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Recent Developments on CO₂ Hydrogenation Performance over Structured Zeolites: A Review on Properties, Synthesis, and Characterization

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Abstract: This review focuses on an extensive synopsis of the recent improvements in the field of CO₂ hydrogenation over structured zeolites including their properties, synthesis methods, and characterization approaches. The role of bimodal mesoporous structures surface oxygen vacancies, and the Si/Al ratio in improving catalytic activity is highlighted. The porosity, thermal stability, and structural integrity are also discussed in the review along with how structured zeolites are affected by electrical and plasma interactions. The synthesis methods are analyzed in detail by comparing the benefits and drawbacks of the bottom-up techniques, such as hard templating, soft templating, and non-templating on the one side; and the top-down approaches, e.g., dealumination, desilication, and recrystallization on the other. This review also draws attention to the necessity of overcoming the difficulties arising from these synthesis techniques, for example, micropore-induced diffusion restrictions and morphological constraints, employing innovative approaches and optimization strategies. Conventional and advanced characterization techniques are pointed out in this respect as crucial for understanding the catalytic mechanism and the dynamic behavior, hence, beneficial in the advancements of research on structured zeolites with higher efficiency and activity. The review ends with a perspective that highlights the necessity of further research in the improvement of synthesis approaches and characterization procedures of the structured zeolites to increase their catalytic activity in CO2 hydrogenation, a critical process of paramount importance in the global effort to reduce excessive carbon emissions and combat climate change..

Keywords: carbon dioxide hydrogenation; structured zeolites; zeolites synthesis and characterization

1. Introduction

Global warming is a significant concern as it is exacerbated by the excessive emissions of greenhouse gases, specifically carbon dioxide (CO₂), which contributes to mounting climate-related issues [1]. CO₂ hydrogenation is gradually emerging as a critical technology for carbon neutrality, which provides a route for CO₂ valorization into valuable chemicals and fuels [2,3]. The process offers a two-fold solution; besides addressing the pivotal issue of CO₂ emissions, it also assists in the sustainable production of heavy hydrocarbons [4]. The selective and optimized transformation of CO₂ represents a current challenge considering its thermodynamic stability and inert properties [5].

Structured zeolites, with their unequaled porous structures and acid-base properties, are used as a catalyst in a whole range of chemical processes, among them is CO₂ hydrogenation. Their ability to catalyze a breadth of reactions—from the Fischer-Tropsch Synthesis (FTS) process to the direct synthesis of aromatics—highlights their generality in catalysis [6]. Figure 1 shows the classes of well-known zeolites (e.g., natural [7], and synthetic [8–10]). Both zeolite types have been widely applied not just in catalysis [11], but even in other industries such as water and wastewater treatment, agriculture, biomedical, laundry detergents, and construction [12–16]. For CO₂ hydrogenation,

zeolites application has received considerable attention over the last decade. Figure 2 shows the distribution of number of articles displayed on google scholar when the phrase "CO_2 hydrogenation over zeolites" is used to search articles. The trend clearly indicates an unprecedented growth in the application of zeolites for CO_2 conversion reactions, particularly over the last decade where an exponential trend is seen. The recent signs of progress have mainly concentrated on the improvement of the zeolites through careful control of their compositions, porous characteristics, and coupling of thermal and mechanical properties that render promotion of reaction selectivity and enhance the production of longer-chained hydrocarbons such as aromatics, liquid fuels, and alcohols, and heavy olefins [5,17]. It should be noted that zeolites by themselves have been widely studied for various applications, nonetheless, the recent developments in the field of CO_2 catalysis and growing interest of researchers in the application of zeolites for CO_2 conversion creates a demand for a review covering the growth in the field, primarily over the last decade, which is the motivation behind this article. This study intends to summarize the recent advances in the area of CO_2 hydrogenation over structured zeolites by offering a synoptic view of the different synthesis techniques, characterization requirements, and catalytic functions. The review critically evaluates the current literature that should bring out new ideas, findings of key innovations, and significant breakthroughs. It will embrace the rudiments of the process, the specific traits of structured zeolites, and their role in augmenting catalytic activity. In addition, there will be reflections upon the challenges and prospects in this field whence one can get ideas on structured zeolites and the way they may be used to reduce the global CO_2 problem.
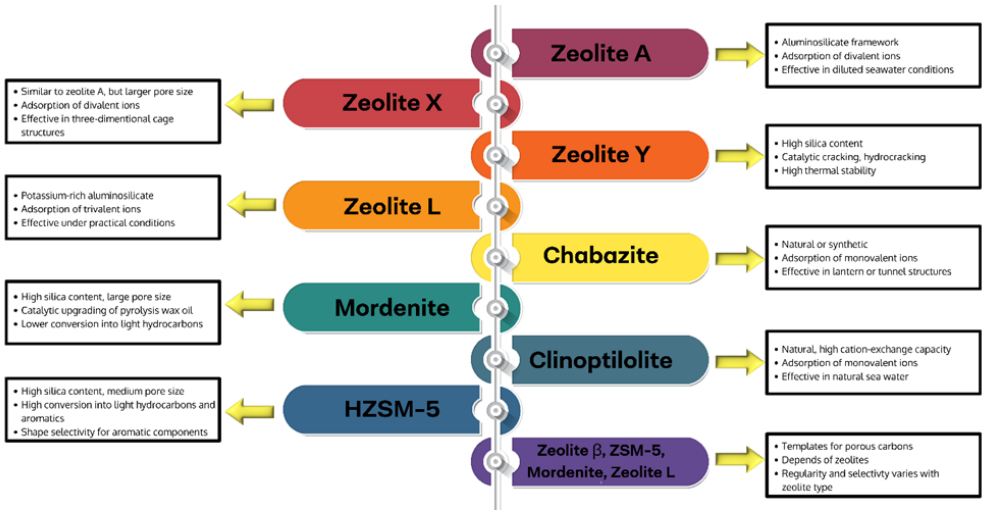

