CATALYSIS RESEARCH

Review Article

Zeolites in CO_2 Activation and Conversion: Mechanistic Consensus, Controversies, and Catalyst Design Principles

Bashir Ahmad Dar[1]*, Naseem Fatima[2], Shamim Ahmad Dar[3]

[1]Department of Chemistry, Government Degree College, Uri, Baramulla, 193123, J&K, India

[2]Department of Physics, Government College Autonomous Kalaburagi, Gulbarga, 585105, Karnataka, India

[3]Department of Zoology, Government Degree College Sogam 192231, India

***Corresponding author:**

Dr. Bashir Ahmad Dar,

Department of Chemistry, Government Degree College, Uri, Baramulla, 193123, J&K, India,

Phone: +918491828956,

E-mail: bashir_15_dar@yahoo.com

Received: January 01, 2026

Published: April 27, 2026

ABSTRACT

Carbon dioxide cycling *via* catalytic conversion into fuels and value-added chemicals has drawn significant attention as a pathway to carbon circularity; however, the efficient activation of this thermodynamically stable molecule remains an overarching fundamental challenge. Zeolites have evolved from mere passive supports into programmable catalytic microenvironments in which framework composition, acid–base properties, pore topology and metal confinement all play roles to dictate CO_2 adsorption, intermediate stabilization and product selectivity. This review provides an assessment of the mechanistic roles presented by zeolite-based materials in important CO_2 conversion pathways, including hydrogenation to methanol and hydrocarbons, cycloaddition with epoxides, and coupling with amines. Specific attention is paid to differentiating between well-known mechanistic aspects and those whose existence is yet to be confirmed. Current evidence indicates that Lewis acidic cations, metal–oxide/zeolite interfaces, and confined metal species are the dominant motifs for primary CO_2 activation. In contrast, Brønsted acid sites more commonly stabilize oxygenated intermediates, mediate proton transfer, and influence downstream transformation chemistry rather than directly protonating CO_2. Across reaction classes, catalytic performance is governed recurrently by metal nuclearity and dispersion, acid–base balance, confinement, and hierarchical porosity. The review also highlights key limitations that have prevented progress towards the rational design of catalysts for translation purposes, including inconsistent benchmarking, operando studies of elementary processes, catalyst deactivation in real feedstocks, and the scalability of highly complex catalysts. The review concludes with a discussion of some exciting new areas such as single-atom catalysts, tandem catalysts, membrane reactors and data-driven design of catalysts.

Keywords: Zeolites, CO_2 Activation, Hydrogenation, Cyclic Carbonates, Heterogeneous Catalysis, Acid–Base Sites

Citation: Dar BA, Fatima N, Dar SA. (2026). Zeolites in CO_2 Activation and Conversion: Mechanistic Consensus, Controversies, and Catalyst Design Principles. Catalysis Research. 5(1):21.

DOI: https://doi.org/10.35702/catalres.10021

INTRODUCTION

The sharp rise in atmospheric carbon dioxide (CO_2) caused by industrial activities and extensive fossil fuel use is among the most urgent environmental issues of the 21st century. In 2024, CO_2 levels in the atmosphere exceeded 424 ppm, marking the highest level ever recorded in human history [1]. Such a significant increase largely drives global temperature changes, ocean acidification, and extreme weather events, highlighting the urgent need for measures to cut CO_2 emissions and reduce ecological impacts [2]. Besides emission reduction, converting carbon dioxide into valuable chemicals and fuels using green technologies is a promising option for carbon storage. This approach not only becomes a source of energy but also enables resource valorization. However, CO_2 is a very stable and essentially non-reactive compound, making it difficult to activate and convert under normal operating conditions. To effectively transform CO_2, molecules must be broken down by selective catalysts and reaction pathways controlled to produce desired products. Over the past decade, zeolites have shown the most promising active-site structures for this purpose, thanks to their unique and adjustable frameworks, acidity, and chemical properties. Their structure offers high surface area, shape- and size-selective cavities, and Brønsted and Lewis acidity—all factors that can limit zeolites' catalytic effectiveness. Adding metal ions or clusters can enhance their catalytic performance and mechanistic control by enabling the selective activation of CO_2, which is a very stable and small molecule [3,4].

From a mechanistic point of view, the polarisation of the C=O bonds in CO_2 is a prerequisite for the binding and the subsequent activation on catalytic surfaces, and this can be done by adsorption onto an electron-rich or electron-deficient site [5]. Zeolites have a vast number of such sites: Lewis acid sites and exchanged metal cations can coordinate and weaken C=O bonds, while Brønsted acid sites are more plausibly involved in hydrogen-bond-assisted adsorption, intermediate stabilization, and proton-transfer steps than in direct primary activation of CO_2 itself. The success of these processes depends to a great extent on the topology of the framework, the size of the pores, and their connectivity, which determine CO_2 diffusion, adsorption, and access to reaction sites [6]. Innovations in this area have revolved around the modification of zeolites with hierarchical pores, metal (Cu, Zn, Fe) impregnation, and post-synthetic functionalization with organic linkers to achieve controlled acidity, hydrophobicity, and CO_2 adsorption capacity [7]. These methods have allowed the production of methanol, formic acid and cyclic carbonates from CO_2, besides improving mass transport and lowering the diffusion resistances. On top of this, the problem of how to engineer zeolite-based catalysts that would exhibit these features and also be stable under real industrial conditions is still far from being solved. A deep insight into the relationships between the metal sites, the acidity of the framework, and the mechanisms of CO_2 activation will surely pave the way towards the design of new catalysts [8]. This article reviews the comprehensive experimental account of the latest advances and challenges of zeolites in the activation and conversion of CO_2, with the focus shifted to the interplay of structure-properties-reactivity. This comparative analysis also reveals the ways a zeolite catalyst functions, and it also serves as a tool for the design of novel zeolites with CO_2 utilization capability, an important step towards a circular carbon economy.

Although substantial progress has been made in developing zeolite-supported catalysts for CO_2 conversion, the field still lacks a unifying mechanistic framework that links zeolite composition, acid–base functionality, confinement, and interfacial architecture to catalytic performance across different reaction classes. Reported activities and selectivity are often difficult to compare directly because they are strongly influenced by catalyst topology, porosity, metal dispersion, acid-site distribution, and reaction conditions [3,4]. In addition, the relative roles of Lewis acidic centers, Brønsted acidity, metal–zeolite interactions, and confinement effects remain unevenly resolved across hydrogenation, cycloaddition, and tandem conversion pathways. Consequently, parts of the literature remain either mechanistically fragmented or prone to overly broad generalization [6]. This review, therefore, aims not merely to catalogue reported catalysts but to distinguish mechanistic consensus from ongoing debate, extract transferable structure–property–reactivity principles, and identify practical design rules for the next generation of zeolite-based CO_2 conversion catalysts.

REVIEW METHODOLOGY

This review was designed as a targeted, mechanistically oriented assessment of zeolite-based approaches to CO_2 activation and conversion. The references included in the study are predominantly based on papers published in peer-reviewed journals and databases, covering mostly the years between 2015 and 2025, while selecting several fundamental papers before that time if they provide valuable mechanistic insight.

