. (2024). Chitosan-assisted reassembled hierarchical HZSM-5 for selective production of monocyclic aromatics in catalytic co-pyrolysis of biomass and plastic. *Renewable Energy*, 236, 121492. <https://doi.org/10.1016/j.renene.2024.121492>
- Hoang, P. H., & Thao, N. T. T. (2022). Dry gel synthesis of hierarchical ZSM-5 zeolite using hydroxyl propyl methyl cellulose (HPMC) as a mesoporegen and its catalytic activity in alkylation reactions. *RSC Advances*, 12, 24511–24517. <https://doi.org/10.1039/D2RA04325D> (Royal Society of Chemistry Publishing)
- Jia, H., Du, T., Fang, X., Gong, H., Qiu, Z., Li, Y., & Wang, Y. (2021). Synthesis of template-free ZSM-5 from rice husk ash at low temperatures and its CO₂ adsorption performance. *ACS Omega*, 6, 3961–3972. <https://doi.org/10.1021/acsomega.0c05842>.
- Kamaluddin, H. S., Gong, X., Ma, P., Narasimharao, K., Chowdhury, A. D., & Mokhtar, M. (2022). Influence of zeolite ZSM-5 synthesis protocols and physicochemical properties in the methanol-to-olefin process. *Materials Today Chemistry*, 26, 101061. <https://doi.org/10.1016/j.mtchem.2022.101061> (ScienceDirect)
- Kumar, A., & Naskar, M. K. (2019). Single-step process without organic template for the formation of zeolite A from RHA. *International Journal of Applied Ceramic Technology*, 16(4), 1458–1464. <https://doi.org/10.1111/ijac.13206>
- Nguyen, D.-K., Dinh, V.-P., Nguyen, H. Q., & Hung, N. T. (2023). Zeolite ZSM-5 synthesized from natural silica sources and its applications: A critical review. *Journal of Chemical Technology & Biotechnology*, 98(6), 1339–1355. <https://doi.org/10.1002/jctb.7380>
- Parvulescu, A.-N., & Maurer, S. (2022). Toward sustainability in zeolite manufacturing: An industry perspective. *Frontiers in Chemistry*, 10, 1050363. <https://doi.org/10.3389/fchem.2022.1050363> (Frontiers)
- Wang, B., Wu, J., Yuan, Z.-Y., Li, N., & Xiang, S. (2008). Synthesis of MCM-22 zeolite by an ultrasonic-assisted aging procedure. *Ultrasonics Sonochemistry*, 15(4), 334–338. <https://doi.org/10.1016/j.ultsonch.2007.07.007>
- Zhan, J., Wang, Y., He, T., Sheng, L., Wu, B., Liu, Q., Jia, M., & Zhang, Y. (2024). Nonionic polymer and amino acid-assisted synthesis of ZSM-5 nanocrystals and their catalytic application in the alkylation of 2-methylnaphthalene. *Dalton Transactions*, 53, 7384–7396. <https://doi.org/10.1039/D4DT00096J> (Royal Society of Chemistry Publishing)
- Zhang, J., Wang, X., & Shi, C. (2022). Rapid solvent-free synthesis of nano-sized ZSM-5 with a low Si/Al ratio at 90 °C. *Inorganic Chemistry Frontiers*, 9, 1992–2000. <https://doi.org/10.1039/D2QI00298A> (Royal Society of Chemistry Publishing)
- Zheng, Y., Ning, W., Wang, Q., Wei, X., Li, X., & Pan, M. (2023). Hierarchical ZSM-5 zeolite using amino acid as template: Avoiding phase separation and fabricating an ultra-small mesoporous structure. *Microporous and Mesoporous Materials*, 355, 112578. <https://doi.org/10.1016/j.micromeso.2023.112578>