Figure 1. Types of Zeolites and their Synthesis, Application, and Performance.
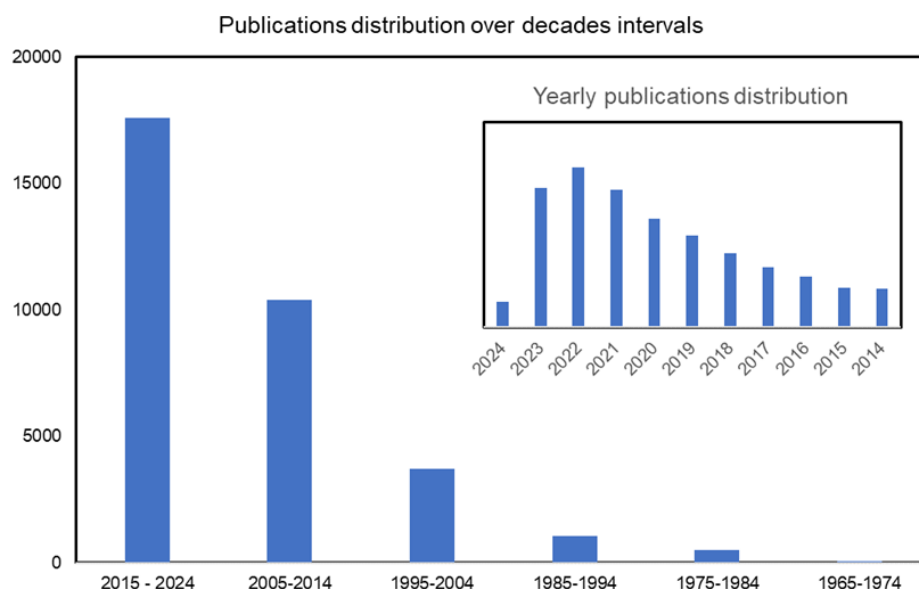
Figure 2. Number of publications displayed by google scholar search using phrase "CO_2 Hydrogenation over zeolites".

2. Influential Parameters

Structured zeolites possess a variety of important characteristics that enable them to function as active agents in catalytic processes, gradually making them a pivotal part of CO_2 hydrogenation prospects. Such zeolites provide specific pore structures, balanced density of acid/basic sites and compositions making them a suitable choice for a controlled catalytic activity and improved product selectivity in converting CO_2 into valuable chemicals. Their capacity for supporting and stabilizing active metal sites, which is aggravated by their adjustable acidity and thermal stability, defines their necessity in the approaches for effective and sustainable processes [18,19]. Selected examples are presented further to highlight this key aspect of structured zeolites in CO_2 conversion.

2.1. Interplay of Composition, and Preparation

Popova et. al. [20] uniquely synthesized a 10Ni5Ru-ZSM-5 catalyst, which presented high activity and selectivity towards methane. The process ultimately produced unique metal oxides with defined dispersion on a zeolite support. This type of catalyst is then very fitting for use in methane production directly from CO_2. Similarly, the formation of hollow Cu@ZrO_2 catalysts stemmed from Zr-MOF by Han et. al. [21] also stood out due to the existence of highly distributed Cu nanoparticles and the balanced presence of Cu^0/Cu^+ sites, establishing the great potential of such zeolites to carry out a selective and efficient CO_2 conversion to methanol. Matveyeva et. al. [22] concentrated on the production of $CeFeO_3$ and its subsequent utilization in CO_2 hydrogenation. They discovered that at lower temperatures (300-400°C), the inclusion of NH_4NO_3 resulted in a 7-12 wt% increase in the quantity of $CeFeO_3$, resulting in greater CO_2 conversion rates when compared to $LaFeO_3$ at a temperature of 600°C. This work demonstrated the capacity of utilizing rare-earth orthoferrites in combination with such zeolites devised via solution combustion synthesis (SCS) to augment the efficiency of CO_2 hydrogenation. In addition, Koh et. al. [23] examined the efficacy of mesoporous CZM/KIT-6 catalyst for the production of methanol. It was noted that the conversion of CO_2 dropped as the weight-hourly space velocity (WHSV) rose but improved with higher operating conditions, and the methanol output was 24.4% during a stability experiment lasting 120 hours. Paviotti and colleagues [24] fabricated Ni-based catalysts via wet impregnation supported on silica originated from rice husk for CO_2 methanation. The incorporation of Ru into these catalysts revealed improved reducibility of NiO and particle size reduction. Evaluated at 250 to 400 °C, Ni5Ru demonstrated to be

a well-selective catalyst, yielding the highest methane production rate with the least amount of active metal loading. The study highlights the possibility of converting agricultural by-products into catalyst supports, leading to the sustainable strategy of the circular economy.

2.2. Bimodal Mesoporous Structure and Surface Oxygen Vacancies

The combination of bimodal mesoporous structures and surface oxygen vacancies in structured zeolites is an important frontier of research. These attributes, mostly with the presence of active metal particles, are the main factors behind the improved catalytic activity. Zhou et. al. [25] synthesized surface-active sites on the mesoporous $Co/CeO_{2-\delta}$ catalysts, and these active sites included Co atoms, surface oxygen vacancies, and interfacial structures of Co^0-$CeO_{2-\delta}$. They were controlled by a dosage of Co species, which made CO_2 hydrogenation better. The catalyst with 12% Co loading ($Co/CeO_{2-\delta}$) at 1 atm and 400°C shows a CO_2 conversion of 59.7% and a CH_4 selectivity of 95.7% while being very stable after 9 cycles. At 1 atm and 400°C, the CO_2 conversion and CH_4 selectivity on a $Co/CeO_{2-\delta}$ catalyst with 12% Co loading achieved 59.7% and 95.7% respectively with great stability after 9 cycles. Liu et. al. [26] manufactured ordered-mesoporous 10N3COMA composite, loaded with 10 wt% and 3 wt% for NiO and Co_3O_4 accordingly, as a CO_2 methanation catalyst at 400°C. Further elevating the temperature to 500°C, such a catalyst displayed the best sintering resistance due to the confinement effect of its fine-ordered mesostructured properties. Zhou et. al. [27] reported about the synthesis of Co/SiO_2 mesoporous catalysts via grind-impregnation pathway. After loading it with 10% Co by weight, they discovered that the particle porosity, active sites, and crystallized Co^0 particles progressed when the crystallization temperature of the SiO_2 support was increased. Their best catalyst, CK100, showcased the following catalytic properties; CO_2 conversion of 44.3% at a rate of 3.29×10^{-5} mol/g_{cat}/s, CH_4 selectivity of 86.5%, and CO selectivity of 13.5%. Wang et al. [28] emphasized the significance of optimizing the characteristics of oxygen vacancies and acid sites in multifunctional catalysts through synergistic tailoring. They showed that by raising the number of oxygen vacancies in Cr_2O_3 and coupling it with the acidic zeolite H-ZSM-5, they obtained a 25.4% and 80.1% for CO_2 conversion and aromatics selectivity respectively, at 350°C. Their research highlighted the crucial significance of the acid site characteristics in zeolites, namely the aluminum species found at the junction of straight and sinusoidal channels, in improving the selectivity of aromatic compounds.