The literature search was done using various keyword combinations such as "zeolite CO_2 activation," "CO_2 hydrogenation zeolite," "metal-exchanged zeolite CO_2," "cyclic carbonate zeolite," "CO_2 amine coupling zeolite," "hierarchical zeolite CO_2," "operando spectroscopy zeolite CO_2," and "single-atom zeolite CO_2 catalysis." Preference was given to original research articles describing catalyst preparation and characterization methods, experimental evidence related to mechanisms and catalytic performance, rather than review papers used only for contextual discussion. The literature was comparatively assessed according to the following criteria:

(i) type and localization of active centers (Brønsted, Lewis, metal, interfacial), (ii) topology and porosity of zeolite structures, (iii) direct experimental evidence about elementary stages and/or intermediates using techniques like operando/in situ spectroscopy, isotope labelling experiments, kinetic analysis, and density functional theory calculations, (iv) performance indicators like selectivity, space-time yield, turnover frequency, and stability, and (v) applicability, including catalyst longevity, regeneration, and scale-up.

STRUCTURAL AND CHEMICAL FEATURES OF ZEOLITES

Zeolites are a group of crystalline aluminosilicates with a three-dimensional network made up of connecting SiO_4 and AlO_4 tetrahedra. The replacement of Si^{4+} by Al^{3+} in the tetrahedral framework results in a negatively charged unit that is usually balanced by cations derived from outside the framework, e.g., H^+, Na^+, or transition metal ions [3]. This structural makeup is the source of their wide structural variety and also their chemical modifiability, which are indispensable properties for the activation of CO_2 catalytically.

Framework Composition

The Si/Al ratio in zeolites substantially influences their properties, like acidity, hydrophobicity, and thermal stability. In general, low-silica zeolites contain more Brønsted acid sites due to the larger number of AlO_4 units present, whereas high-silica zeolites are more hydrophobic and thermally stable [8]. The structural features of the framework, i.e., pore size, channel connectivity, and cage geometry, determine the molecular diffusion as well as access to the active sites. Hierarchical zeolites that combine micropores with meso- or macropores have been created to overcome the limitations of diffusion and improve mass transport, thus allowing higher catalytic efficiency in CO_2 conversion reactions [7].

Acid–Base Properties

The acid–base character of zeolites is key for their catalytic function; however, it should be properly interpreted within the scope of CO_2 activation mechanisms. Generally, zeolites possess Brønsted acidic sites, which are usually represented by bridged Si–OH–Al pairs, and Lewis acid sites as depicted in Figure 1, which typically include extra-framework cations, coordination-inactive metals, or defect areas. The roles played by the latter and former types of sites in the reaction cannot be considered similar [9]. In most cases, the activation of CO_2 in zeolite catalysts involves the involvement of Lewis acidic cations and metal centers, which can coordinate to the oxygen atoms of CO_2 molecules and distort their linear structure. In turn, the secondary processes that accompany this stage, such as the stabilization of oxygen-containing products, the transfer of protons, and further reactions, are often linked with Brønsted acidic sites. Thus, the presence of high acidity does not necessarily mean an effective activation of CO_2 [10].

The activity of zeolite-based catalysts, as well as the success of the CO_2 activation process, relies less on "high acidity" than on the rational distribution and location of metal and acid–base sites. High acidity may cause unwanted side reactions and result in coke formation; thus, it is better to achieve a balance between both types of acidity [11].

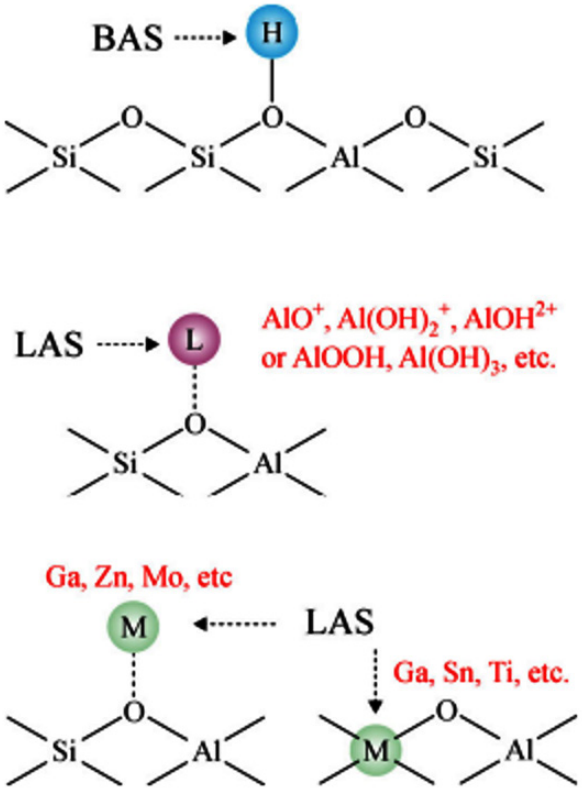

Figure 1: Depiction of acid sites in zeolites: Brønsted acid sites, Lewis acid sites, and metal addition-induced modified Lewis sites, all of them being different catalytic functionalities. Adopted from [11].

Metal Exchange

Metal-exchanged zeolites are the most effective materials to achieve CO_2 activation, as the metal cations provide a new dimension to the electronic properties of the material. The transition metal ions like Cu, Zn, Fe, or Ni would bind with CO_2, helping electron transfer and therefore lowering the activation energy of hydrogenation or cycloaddition reactions [4]. The development of single-atom metal sites in the zeolite framework is considered a breakthrough that leads to ultimate atom efficiency, homogenous active sites, and gives an opportunity for the exact control of the reaction pathways [12].

Hierarchical Structures

The concept of hierarchical zeolites is based on the natural microporosity of the material combined with secondary meso- or macropores, which significantly reduce diffusion limitations and increase the accessibility of the active sites. The methods of desilication, dealumination, and template-assisted synthesis enable the determination of pore size distribution, acidity, and surface properties with a high degree of precision. The application of these hierarchically structured materials is particularly effective for CO_2 conversion techniques where the reaction involves larger intermediates or more reactants; thus, the catalytic efficiency and product selectivity are improved [13]. Therefore, the catalytic performance of zeolites in CO_2 conversion is to a large extent determined by their structural and chemical characteristics. The compositional and acid-base features of the framework, metal exchange, and hierarchically porous architectures all contribute to CO_2 adsorption, activation, and diffusion and thus, catalytic activity and selectivity. An insight into these structure-property relations is indispensable for the design of zeolite catalysts that exhibit not only high efficiency and stability but also tunable selectivity that allows for sustainable CO_2 valorization.

MECHANISTIC INSIGHTS OF CO_2 ACTIVATION OVER ZEOLITES

CO_2 is a linear molecule that is thermodynamically stable; consequently, its activation in an effective manner necessitates sites that polarise the molecule (weaken C=O bonds) and/or provide electron/proton transfer pathways for the formation of reactive intermediates. Zeolites constitute highly tunable catalytic platforms for CO_2 activation due to the following reasons: (i) their acid–base properties (Brønsted and Lewis

sites) being tunable by changes in the framework composition and cation exchange, (ii) the ability to host dispersed metal species (including single-atom sites) that can be the source of redox/hydrogenation functionality, and (iii) their confined pore architectures that influence adsorption geometry, intermediate stabilization and residence time [14].

Adsorption and Activation of CO_2

CO_2 interacts with zeolite materials in various modes of the experiments observed. In high-silica zeolites, these gases are mainly physisorbed via dispersive interactions; adsorption capacity and isosteric heat correlate with the Si/Al ratio and pore topology [15]. The oxygen atom of CO_2 that binds to a Lewis acid site highly polarises the C–O bonds, leading to chemisorption of surface species such as carbonate- or bicarbonate-type arising under various experimental conditions [16,17]. The spectroscopic and DFT investigations demonstrated that the energies of the following reaction steps decrease upon such binding. Protonic (Si–OH–Al) sites take part in CO_2 capturing mostly through the formation of hydrogen-bonded bicarbonate/carbonate species rather than free "carbocations"; the direct protonation resulting in true carbocations is not confirmed by operando studies on typical zeolites. Brønsted sites, however, can stabilize oxygenated intermediates and help proton transfer steps during hydrogenation [14]. With transition metal (Cu, Zn, Fe, etc.) - either as a few dispersed clusters, an oxide particle, or a single atom - that creates a metal centre/redox centre which binds and activates CO_2 more strongly than pure zeolites. Single-atom catalysts (SACs) implanted into the framework of zeolite have been proven to provide a very clear coordination environment that facilitates CO_2 activation and decreases the activation barrier compared to bulk metal particles [10]. The combined results of operando IR (DRIFTS), XAS, and AP-XPS studies indicate that the interaction of CO_2 with metal-bearing zeolitic catalysts typically results in the formation of carbonate/bicarbonate and formate-type surface species, with the latter being predominantly observed under hydrogenation conditions [18].

Hydrogenation Pathways Over Metal–Zeolite Systems

Several techniques and theories, including operando spectroscopy, transient kinetics, and DFT, used in mechanistic and microkinetic work, have synergistically arrived at a consensus sequence for CO_2 → methanol on many metal–support or metal-in-zeolite systems:

1. CO_2 adsorption and activation at metal–support interfaces or at metal sites within the zeolite.
2. The hydrogenation of CO_2 to formate on the surface (HCOO*) — because many operando studies find HCOO* as an early, relatively stable intermediate [18,19]
3. Further hydrogenation via formyl (HCO*) / methoxy (CH_3O*) groups on the surface; most of the time, the methoxy groups are considered the penultimate intermediates before the release of methanol [14,20]. The direct detection of free formaldehyde as a stable intermediate is seldom; most of the evidence favours surface-bound oxygenates.
4. The product formation and desorption (CH_3OH) or additional conversion (in tandem systems, methanol can be converted over a zeolite to hydrocarbons *via* MTH chemistry [15].

The bifunctional catalyst idea, metal (for H_2 activation and C–O/C–H hydrogenation) + acid/oxide (for CO_2 adsorption, intermediate stabilization and downstream conversion), receives robust support from both model and applied studies. Research on Cu-based catalysts, for instance, reveals that formate intermediates are hosted by partially reduced Cu species (Cu^0/Cu^+), which are then hydrogenated at metal sites while the support/acid sites facilitate intermediate stability and selectivity [18,19]. In the same manner, tandem catalysts of Zn-doped ZrO_2 and zeolite demonstrate both experimentally and computationally that the sequence carbonate → formate → methoxy is the one that happens at the oxide sites before the zeolitic conversion [20]. The zeolite framework is not just a simple support structure:

Confinement effects change adsorption geometries and increase local concentrations of intermediates, which can stabilize polar oxygenates and direct C–C coupling pathways in tandem systems [15].

Acid–base cooperativity (controlled Brønsted/Lewis site distribution) essentially tunes the energy landscape of the hydrogenation *vs*. RWGS (reverse water-gas shift) pathways, thus affecting selectivity towards methanol or CO/hydrocarbons [14].

Designed hierarchical porosity works to remove mass-transport limitations and coke formation in the downstream methanol-to-hydrocarbon steps [20].

The mechanistic map of metal-in-zeolite and oxide-plus-zeolite tandem systems, in practical terms, is shown in Figure 2. Reaction pathways for CO_2 hydrogenation: CO_2 adsorption/activation (carbonate/bicarbonate/formate formation) → HCOO* (formate) → HCO*/CH_3O* (surface-bound oxygenates) → CH_3OH (desorption) / further conversion in zeolite (Figure 2).

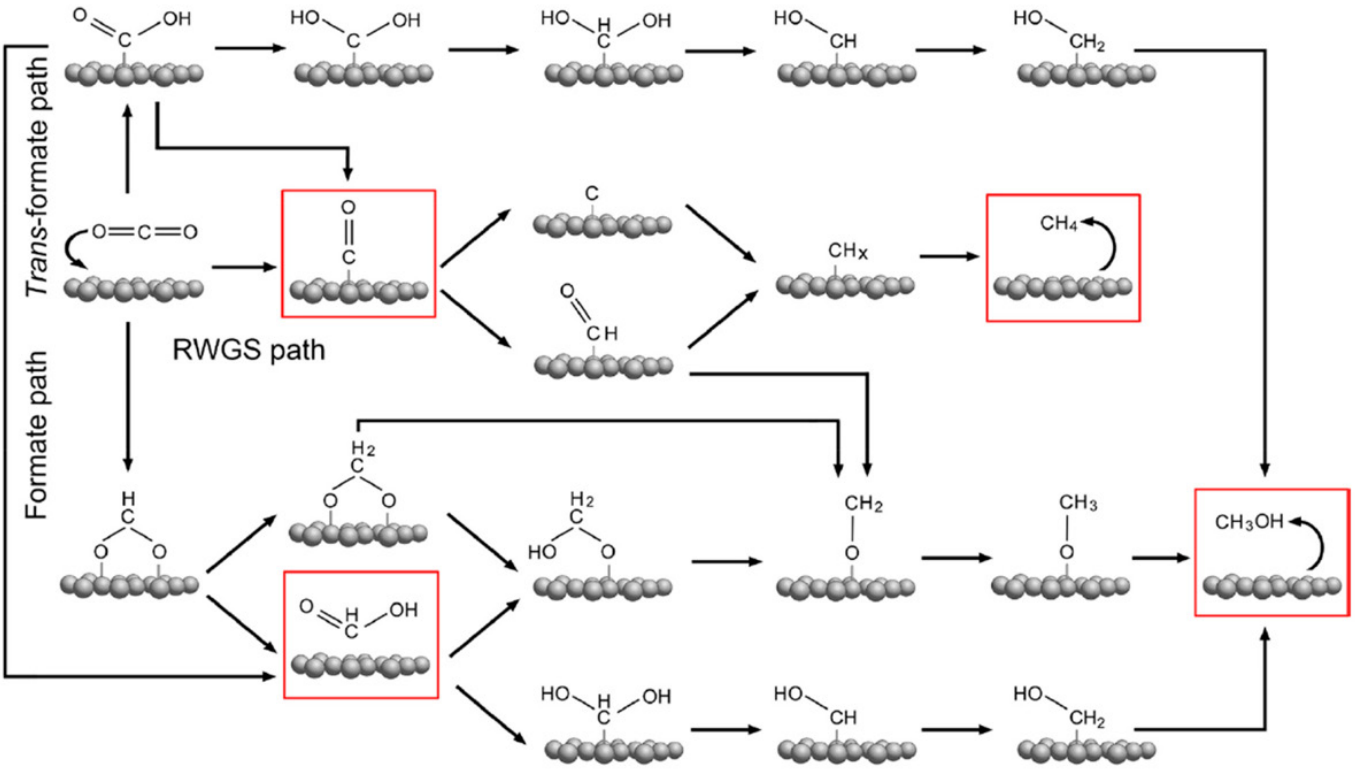

Figure 2: Reaction pathways for CO_2 hydrogenation to methanol over zeolite-supported metal catalysts, showing formate, RWGS, and transformate routes with key intermediates and catalyst surface interactions. Adopted From [21]

Cycloaddition of CO_2 with Epoxides to Form Cyclic Carbonates

The cycloaddition of carbon dioxide (CO_2) with epoxides to make cyclic carbonates is the most atom-efficient and one of the most industrially relevant ways of CO_2 utilization. The reaction is a clean one-step process into the products of high value under relatively mild conditions, avoiding the use of toxic reagents like phosgene. Zeolite-based catalysts have become potent heterogeneous systems for this purpose due to their adjustable acid-base properties, metal ion-exchange ability, and shape-selective microporous structures, which are not only favourable for reactants' confinement but also promote their cooperative activation [22].