2.3. Si/Al Ratio

A higher Si/Al ratio favors the catalytic performance of structured zeolites in CO_2 hydrogenation. This ratio influences the zeolites' acidity/basicity, metal-support interactions, and pore structure; all of which play significant roles in the efficiency and selectivity of the hydrogenation reactions. A study carried out by Kosinov and colleagues [29] on the SSZ-13 (CHA) zeolite membranes exemplified the key role played by the Si/Al ratio. They found out that silica membranes with a below-average Si/Al ratio were effective in the pervaporation dehydration of ethanol/water mixtures. In contrast, membranes with a higher silica content, such as high-silica membranes with a relatively high Si/Al ratio, are better performed for separating gas mixtures of CO_2/CH_4. Their research delivers a clear message on how the Si/Al ratio in zeolite membranes affects the separation performance; therefore, this approach may be used for the enhancement of CO_2 hydrogenation processes. Bacariza and coworkers [30] looked into the influence of Ni loading and Si/Al ratio on the behavior of framework zeolites during the dry reforming of methane (DRM). It was revealed that the ratio of Si/Al influenced tremendously the catalytic activity, which showed outstanding results of low alkalinity and higher reducibility at lower temperatures. Besides, the catalyst composed of 15 wt.% Ni and a USY zeolite, characterized by robust metal-support interactions due to nickel nanoparticles situated in mesoporous cavities, demonstrated superior conversions and sustained stability over time at high temperatures. This research indicates the importance of the Si/Al ratio, a vital factor in structured zeolite modification, in dictating the performance of zeolites. Moreover, the study by Borgschulte et. al. [31] demonstrated that the nanostructure of the catalyst-sorbent system plays a pivotal role in shaping the kinetics of the Sabatier reaction when using sorption catalysts. They found that the zeolite support with pores size larger than 5Å enhanced the selectivity of the

methane, while sub-nano-sized pores reduced the overall conversion efficiency and selectivity. The result implies that the nanostructure, which bears the influence of the Si/Al ratio, might be a decisive factor in the efficiency of CO_2 hydrogenation reactions.

2.4. Porosity, Thermal Stability, and Structural Integrity

Zeng et. al. [32] proposed a hydrous zirconia porous structure prepared from a zirconium-based MOF UiO-66 with the help of strong bases. The porous nature of the material had a certain part of the micro-porosity of the original MOF. The absorption of Ni^{II} onto the OH-rich hydrous zirconia prompted the conversion to Ni^0 and subsequently demonstrated remarkable activity in CO_2 hydrogenation to CH_4. After being assessed for 100h on a continuous stream, the turnover frequency of the catalyst increased to 345 h^{-1} with the CH_4 selectivity exceeding 99%. This study points out the potential of MOFs in use as precursors for porous support materials leading to increased solid-gas phase catalysis. For the first time, Xiang et. al. [33] prepared an AFX-type SAPO-56 zeolite impregnated with copper nanoparticles, constructing a bifunctional catalyst for CO_2 transformation to methanol. A CO_2 conversion rate of 16.4% and an 80.9% selectivity for methanol were observed, and the authors emphasized the role of specific Lewis acid sites and the dispersion of copper nanoparticles in the SAPO-56 zeolite. The hierarchical structure had a significant effect on the improvement of methanol productivity, which represents a huge potential for further research and subsequent industrial applications of CO_2 hydrogenation. Lin et. al. [34] investigated the effect of the thermal stability of structured zeolites on different polymorphs of titanium dioxide (TiO_2) on the dispersion of Ru nanoparticles. They discovered that rutile-type TiO_2-supported zeolites were more thermally stable than anatase-type and therefore the selection of support material for CO_2 hydrogenation can play a significant role in the thermal stability of structured zeolites. Cui and coworkers [35] focused on improving the conversion of CO_2 to methanol by utilizing a zeolite-encapsulated catalyst, Cu/ZnOx@Na-ZSM-5, specifically engineered to combat the sintering of copper and enhance stability. The catalyst was created using bimetallic CuZn-HKUST-1 nanoparticles by hydrothermal techniques, leading to a core-shell design that enhances methanol production. This catalyst surpassed conventional Cu/ZnOx and Cu/ZnO/Al_2O_3 catalysts due to the synergistic effect and close interaction of the zeolite framework, which also guarantees sustained long-term efficiency.

2.5. Electrical and Plasma Interactions

Feliz et. al. [36] observed, among other things, that zeolite structures affect the ionic conductivity and dielectric constant of the catalyst in plasma-assisted reactions. Lower ionic conductivity facilitates a better CO_2 conversion (34%) because of decreased plasma density and CO_2 dissociation at ambient pressure and temperatures under 100 °C. Expanding their results, which focused on the critical role of ionic conductivity in CO_2 hydrogenation under dielectric barrier discharge (DBD) plasma, subsequent studies have gone even deeper into this topic. Henckel et. al. [37] utilized Electrochemical Impedance Spectroscopy (EIS) for investigating the interplay between the catalyst and ionomer, as well as the resistance to the transport of hydroxide ions at the cathode, in the process of converting CO to ethylene electrochemically. Their work showed that the selection of the optimal synthesis conditions and factors such as the ionic conductivity brought improved ethylene Faradaic efficiency and cell voltage. This implies that tuning the ionic behavior of zeolites can critically impact the performance of the CO_2 hydrogenation processes. Furthermore, Ashford et. al. [38] reported the use of various alumina-supported metal catalysts in a DBD reactor for plasma-catalytic CO_2 hydrogenation to ethane. The outcome of the investigation revealed that the Ru catalyst achieved the highest selectivity of ethane, which was almost 40%, and this was attained with an improved energy efficiency. Men et. al. fabricated Pt/film/In_2O_3 catalyst and they accomplished a CO_2 conversion of 37.0% and a methanol selectivity of 62.6% in CO_2 hydrogenation under atmospheric pressure. This research experiment shows that the DBD plasma can predominantly prepare the high-energy electrons with the help of the nanoparticles containing the highly-dispersed metal as well as the best

properties of the film, again underlining the imperative role of the electrical and dielectric properties in the design of catalyst.

3. Synthesis Methods

Structured zeolites can be synthesized in many ways, by utilizing precursors in soluble form and reducing them, or by using existing solid compounds and modifying their structures. Overall, these methods can be broadly grouped into two categories; bottom-up and top-down approaches as depicted in Figure 3a.
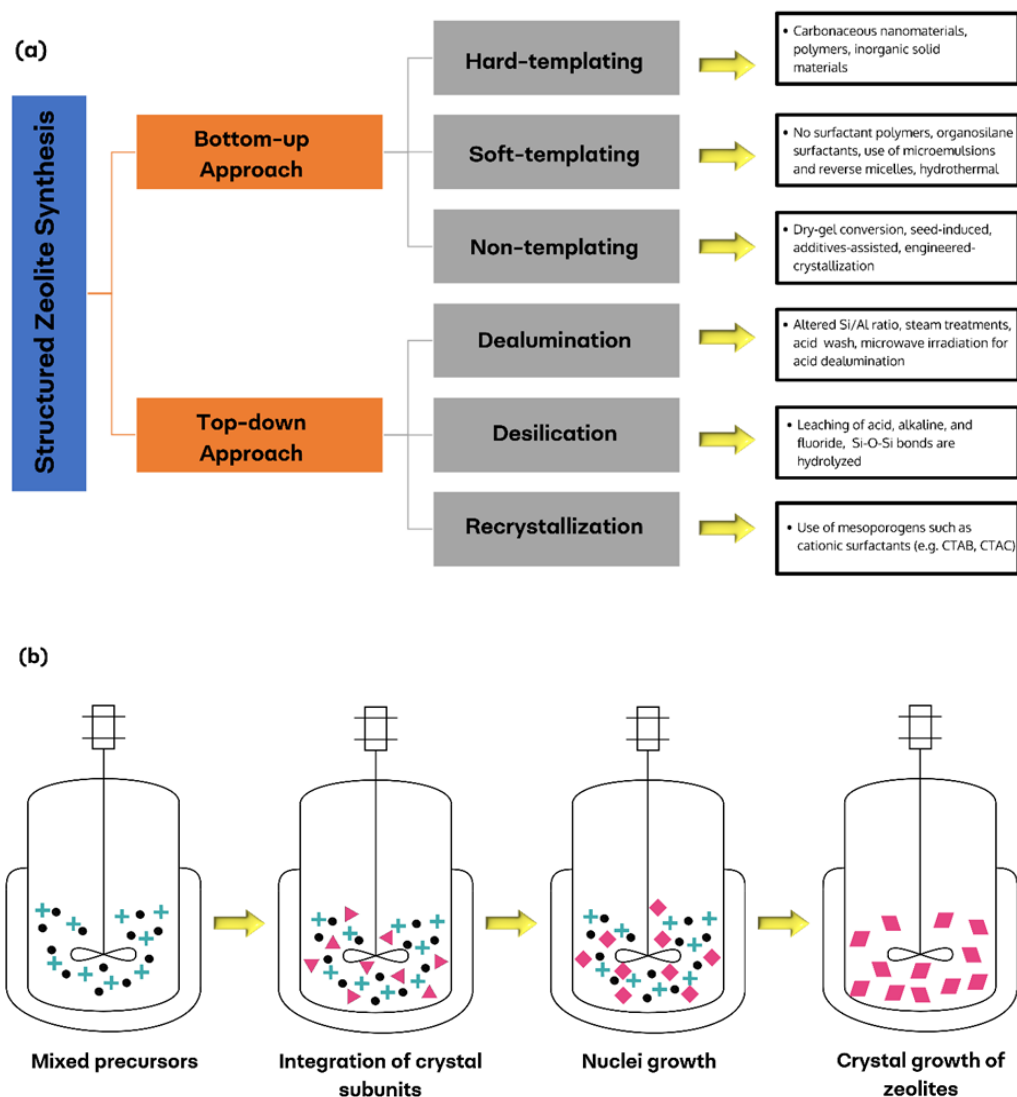

Figure 3. Pathways for Zeolite Synthesis. (a) Novel routes and their preparation principles. (b) Schematic formation of new crystalline phases via Hydrothermal Synthesis in Bottom-Up Approach.

3.1. Bottom-Up Approach

In the bottom-up approach, the syntheses commence with the fundamental constituents, which congregate to construct the ultimate configuration. This methodology is categorized into templating-based methods, where a template is employed to direct the development of the zeolite structure such as the hydrothermal technique presented in Figure 3b. Zhang et. al. [39] performed a study on hierarchical beta zeolites using an organosilane-templated bottom-up synthesis. This method involved the use of organosilanes as soft templates in conjunction with hydrothermal treatments. The study revealed that the soft template route yielded a balance between microporosity and

mesoporosity. The synthesized zeolites had similar Si/Al ratios and were tested for their catalytic performance in the cracking of cumene and 1,3,5-triisopropylbenzene [39]. However, the hydrothermal synthesis route is recognized for its excessive production of wastes and impurities such as CO_2 and N_2-based effluent gases [40]. Hence, alternative 'green' synthesis routes have been sustainably employed to overcome such concerns. Chang and co-workers [41] presented an organic synthesis procedure without fluoride, and a seed-crystal-assisted gel conversion method to synthesize Sn-BEA catalyst. This technique excluded the use of highly poisonous chemicals such as hydrofluoric acid. The study found that seeding zeolite BEA crystals enhanced the crystal growth and led to the BEA topology with the framework Sn. The fabricated Sn-BEA catalyst exhibited impressive performance in particular catalytic processes. Moreover, Pan et. al. [40] suggested the direct employment of inorganic oxides such as calcium carbonate ($CaCO_3$), calcium oxide (CaO), and silica as hard templates, which are often considered eco-friendly options. Wang et. al. [42] concentrated on the one-pot green synthesis of Fe-ZSM-5 with $CaCO_3$ as a precursor via the dry gel conversion approach and their work indicated high propylene selectivity of the catalyst for cracking experiments. El Samrout et. al. [43] developed innovative ways to synthesize support nickel catalysts on mesoporous calcium oxide (Ni-CaO) for use in DRM. Employing silica SBA-15 to reproduce CaO, constituted a new approach in the literature for this oxide. The study showed that the hard-template-based synthesis route was successful in producing active, stable, and selective Ni–CaO catalysts for DRM. Such an approach led to the synthesis of materials with superior porous properties to avoid catalyst deactivation. Other notable green methods include but are not limited to compressed CO_2 accelerated synthesis, nano-crystalline solid acid process, ionothermal synthesis, microwave-assisted synthesis, biomimetic synthesis, sol-gel process using water or bio-based solvents, alkali-activated coal fly ash, and ultrasonic synthesis [44–48].