Lewis acidic sites in zeolites, such as framework Al^{3+} centres or exchanged metal cations (e.g., Zn^{2+}, Co^{2+}, Fe^{3+}), coordinate with the oxygen atom of the epoxide, thus polarising the C–O bond and enhancing its electrophilicity. The step leads to ring opening with reduced steric hindrance and interaction energy. Metal halides such as $ZnBr_2$ or $CoBr_2$ impregnated Zeolite Y are a good example to demonstrate such synergistic activation [23]. By metal halide impregnation, a halide ion (mostly Br^- or I^-) is introduced to accomplish nucleophilic attack at the least sterically hindered side of the epoxide, where the halide thus performs the ring opening, obtaining the alkoxide intermediate. Multiple in situ spectroscopic techniques have been utilized in confirming this step for different halide-modified zeolites [16]. The surface alkoxide binds with the activated CO_2 that is either a basic oxygen site within the zeolite or a nearby metal centre polarised. The nucleophilic oxygen of the alkoxide attacks the electrophilic carbon of CO_2 to produce a carbonate intermediate. The reaction is driven by the release of epoxide ring strain and the high affinity of CO_2 for basic oxygen species [22]. The carbonate intermediate undergoes intramolecular nucleophilic attack to free the halide and produce the five-membered cyclic carbonate product, as shown in Figure 3. Zeolite frameworks support the transition state through spatial confinement and electrostatic interactions [23].

Zeolite-based catalysts are very selective in CO_2 cycloaddition reactions due to the well-defined pore structure that facilitates local reactant concentration and transition-state stabilisation. The steric hindrance of the narrow micropores, however, may prevent the conversion of bulky epoxides [22]. The best performance relies on a delicate equilibrium between Lewis acidity for epoxide activation, nucleophilicity for ring opening, and basicity for CO_2 insertion, as these synergistic functions jointly determine activity and selectivity. Compared to their homogeneous or MOF counterparts, zeolite catalysts are more stable and can be recycled further, although their long-term efficiency can be lessened by halide leaching and pore blockage [23]. Besides that, differences in the experimental conditions—substrate nature, CO_2 pressure, and catalyst preparation—make cross-study comparisons difficult, thereby pointing to the necessity of standardised benchmarking protocols.

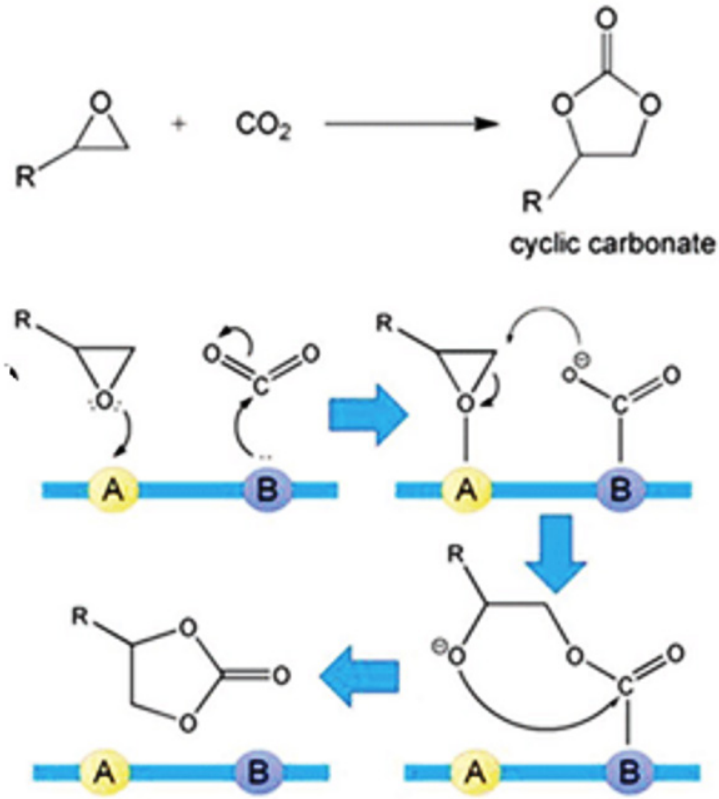

Figure 3: CO_2 cycloaddition catalysis with epoxides in bifunctional zeolite-based systems. Epoxide ring opening is facilitated by site A (a Lewis acid), while site B (a basic or metal site) activates CO_2. Ring closure and intermediate stabilization within the zeolite framework led to cooperative action that generated the cyclic carbonate product. Adopted from [24].

Coupling with Amines

In the coupling reactions of CO_2 with amines on zeolite-based catalysts, the synergy between metal cations and the acidity of the zeolite framework (Brønsted and/or Lewis sites) is most often considered the key factor. To metal centres relating to CO_2 are to enable its activation (e.g. by coordination, polarization, or charge transfer), while the Brønsted acid (or base) sites of the zeolite can help in proton transfer or in the stabilization of the charged/covalent intermediates. Thus, the cooperative procession makes it possible to convert CO_2 to carbamates, isocyanates, and, in the end, to products of a urea-type nature in the confined space of the zeolite matrix. The computational data reveal that the interaction with two sites stabilizes the transition states and hence allows for low activation barriers under mild reaction conditions [25]. Besides, the microporous cages as well as the acid–base character that can be tuned in zeolites are of great help in the concentration of CO_2 (mostly as surface carbonates or carbamate species) and amines, thus, resulting in the formation of the reactive micro-environment that is the main factor for the transformation steps to follow [26]. If only CO_2 is connected (usually through a primary or secondary amine and the product is a carbamate intermediate), the subsequent steps may be:

$$RNH_2 + CO_2 \rightarrow RNHCO_2^-/RNHCOO \text{ (carbamate)} \text{ [27].}$$

When exposed to heat or catalytic dehydration, carbamates may lose water to form isocyanates (RNCO) [28]. The isocyanate intermediate resulting from this then combines with a second amine molecule to yield a urea derivative ($RNHCO_2NR$) [29].

The zeolite framework is: (i) helping the adsorption and activation of CO_2 and amine (through cation-framework interactions), (ii) providing the spaces that are confined and thus intensify the collision frequencies between the reactants and at the same time eliminate unwanted reactions, and(iii) having acid/base pairs that, besides lowering the energetic barriers, stabilize the reactive intermediates [30]. What is more, despite numerous individual reports on carbamate formation, isocyanate generation, or urea synthesis under heterogeneous conditions, there is still no single well-characterised zeolite-only system that basically goes through a full CO_2 → carbamate → isocyanate → urea cascade in one pot under typical heterogeneous/solid-catalyst conditions [31].