The bottom-up approach to structured zeolite synthesis is not without difficulties. A principal issue is the intrinsic fragility of hierarchical zeolite structures that could result in loose intermolecular interactions, thereby affecting mechanical stability and charge transport [49]. This can be an especially serious issue when zeolites are used under the high-temperature and high-pressure conditions characteristic of CO_2 hydrogenation processes. One possible approach suggested by Gourdon [49] is to optimize the strength and performance of the materials by linking the molecules through strong covalent bonding that involves the reaction directly on the surfaces. The poor mechanical strength of self-supported zeolite membranes is also pointed out by Wenten et al. [50] as an essential disadvantage. They proposed that the production of zeolite membranes on inorganic supports may improve the mechanical stability, and by modifying the synthesis techniques, it is possible to obtain thin, defect-free, and of higher perm selectivity LTA zeolite membranes with repeated reproducibility. Furthermore, the bottom-up approach sometimes struggles with the controlled physical and chemical transformations within liquid droplets, a process that is integral to the synthesis of zeolites [50,51]. An alternative method is set forth to be "aerosol-assisted sol-gel" because this one allows one to implement the process of nanomaterial synthesis with more focus on the physical and chemical properties of the resultant zeolites [51]. These changes may produce zeolites with improved structural properties, but the relative enhancement in hydrogenation efficiencies of CO_2 ion carriers has still to be demonstrated. Another limitation is the intercrystalline diffusion challenges that occur as zeolites contain only micropores [52]. The restricted pore size limits the diffusion of the reactant and product molecules, and consequently, catalytic activity is severely suppressed. Pérez–Ramírez et. al. [53] proposed the synthesis of lubricants with larger pores and short diffusion paths, which will make active sites more accessible and hence improve the catalyst performance. Besides that, synthesis pathways have also been studied to prepare a tri-level hierarchical SAPO-34 zeolite, having micro-meso-macro porosity, in the intercrystalline space which overcomes the diffusion limitations and performs well in particular applications such as methanol-mediated to olefin processes [54]. Yang et. al. [55] and Oliveira et. al. [56] recommended the formation of secondary porosity using post-synthetic techniques such as dealumination and desilication which are both now under the umbrella of the top-down approach. This results in a porous hierarchical

pore system, which facilitates the diffusion of large molecules and enables more complex catalytic reactions.

3.2. Top-Down Approach

The top-down approach, which has come up as a vital strategy, designs structured zeolite structures and modifies them for better performance by altering pre-existing zeolites to attain the desired characteristics and frameworks. Recent studies have shed light on this approach in the synthesis of structured zeolites with enhanced properties for CO_2 hydrogenation. The one-pot top-down method to grow mesoporous zeolite for CO_2 adsorption reported by Tran et. al. [57] was essential to biogas refinement. The synthesis results were successful and the formation of mesopores was confirmed by the XRD and pore size distribution analysis which in turn enhanced the CO_2 adsorption capacity, a critical factor in biogas refinement. The top-down hydrothermal reaction, which involved a 3M NaOH solution at 96°C, was employed by Hong and Um [58] to convert natural zeolite into Na-zeolite P (NaP zeolite). The specific surface area of NaP zeolite happened to be significantly higher than that of the natural one (95.95 m²/g against 31.35 m²/g). In this case, the cation exchange capacity (CEC) of NaP zeolite was also significantly increased (310.89 cmol/kg) compared to that of natural zeolite (119.19 cmol/kg). This indicated that NaP zeolite has a higher capacity for removing Cs, Sr, and Ni from the water. Konnov et. al. [59] proposed a new top-down synthesis strategy, which allowed the preparation of single-site Mo-containing ZSM-5 zeolite nanocrystals. The synthesized zeolite was able to retain its structural integrity and atomically dispersed Mo even in extreme conditions, demonstrating its potential in catalytic conversions. Additionally, Kuznetsov et. al. [60] described the production of highly active nano zeolites via mechanical milling, recrystallization, and dealumination methods. The studied catalysts after post-treatment display significantly higher activity than the original ones due to the enormous amount of acid sites and high specific surface. The discovered transformation of the zeolite pore structure in the course of post-treatment also promotes the catalyst resistance to deactivation. This phenomenon is demonstrated in the rapidly proceeding reactions such as the cracking of hydrocarbons.

The top-down methodology for synthesizing zeolites for CO_2 hydrogenation also encapsulates a set of distinctive challenges that command innovative solutions to enhance their catalytic performance. Firstly, inadequate characterization methods used for zeolites synthesized by the top-down approach prove to be one of the serious limitations. This hampers the accurate localization of the active sites led to their synthesis, which is extremely important for the perception and optimization of the catalytic properties [61]. Dapsens et al. [62] stated that new analytical and modeling instruments (e.g., DNP MAS NMR) can offer an insight into the site location and stability that is critical for future catalyst design. Desilication with different bases and dry milling for incorporating metal nanoparticles inside zeolite also play a crucial role in investigating the active sites [63]. Such a technique ensures the correct incorporation of single atoms within the frameworks, as shown in Ni-Nx and Fe-Nx catalysts for electrochemical CO_2 to syngas conversion [64]. Another challenge, secondly, is morphological constraints and size-confinement effects that can limit the catalytic performance. The work of Kosari et. al. [65] identified the morphological architecture of supports as a direct tactic to address these challenges. Reengineering multi-void mesoporous silica sphere (MVmSiO₂) spheres using a top-down approach and with a core-shell porosity design to build a maze-like nanoreactor, gave them the ability to demonstrate increased catalytic performance in CO_2 hydrogenation to methanol. This method will explain how the optimal shape and pore size of zeolite has a positive effect on the diffusion of reactants and products to decrease the reaction rate and increase conversion so the catalytic reaction is accelerated. Apart from morphological optimization, experimental characterizations with the help of density functional theory (DFT) calculations are also used to elucidate the size changes of the confined small nanoparticles in catalytic reactions [66–69]. Lastly, the top-down approach often leads to the generation of a high number of oxygen functionalities on carbon surfaces, which negatively affect CO_2 hydrogenation over structured zeolites due to the formation of oxy-carbides [70]. Tuncer and Kizilkaya [71] revealed that the top-down method of Fe doping on Co(111) surfaces suppresses oxygen eviction from cobalt surfaces,

forming oxide phases on bimetallic FeCo catalysts, hence, potentially restricting hydrogenation reactions. Heo and Park [72] presented that the thermal reduction process is capable of removing oxygen functionalities, thus increasing CO_2 affinity and uptake on the carbon surfaces.

4. Characterization Techniques

Catalyst characterization techniques have now become essential instruments in acquiring a high level of understanding regarding the catalytic mechanism, performance, and the complex behavior of catalysts in operation. The methods illustrated in Table 1 have been used to identify the structural and electronic properties of catalysts, the nature of active sites, and the interaction of CO_2 and other reaction species on the surface of the catalyst, and understand the adsorption and redox properties of the catalytic system. These techniques have enabled researchers to observe real-time changes in catalyst composition and structure during the hydrogenation process, providing valuable information that guides the design of more efficient and selective catalysts.

Table 1. Different Characterization Techniques for Structured Zeolites for Catalytic Reactions such as CO_2 Hydrogenation.

Definition	Method	Application
Molecular and Chemical Structure Analysis [73–75]	Fourier-transform infrared (FTIR) spectroscopy	Quantify absorption spectra in chemical bonds and functional groups in molecules
	Raman spectroscopy	Postulate information about molecular vibrations, crystal structures, and phase transitions
	Nuclear Magnetic Resonance (NMR) spectroscopy	Detect magnetic properties (physical/chemical) of atoms
	Small-angle X-ray Scattering (SAXS)	Examine nanomaterial structures
Crystallographic and Phase Analysis [20,76]	X-ray diffraction (XRD)	Assess crystalline structures, crystal phases, and crystal defects
	Powder X-ray Diffraction (PXRD)	Analyze powdered crystalline materials for crystal structure identification
	Selected Area Electron Diffraction (SAED)	Obtain crystallographic information from a sample area
Surface and Elemental Analysis [73,74,77]	X-ray photoelectron spectroscopy (XPS)	Examine the chemistry of the surface, including aspects such as elemental composition, chemical and empirical states, and the electronic state of elements
	X-ray Absorption Spectroscopy (XAS)	Determine local geometric/electronic structural order
	Auger Electron Spectroscopy (AES)	Detect emitted energy of electrons from the catalyst surface
Microscopy and Imaging [74]	Scanning Electron Microscopy (SEM)	Generate high-resolution images of the surface,
	Transmission Electron Microscopy (TEM)	internal structure, morphology, and crystallography of nanomaterials
Thermal Analysis [78–81]	Temperature-Programmed Reduction-Thermogravimetric Analysis (TPR-TGA)	TPR: Measure the change in chemical state upon heating
		TGA: Measure changes in physical and chemical states upon heating
	Temperature-Programmed Desorption (TPD)	Investigate adsorption and desorption behaviors on surface interactions and binding energies
	Temperature-Programmed Oxidation (TPO)	Evaluate oxidation behaviors, particularly in carbonaceous materials, catalyst deactivation investigations
	Temperature-Programmed Reaction (TPRe)	Study reaction kinetics, and catalytic stability under different thermal environments

Temperature-Programmed Surface Reaction (TPSR)	Focus on surface reactions; mechanisms of surface-mediated reactions
Temperature-Programmed Reduction/Oxidation (TPR-O)	Explore redox properties for redox reactions
Temperature-Programmed Ammonia Desorption (TPAD)	Observe ammonia-desorption for acid catalysis

Building upon the fundamental knowledge acquired from spectroscopic techniques, recent studies have achieved significant progress in the process of converting CO_2 into high-value-added products using structured zeolites. Song and co-workers [81] designed zeolites with nanocrystals of 60-150 nm via the soft-template approach. Analyzed using advanced techniques like XRD and FTIR in Figure 4a,b, the zeolites exhibit superior catalytic performance in various chemical reactions, including benzene alkylation and polymer cracking, due to their extensive surface area and acid sites. A study by Ticali et. al. [73] revealed the suitability of the combination coating of Zn-doped ZrO_2 with H-ZSM-5 and H-SAPO-34 zeolites to methanol-to-hydrocarbon reaction. The test results disclosed that the 30% ZnZrZnOX amended together with the zeolite ZSM-5 provides the perfect performance of the system, which allowed for the C_3 production to be 1.5 mol kg^{-1} h^{-1}. This study, presumably employed NMR spectroscopy in addition to FTIR spectroscopy, PXRD, and XAS (see Figure 4c,d) to conduct a thorough structural examination, serves as evidence for how Zn-doping can give the solution a boost in terms of the quality of the catalyst performed with no zinc leaching observed.
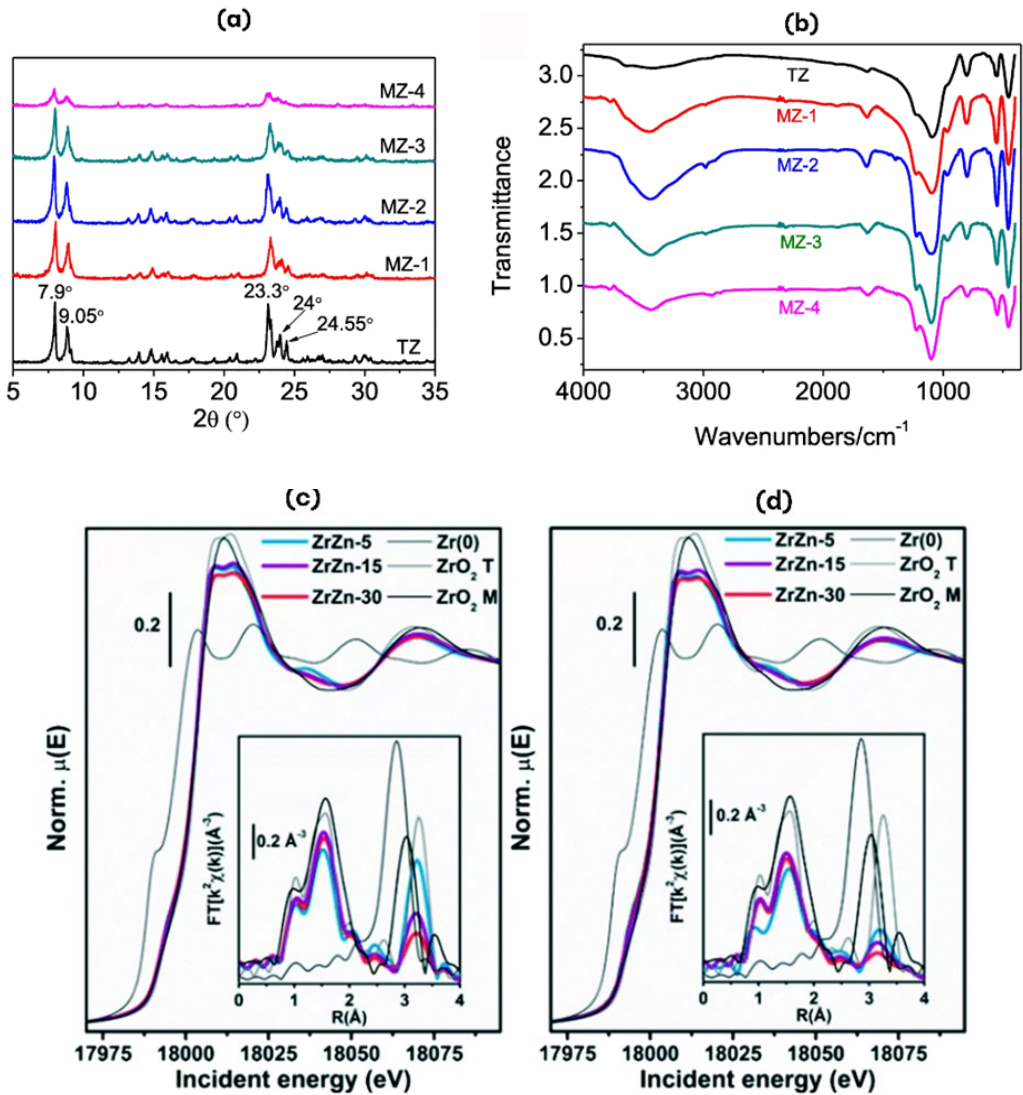
Figure 4. Various catalyst characterization techniques employed. (a) Crystallographic and Phase Analysis of MZ and TZ samples via XRD where they both showed similar diffraction peaks [81]. (b) Molecular and chemical structure analysis via FTR for MZ and TZ samples [81]. (c), (d) Surface and elemental analysis via XAS on the integrated ZrZn-X/ZSM-5 systems [73].