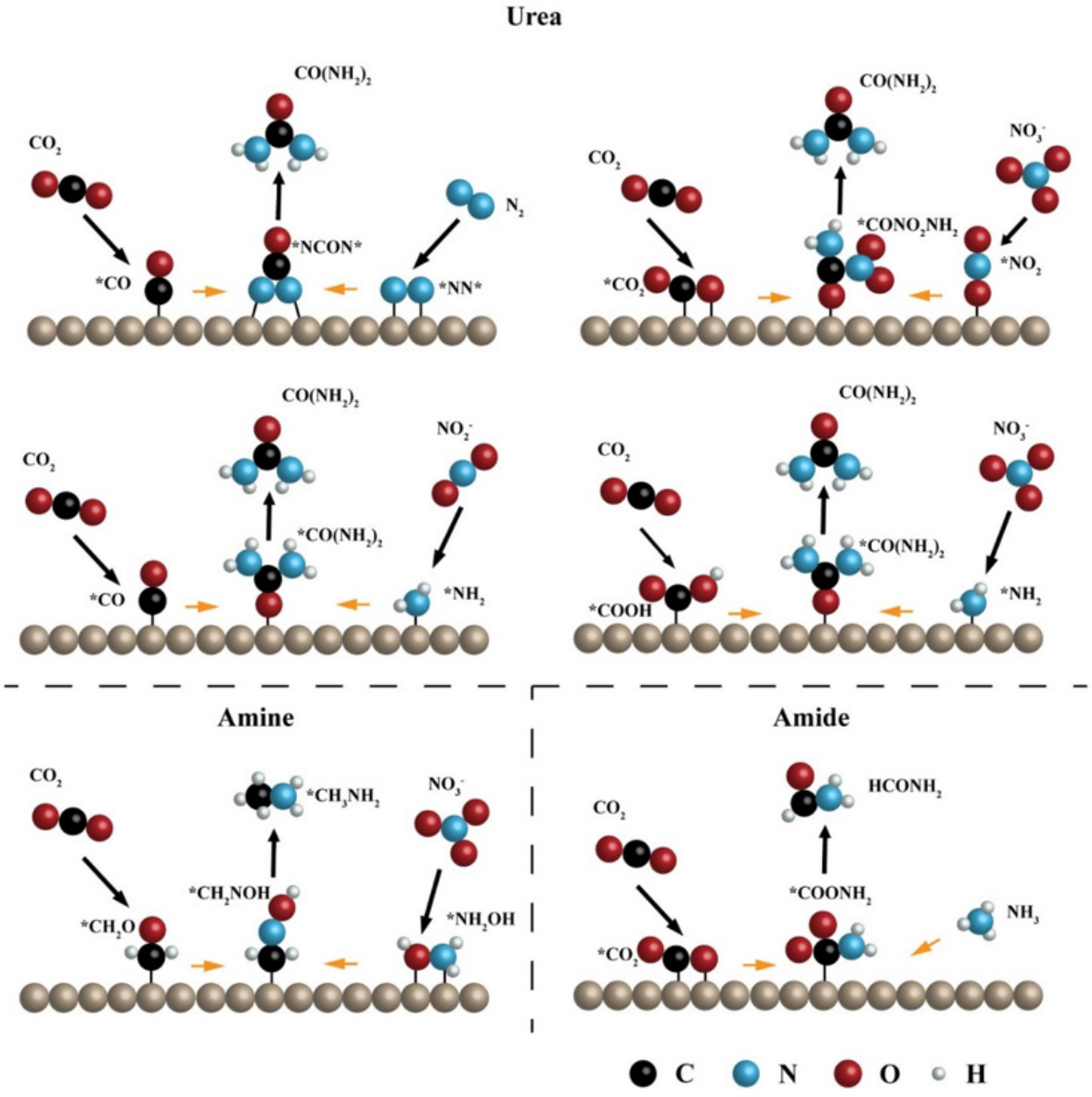

Figure 4: Reaction pathways of urea decomposition on amine- and amide-functionalized surfaces, highlighting key intermediates and product evolution under catalytic conditions. Adapted from [32,33].

All these mechanistic details emphasize the mutual support the metal sites, the acidic/basic framework sites and the pore confinement play to each other, which in turn regulate the activity, selectivity and efficiency of zeolite-mediated CO_2 conversion reactions [32].

Synergistic Effects of Framework Topology and Pore Architecture

Zeolite structures are essential in nature for CO2 conversion, as they not only change the confinement of CO2 molecules but also help to open new sites. This is well demonstrated by the hierarchical zeolites that have both micropores and mesopores, as they increase molecular diffusion, thus mass-transfer limitations drop and site blockage that is particularly severe in multi-step reactions such as CO_2 hydrogenation to methanol or hydrocarbons is eliminated [34]. On the other hand, microporous frameworks may strengthen CO_2 adsorption energies via van der Waals interactions, thus effectively concentrating the reactants near the active sites and facilitating the initial activation stage [30]. The combination of metal sites (such as Cu^{2+}, Fe^{3+}, Co^{2+}) and the acidic framework leads to the formation of the metal site, which activates CO_2 or H_2, while the acidic framework stabilizes reaction intermediates. The interactive operation thus enables the zeolite to perform efficiently the catalytic multi-step reactions, like CO_2 hydrogenation, cycloaddition with epoxides, and coupling with nucleophiles, under relatively mild conditions [35].

Mechanistic studies show the activation of carbon dioxide over zeolite is a very complicated process that involves the interaction between adsorption sites, metal centres, and the framework structure. This catalysis is very efficient when the polarisation of C=O bonds at Brønsted and Lewis acid sites takes place, the reaction intermediates are stabilized, and the mass transport is enhanced through the hierarchical pore systems. Understanding of these mechanisms offers the ground for the rational design of zeolite catalysts for selective and efficient CO_2 conversion into fuels and chemicals.

Mechanistic Consensus Versus Unresolved Questions

Many mechanistic features of zeolite-mediated CO_2 conversion can now be regarded as relatively well established. First, direct activation of CO_2 is more consistently associated with Lewis acidic cations, redox-active metal centers, framework defects, or metal–oxide/zeolite interfacial sites than with Brønsted acid sites alone. Second, under hydrogenation conditions, carbonate, bicarbonate, formate, and methoxy-type surface species are repeatedly observed, with formate frequently emerging as a kinetically relevant intermediate in methanol-directed pathways. Third, in epoxide cycloaddition reactions, cooperative bifunctionality, typically involving epoxide activation at a Lewis acidic site and nucleophilic ring opening, is one of the most consistently supported mechanistic features across catalyst classes [30,32].

However, several important questions remain unresolved. The identity of the kinetically dominant surface intermediate can vary with catalyst composition, pressure, co-fed water, and surface coverage, indicating that a single universal hydrogenation pathway should be treated cautiously. Similarly, it is still not fully resolved to what extent zeolite confinement alters intrinsic elementary-step energetics, rather than simply affecting local concentration and residence time. In tandem CO_2-to-hydrocarbon systems, another open question is whether zeolite topology primarily governs intermediate transport and secondary transformation chemistry or whether it also exerts a more direct influence on upstream oxygenate formation at the metal–zeolite interface. These uncertainties underscore the need for closer integration of operando spectroscopy, isotopic transient studies, kinetic analysis, and microkinetic modelling under realistic operating conditions.

Comparative Insights into Catalyst Performance

A critical comparison of zeolite based catalysts reveals that their performance advantages are not uniform but arise from distinct structural and mechanistic features. Systems such as Cu/Zn zeolites achieve high methanol selectivity because dispersed Cu species stabilize formate intermediates while Lewis acid sites polarize CO_2, creating a cooperative environment for hydrogenation. In contrast, halide modified zeolites excel in cycloaddition reactions, where Lewis acidic sites activate epoxides and halide ions facilitate ring opening, though these systems often suffer from halide leaching and pore blockage. Single atom Fe zeolites demonstrate strong CO_2 activation and atom efficiency due to their uniform coordination environment, but their long term stability under industrial conditions remains uncertain. Hierarchical zeolite frameworks consistently improve mass transport and reduce coke formation by combining micropores with meso or macropores, though their synthesis can be complex and difficult to reproduce at scale.