As Popova et. al. [20] analyzed in Figure 5, the effect of the reaction conditions on CO_2 hydrogenation was investigated using Ni- and Ru-based ZSM-5 modified catalysts. It appeared that 10Ni5Ru pure zeolite type ZSM-5 was among the most active and highly selective materials in the process of methane production and achieved equilibrium conversion, and 100% selectivity at an operating temperature of 400°C. Among other methods used were Raman spectroscopy, XRD, SAXS, and SAED. Xiang et. al. [74], while primarily using XRD, SEM, and XPS, also included NMR spectroscopy in its comprehensive analysis of creating a Ni-doped ETS-10 zeolite catalyst for CO_2 methanation with a CO_2 conversion rate of 39.7% and CH_4 selectivity at 280°C. The catalyst of the hierarchical structure and its CO_2 adsorption-activation capability was realized to be of great importance through the study and a new way for the fabrication of highly efficient catalysts. By utilizing FTIR spectroscopy, Azzolina-Jury and Thibault-Starzyk [82] presented a new catalyst where Ni-doped Zeolite H-USY was used for plasma-assisted CO_2 hydrogenation. Mainly, the study identified CO, which became the product, with methane and other linear hydrocarbons being the result of the hydrogenation of linear carbonyls on nickel surfaces. These findings therefore give us a novel insight into what role the plasma plays in CO_2 hydrogenation. García-Hurtado et. al. [83] addressed zeolite structure and crystal size impact via XRD and NMR spectroscopy on CO_2 hydrogenation with K-promoted iron oxide and zeolite-based bifunctional catalyst. The study established that the sample with K/Fe_3O_4-MFI gave the highest hydrocarbon yield while CHA and BEA favored the production of C_1-C_4 fractions with high olefin selectivity. The outcome of this research where zeolite structure affected product selectivity provides evidence for the crucial role in this process. Lin et al. [84] manufactured an advanced catalyst characterized by XRD and NMR spectroscopy, which contains Cr_2O_3 and twin-structured ZSM-5 zeolite that was used for the direct conversion of CO_2 and H_2 into valuable aromatics such as para-xylene.
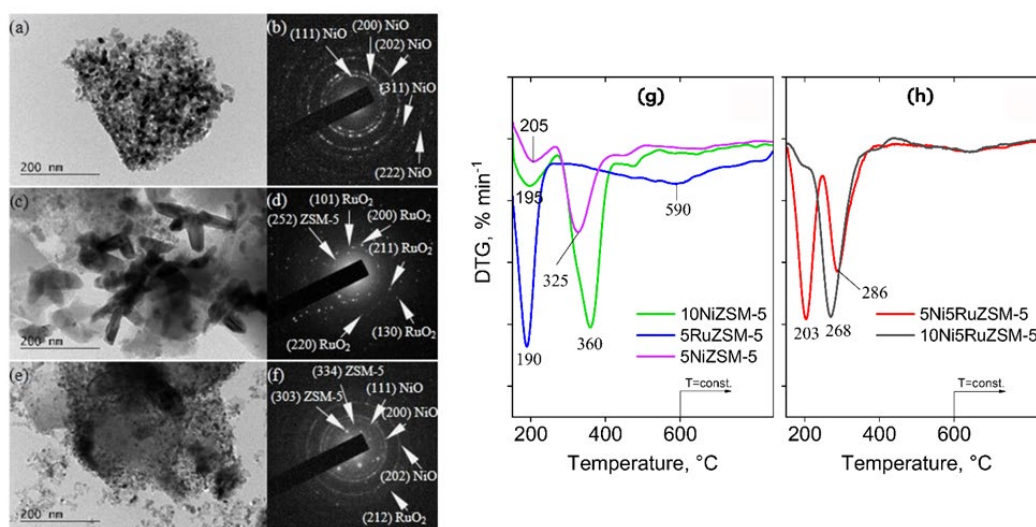

Figure 5. Microscopic Imaging and thermal analyses of Ni/Ru modified ZSM-5 Zeolites for CO_2 hydrogenation to methane by Popova et. al. [20]. (a), (c), (e) Morphological studies via TEM imaging of 10NiZSM-5, 5Ru10NiZSM-5, and 10NiZSM-5 respectively. (b), (d), (f) Electron diffraction patterns via TEM imaging of 10NiZSM-5, 5Ru10NiZSM-5, and 10NiZSM-5 respectively. (g), (h) Reduction temperature profiles via TPR-DTG analyses for monometallic and bimetallic Ni- and Ru-modified zeolites respectively.

Zhang et. al. [85] reported an in-situ spectroscopic study, utilizing Raman spectroscopy and XRD, on the chemical reaction structure of iron active phases regarding CO_2 hydrogenation. This

study provided a panoramic view of the transformation of iron oxides (α-Fe_2O_3 and γ-Fe_2O_3) to iron carbides, with χ-Fe_5C_2 showing higher selectivity to lower olefins. Wang and co-workers [28] accelerated methanol-mediated CO_2 hydrogenation into aromatics by increasing the oxygen vacancy density in chromium oxide (Cr_2O_3). The study proved that the combination of Cr_2O_3 with the acidic zeolite H-ZSM-5 yields high levels of CO_2 conversion as well as selectivity to aromatics. Therefore, this study presented a breakthrough method of combinatorial co-tuning of the catalyst parts for better performance as illustrated in Figure 6. Finally, the characterization of structured zeolites via temperature-programmed methods has provided substantial insights into their adsorptive and redox capabilities, alongside their catalytic efficiency. Cimino et. al. [86] have highlighted a paradigm on how temperature-programmed catalytic approaches can be employed in the pursuit of better catalytic performance. The study on Ru/Ce/Ni foams for CO_2 methane fixation highlighted that the porous CeO_2 construction and the dispersion of the Ru particles, in the Ni foam was the cause for much performance improvement, and showed the efficiency of this kind of optimization methodology.
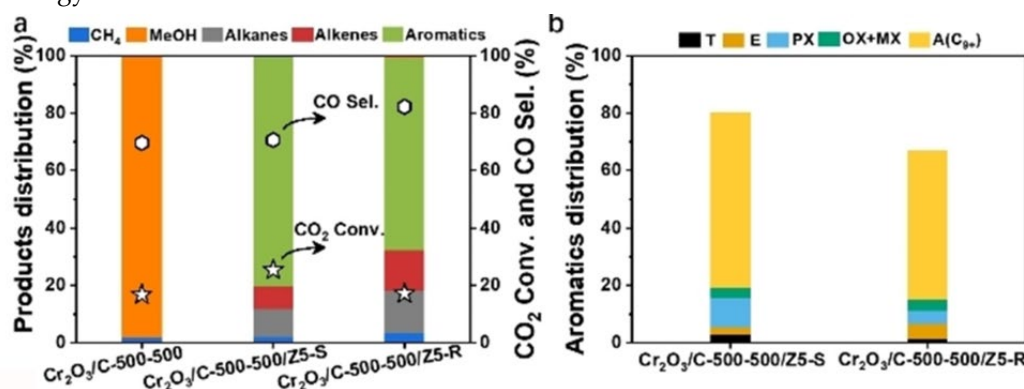

Figure 6. (a) (b) Catalytic performance of methanol synthesis over Cr_2O_3-based catalysts with 80.1% aromatics selectivity and CO_2 conversion of 25.4% at 350 °C, 3 MPa, H_2/CO_2=3 (Ar of 5 vol% as internal standard), 20 mL min−1, TOS=24 h [28].

The in-depth characterization of structured zeolites, leveraging advanced techniques such as spectroscopy, microscopy, and thermal analysis, has been instrumental in decoding their intricate structural and chemical nuances. Pioneering case studies have shown the extremely crucial role of metal-metal oxide interaction and transition metal doping in making the catalyst more stable and efficient [87,88]. These insights are highly important, as they make known the molecular behavior of zeolites and provide understanding for the development of catalysts of much higher activity and selectivity. On the performance aspect, the optimization knowledge of reaction parameters such as temperature, pressure, CO_2/H_2 feed ratio, etc., as well as the construction of modified kinetic models have provided a more detailed method for the optimizing production of desired hydrogenation products [83,89–91]. Overall, these techniques not only lead to a deeper understanding of catalytic materials and processes but also define the basis for the development of more productive and environmentally friendly ways to convert CO_2 to valuable substances.

5. Conclusion

This review has discussed the recent achievements of CO_2 hydrogenation performances of structured zeolites, emphasizing influencing properties, synthesis pathways, and characterization methodologies. The interaction between composition and preparation methods is a significant consideration in the activity of structured zeolites in CO_2 hydrogenation. The development of a bimodal mesoporous structure combined with the existence of surface oxygen vacancies results in a substantial improvement of the catalytic activity. Further, the Si/Al ratio, porosity, thermal stability, and structural integrity of zeolites are also crucial parameters, which determine performance and durability in catalysis. Moreover, electrical and plasma interactions add novel ways to enhance the reactivity, selectivity, and efficiency of these catalysts. In terms of catalyst syntheses for structured

zeolites, we have explored both bottom-up and top-down approaches. The bottom-up techniques like hard templating, soft templating and non-templating are crucial in dealing with the diffusion limitations that are commonly associated with the microporous zeolites. The formation of the hierarchical structures and mesopore integration technology are the prospective routes for improving catalytic activity. However, dealumination, desilication, and recrystallization, among other top-down approaches, though bound by thermodynamic constraints as well as morphological restrictions, represent opportunities to boost the catalytic performance of structured zeolites for CO_2 hydrogenation. The introduction of advanced characterization tools, morphological optimization, and modern thermal reduction technologies can overcome these shortcomings making the catalysts more efficient and commercially viable. The role of catalyst characterization using spectroscopic techniques allows continuous evaluation of the real-time features that the catalyst composition and structure possess, which is imperative in designing more selective and efficient catalysts.

Looking forward, the field of CO_2 hydrogenation over structured zeolites is poised for significant advancements. Further development of synthesis approaches, together with sophisticated characterization methods, is fundamental for realizing the whole potential of zeolite as an efficient catalyst. With the world moving towards greener and more sustainable options, structured zeolites play a more and more significant part in holistically converting CO_2 to high-value-added chemical products. Future investigations should be aimed at the elimination of the current drawbacks and the development of novel innovations for increasing the efficiency and selectivity of these catalysts, thus promoting the global strategy of carbon footprint reduction and climate change mitigation.

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

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