Taken together, these comparisons highlight that superior catalytic performance is not simply a function of acidity or porosity alone. Instead, it emerges from carefully engineered combinations of metal dispersion, acid–base balance, confinement effects, and hierarchical architecture. Recognizing these mechanistic origins of performance provides a clearer foundation for rational catalyst design and helps explain why certain systems outperform others across

different CO_2 conversion pathways.

5. APPLICATION OF ZEOLITES IN CARBON DIOXIDE (CO_2) CONVERSION

To clarify the mechanistic insights of zeolite catalysts used for CO2 conversion, it is indispensable to consider some representative examples and their applications. Basically, the four features of stability, acidity, pore structure, and metal incorporation are responsible for the high versatility of these materials. Zeolites are the catalysts that bring these methods to reality since they allow hydrogenation, cycloaddition with epoxides, and coupling with nucleophiles in CO_2 conversion.

CO_2 Hydrogenation to Methanol and Formic Acid

Metal-modified zeolites act as good candidates to realize the goal of CO_2 hydrogenation, generating methanol and formic acid due to their metal-site hydrogen activation combined with framework stabilization of the reactive intermediates of the zeolite. As an instance, copper/zinc-ZSM-5 shows high selectivity for methanol as a result of the copper sites and the acidic ZSM-5 framework concerted interaction, whereas its hierarchical architecture enhances the diffusion and depresses the coking process [36]. Likewise, Fe-BEA makes use of Fe^{3+} sites to convert CO_2 into formic acid via redox-active pathways [37], and Cu/SAPO-34 achieves high methanol selectivity via strong Cu^{2+} framework interactions that stabilize intermediates and enhance catalyst durability [36]. Generally, these catalysts are operating in bifunctional systems, where metal oxides activate CO_2, and the acid sites of the zeolite catalyze the subsequent hydrogenation steps, thus leading to higher overall efficiency and product selectivity.

Taken together, these studies show that superior hydrogenation performance is rarely dictated by metal identity alone. Instead, the most effective zeolite-based systems consistently combine high metal dispersion or site isolation, intimate proximity between hydrogenation-active metal/oxide domains and zeolitic acidic environments, and sufficient pore accessibility to avoid diffusion-limited water accumulation and secondary over-conversion. Catalysts with well-controlled interfacial architecture generally outperform compositionally similar but structurally less organized systems, indicating that metal nuclearity, interfacial density, and transport accessibility are often more decisive than nominal loading or acidity alone.

CO_2 Cycloaddition with Epoxides

Zeolites are excellent catalysts for the cycloaddition of CO_2 with epoxides to yield cyclic carbonates. Lewis acid sites (extra-framework metal cations or framework Al) activate the epoxide, Brønsted sites and basic oxygen atoms help in CO_2 activation, and the confined pore environments increase the local concentration of the reactants as well as the selectivity [38]. One of the representative systems is H-BEA, which has Brønsted/Lewis acid functionality and hierarchical porosity for high carbonate yields [39]; SAPO-34 (and hierarchically modified SAPO materials) that show excellent selectivity for small, rigid epoxides (e.g., epichlorohydrin) due to optimal pore geometry and tunable acidity [40].

When Zn is incorporated into ZSM-5, the Lewis acidity and the epoxide-activation ability are increased; Zn-modified zeolites and Zn-containing ZSM-5 catalysts have been found to facilitate the CO_2 cycloaddition of epoxides to cyclic carbonates with high yield and selectivity. This is in agreement with the spectroscopic evidence for Zn-induced Lewis sites and various catalytic studies on Zn-bearing zeolitic materials [40].

Across cycloaddition systems, catalytic performance appears to depend less on the absolute strength of acidity than on the cooperative accessibility of complementary functions. The most effective catalysts typically combine Lewis acidic sites for epoxide activation, nucleophilic species for ring opening, and pore environments that stabilize transition states while remaining accessible to bulky substrates. Accordingly, hierarchical or defect-engineered zeolitic systems often outperform purely microporous analogues, not because they are intrinsically more acidic, but because they better balance activation, transport, and confinement.

CO_2 Coupling with Amines

Zeolite-based materials provide bifunctional acid–base sites that boost CO_2 adsorption and polarisation, and at the same time, they stabilize the resulting carbamate intermediates. Although the catalytic direct synthesis of urea derivatives from CO_2 and amines is primarily achieved using mixed-oxide or transition-metal systems, zeolites serve as ideal supports and co-catalysts, enhancing dispersion, microenvironment control, and product selectivity. One of the examples is the amine-grafted zeolite 13X and similar frameworks, which absorb CO_2 chemically through the formation of surface carbamates, as evidenced by spectroscopic studies [41]. Likewise, Co- or Fe-modified SAPO and ZSM-5 zeolites commit the coupling of CO_2 with amines or amino-epoxides by supplying more Lewis acid sites that both activate CO_2 and facilitate the nucleophilic

attack, thus giving rise to the selective formation of carbamate intermediates at close to atmospheric temperatures and pressures [42,43].

Actually, oxide-based hybrid catalysts have been able to directly synthesize urea from CO_2 and amines or ammonia, thus revealing mechanistic parallels that may guide the development of future zeolite-integrated systems [44,45]. All these works together point out that, in the first place, zeolites are not capable of completely converting CO_2 to urea. However, their adjustable acid–base nature and framework confinement make them a promising platform for designing recyclable, cooperative catalytic systems for CO_2 valorization into nitrogen-containing fine chemicals.

In amine-coupling and related adsorption–conversion pathways, performance is governed primarily by the co-adsorption environment rather than by isolated site strength alone. Catalysts that provide accessible Lewis acidic centers, moderate local polarity, and sufficient pore volume to accommodate both CO_2 and amine-derived intermediates generally show superior reactivity and selectivity. These observations suggest that, in this reaction class, zeolites function less as simple acid catalysts and more as structured adsorption–reaction environments that control reactant organization and intermediate stabilization.

CO_2 Hydrogenation to Light Olefins and Aromatics

Among zeolites, H-ZSM-5 in particular is indispensable in the methanol-to-hydrocarbon (MTH) process, whereby methanol, which is typically obtained from CO_2 hydrogenation, is converted into light olefins and aromatics. The medium-pore MFI structure of H-ZSM-5 and its strong Brønsted acidity are the reasons why high methanol conversion as well as considerable selectivity to hydrocarbons, including aromatics and olefins (e.g. hierarchical H-ZSM-5 resulted in >85 % selectivity to aromatics in a particular study), can be achieved [46]. Likewise, SAPO-34 zeolites are characterised by the CHA topology and are extensively employed for methanol-to-olefins (MTO) processes, thus when methanol is the feed, they show great selectivity to light olefins such as ethylene and propylene (e.g. selectivity ~85 % for light olefins in modified SAPO-34 [47, 48]. The combination of metal catalysts for CO_2 hydrogenation with these zeolite catalysts for subsequent MTH or MTO reactions is an alluring route for the production of hydrocarbons from CO_2.

For tandem CO_2-to-hydrocarbon systems, catalyst performance depends critically on whether the architecture allows efficient relay of oxygenate intermediates between hydrogenation-active domains and hydrocarbon-forming zeolitic sites. The most effective systems are not simply bifunctional in composition, but spatially integrated in a way that minimizes intermediate loss, suppresses over-hydrogenation, and balances residence time against diffusion escape. As a result, interfacial proximity, pore hierarchy, and acid strength distribution often determine product selectivity more strongly than bulk composition alone.

CO_2 Capture and Separation

Firstly, zeolites act as catalysts; however, they can also be utilized as efficient materials for capturing and separating CO_2, which essentially makes them a double-edged weapon in CCU scenarios. A case in point, SAPO 34 derived membranes have been fabricated for the sole purpose of CO_2 separation, and they are characterized by high permeance and CO_2/CH_4 selectivity (for instance, selectivity values were found to be > 170 while permeances were about 2×10^{-6} $mol\cdot m^{-2}\cdot s^{-1}\cdot Pa^{-1}$) [49]. On the other hand, platelet or bead forms of ZSM 5 (along with ion-exchanged variants) have been utilized as CO_2 adsorbents, demonstrating carbon dioxide adsorption capacities in the range of 1.4 mmol g^{-1} at 25 °C and 1 bar of pressure (Modification of the Zeolite ZSM-5 Adsorbent for CO_2 Capture [50]. These are examples of how zeolite-based materials can prevent the release of CO_2 gases into the atmosphere by capture/separation, thus making it possible to use the CO_2 obtained in chemical conversion processes at a later stage.

As summarized in Table 1, catalytic performance in zeolite-mediated CO_2 conversion is governed less by nominal catalyst composition alone than by the nature, accessibility, and spatial organization of the active motif. Highly selective hydrogenation systems benefit primarily from site isolation or stabilized metal–oxide interfaces, whereas cyclic carbonate synthesis is more consistently promoted by cooperative Lewis acid–nucleophile functionality and improved pore accessibility. In tandem systems, the decisive factor is often not simply bifunctionality, but the efficient relay of oxygenate intermediates between sequential catalytic domains.

Table 1: Comparative structure–property–reactivity analysis of representative zeolite-based catalysts for CO_2 activation and conversion

Catalyst/ system	Active motif/zeolite function	Reaction	Representative performance/conditions	Likely origin of performance	Main limitation	Mechanistic significance	Ref.
Cu@FAU	Mononuclear Cu–O species confined in FAU cages	CO_2 hydrogenation → methanol	Methanol selectivity up to 89.5%; STY = 12.8 mmol $gcat^{-1}$ h^{-1} at 513 K, 3 MPa, H_2/CO_2 = 3:1	Site isolation and cage confinement stabilize oxygenated intermediates and suppress Cu aggregation	Lower productivity than some interfacial nanoparticle systems; possible water sensitivity during long-term operation	Demonstrates the catalytic value of single-site confinement for selective methanol synthesis	51
Cu/ZnO_x@Na-ZSM-5	Confined Cu/ZnO_x interfacial domains within Na-ZSM-5	CO_2 hydrogenation → methanol	STY = 44.88 gMeOH gCu^{-1} h^{-1} with high durability	Strong Cu–ZnO_x interfacial synergy and confinement-enhanced structural stability	Selectivity may remain sensitive to water accumulation and local acid–base environment	Highlights the importance of interfacial architecture and confinement, beyond metal identity alone	52
Zn-exchanged ZSM-5	Framework-associated Zn^{2+} Lewis acid sites	CO_2 + epoxide → cyclic carbonate	Efficient styrene carbonate formation from styrene oxide and CO_2	Lewis acid activation of epoxide facilitates ring opening and CO_2 insertion	Activity depends on nucleophile availability and substrate sterics	Supports the central role of Lewis acidity in epoxide cycloaddition	7
KI/Y zeolite	I^- nucleophile combined with zeolite confinement	CO_2 + styrene oxide → styrene carbonate	100% conversion/yield at 100 °C, 50 bar CO_2, 6 h	Synergy between I^- nucleophilicity and pore-confined substrate activation	Requires relatively high CO_2 pressure; possible halide leaching on reuse	Clear example of cooperative bifunctional catalysis in cyclic carbonate synthesis	53
Hierarchical H-BEA	Brønsted/Lewis acidic zeolite with micro–mesoporous hierarchy	CO_2 + epoxides → cyclic carbonates	Yields >90% for small epoxides at 80–120 °C	Improved diffusion and accessibility of internal active sites	Hierarchical synthesis may introduce structural heterogeneity	Shows that transport accessibility can rival acid-site density in importance	54
Amine-functionalized SAPO-34	CHA framework with confined adsorption environment and basic/tethered functionality	CO_2 + epoxides → cyclic carbonates	Cyclic carbonate yields >95% under mild conditions	Strong CO_2 adsorption, favorable confinement, and cooperative substrate activation	Small-pore topology may restrict bulky substrates and slow diffusion	Illustrates how framework topology and local functionality jointly govern CO_2 fixation	55
Fe-ZSM-5	Framework-associated Fe^{3+} / Lewis acidic sites	CO_2 + amines → carbamates / urea-related products	Reactivity reported under relatively mild conditions (typically ≤120 °C, moderate CO_2 pressure)	Fe^{3+} sites likely assist CO_2 polarization and stabilization of amine-derived intermediates	Mechanistic evidence remains less mature than for hydrogenation or cycloaddition systems	Suggests zeolites can act as structured adsorption–reaction environments, not only acid catalysts	56, 57

Note: STY = space–time yield; MTH = methanol-to-hydrocarbon. Performance values are reported as described in the respective original studies and should be interpreted comparatively rather than as directly normalized benchmarks across all catalyst systems.

Key Insights from Comparative Analysis

Zeolite-based catalysts exhibit exceptional versatility in CO_2 conversion due to the coupling of framework acidity, shape selectivity, and the ability to spatially organize active metal or ionic sites [59]. However, comparative analysis reveals that performance is governed less by composition alone and more by the structure of active motifs within the zeolite environment [6]. For CO_2 hydrogenation, mononuclear Cu species confined within FAU supercages consistently deliver high methanol selectivity (~90%), primarily due to site isolation that suppresses Cu aggregation and stabilizes oxygenated intermediates (e.g., formate, methoxy) [60]. In contrast, Cu/ZnO_x interfaces confined within ZSM-5-type frameworks achieve significantly higher productivity because ZnO_x promotes H_2 activation and modifies the Cu electronic structure, while confinement maintains interfacial integrity under reaction conditions [61]. This comparison highlights a key trade-off: Single-site confinement favours selectivity, whereas interfacial architectures enhance activity and turnover frequency [59].

In oxygenate-mediated pathways, framework-associated Zn^{2+} species in ZSM-5 function as Lewis acid centers, facilitating epoxide activation rather than direct CO_2 activation, with CO_2 insertion occurring subsequent to ring opening [7]. This reinforces that Lewis acidity, not Brønsted acidity, is the dominant driver in cycloaddition chemistry, while Brønsted sites primarily stabilize intermediates and facilitate proton transfer rather than directly activating CO_2 [7,62]. Bifunctional systems such as KI/Y zeolite and β-zeolite–ionic liquid hybrids further demonstrate that cooperative catalysis between nucleophiles (I^-), Lewis acid sites, and confinement effects can achieve >90% cyclic carbonate yields under solvent-free conditions [63]. Here, pore confinement enhances local reactant concentration and transition-state stabilization, underscoring that the reactor microenvironment is as critical as active-site identity [64]. Hierarchical zeolites (e.g., mesoporous β or H-BEA) illustrate that mass transport limitations can rival intrinsic catalytic activity, with improved diffusion pathways increasing the effective utilization of internal acid sites, particularly for bulkier substrates [55]. This underscores that accessibility—not just site density—controls observed reactivity [55]. For CO_2–amine coupling, Fe- and Co-exchanged zeolites operate through cooperative metal–acid/base interactions, where framework-associated metal centers polarize CO_2 and stabilize amine-derived intermediates [57]. However, compared to hydrogenation and cycloaddition systems, mechanistic understanding remains less resolved, indicating a need for more operando-level evidence [57].

Finally, tandem systems such as ZnO–ZrO_2/H-ZSM-5 demonstrate the importance of spatially integrated bifunctionality, where oxide domains catalyze methanol formation and zeolitic Brønsted sites convert oxygenates via MTH chemistry to hydrocarbons (C_5^+, aromatics) [59]. Performance in these systems is highly sensitive to oxide–zeolite proximity, intermediate diffusion rates, and coke formation, highlighting the complexity of multi-step reaction coupling [65].

KINETIC AND THERMODYNAMIC CONSIDERATIONS IN CO_2 CONVERSION OVER ZEOLITE-BASED CATALYSTS

The essential factors that control the catalytic conversion of CO_2 are kinetic barriers and thermodynamic constraints. In the case of zeolite-based systems, knowledge of those factors is a recurring determinant for productivity and selectivity of different CO_2 conversion pathways, such as hydrogenation, cycloaddition, and coupling reactions. Zeolite structures have the peculiar features of Brønsted and Lewis acid sites, metal centres, and pore confinement effects working together to lower activation barriers and stabilize intermediate species. But the energy landscape that is in use depends to a very large extent on the catalyst composition, the dispersion of the metal, the acid–base balance, and operating conditions like temperature, pressure, and the H_2/CO_2 ratio [7].

Activation Energies and Reaction Pathways

Computational and operando kinetic studies have led to the conclusion that the creation and hydrogenation of surface formate (HCOO) are the rate-limiting steps in the $CO_2 \rightarrow CH_3OH$ reaction over Cu-based or metal-modified zeolites. The activation energies that have been reported mostly vary between 40 and 90 kJ mol^{-1}, the exact value being dependent on surface structure, coverage, and solvation corrections. These barriers can be altered through the Cu–ZnO–ZrO_2 interfaces or metal–zeolite encapsulation optimization, leading to an increase in hydrogen spillover and formate stabilization [66]. By contrast, activation energies for non-reductive CO_2 transformations, such as epoxide–CO_2 cycloaddition, are much lower – they normally fall within the range of 10–40 kJ mol^{-1}. This is attributable to the fact that the epoxide substrate undergoes ring-strain release, and Lewis acid and nucleophilic sites work cooperatively. In addition, zeolite-supported systems that have ionic liquids or halide promoters incorporated can follow this pattern, thus allowing the catalysis to be carried out efficiently at low temperatures (25–150°C) [21].

Rate-Determining Steps and Condition Dependence

The rate-determining step (RDS) in CO_2 conversion varies depending on the reaction environment and catalyst composition; thus, it is not a single RDS. Hydrogenation of surface formate to HCO* or the following hydrogen addition steps, in most instances, is the RDS in Cu–ZnO–ZrO_2 and Cu-encaged zeolite systems under conditions of moderate temperatures and pressures [61]. At conditions where the RWGS reaction dominates (high T, low H_2/CO_2), the formation of CO becomes kinetically preferred, and the step that controls the process is the desorption of CO*. In cycloaddition reactions, the ring-opening of the epoxide is the step with the highest energy barrier when the availability of the nucleophile is limited. The stronger nucleophiles or immobilized halides can change the direction of RDS to CO_2 insertion or ring-closure. This phenomenon was demonstrated in hybrid zeolite catalysts modified with ionic liquid, where the RDS shifted toward ion insertion and ring-closure [62]. These

discoveries bring two major design strategies into focus: (i) the modification of metal–zeolite interfaces so that hydrogenation can proceed with a minimal barrier, and (ii) the provision of enough nucleophilic activity and pore accessibility for the incorporation of CO_2 to occur efficiently.

Apparent *vs*. Intrinsic Kinetics

It is not uncommon for experimental activation energies to be quite off from intrinsic barriers derived from DFT because the coverage effects, adsorbate–adsorbate interactions, and mass-transport limitations that are present can alter the apparent energy profile. The confinement in a zeolite not only increases the local reactant concentrations but also stabilizes polar intermediates, which is why apparent activation energies are often lowered. Nevertheless, the diffusion limitations in micropores or at pore mouths may overshadow the surface-reaction-limited activities, and the overall rate becomes transport-limited. For this reason, kinetic parameters obtained from experiments should always be accompanied by gas-hourly space velocity (GHSV), particle size, and CO_2 partial pressure to ascertain the intrinsic catalytic performance and rule out transport effects [63].

Thermodynamic Feasibility

From the point of thermodynamics, CO_2 hydrogenation to methanol

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$

It is an exergonic process under industrial conditions. On the other hand, due to Le Châtelier's principle and the competing reverse water–gas shift (RWGS) reaction, the reaction equilibrium moves in the opposite direction at high temperatures and low pressures [64]. Therefore, operation at temperatures of 200–300 °C and pressures of 2–5 MPa is ideal to achieve maximum methanol selectivity. On the other hand, CO_2 cycloaddition with epoxides is a fundamentally exothermic process, and the reaction is thermodynamically feasible even at atmospheric pressures because the release of the ring-strain acts as a natural driving force. Here, the catalyst merely serves the purpose of reducing kinetic barriers and improving selectivity without changing the equilibrium [65].

Implications for Catalyst and Reactor Design

The amalgamation of kinetic and thermodynamic knowledge pinpoints the improvements that could be made to the recycling of CO_2 by using zeolite catalysts. Generate intrinsic activity by single-atom sites, metal–oxide–zeolite interfaces, and specifically designed acid–base site distributions to not only stabilize but also facilitate the intermediates [7]. Creating hierarchically porous structures to break the diffusion barriers and ensure that the measured rates actually refer to intrinsic kinetics. Using pressure temperature conditions that are in agreement with the zones of favourable equilibrium, and at the same time allowing the suppression of the side reactions such as RWGS and coking. The integration of DFT/microkinetic modelling with operando spectroscopy provides an unmediated way for finding RDS, surface coverage, and dynamic restructuring under reaction conditions vital for rational catalyst design [66]. In essence, the detailed comprehension of reaction energetics, mass transport, and surface dynamics in the context of zeolitic environments paves the way for the design of groundbreaking catalysts capable of transforming CO_2 volumetrically under technologically relevant conditions while maintaining high selectivity and conversion.

CATALYST STABILITY AND SCALABILITY OF ZEOLITE-BASED CO_2 CONVERSION CATALYSTS

To bring zeolite-based CO_2 conversion catalysts to commercial practice from mere laboratory demonstrations, it is essential to make them stable over a long period and scale up their production to an industrial level. Stability issues of the catalysts mainly involve: (i) metal leaching and loss of hydrothermal stability, (ii) coking and sintering in long-term operations, and (iii) decrease of performance after post-synthetic modifications, as well as in the case of use of realistic gas feeds. The authors of this article point out these problems, the solutions to them, as well as the scale-up issues with direct support from the literature, as the present-day knowledge in this field.

Metal Leaching and Hydrothermal Stability

Metal leaching is the major cause of the catalyst activity drop in ion-exchanged and supported zeolite catalysts. Two main strategies for their stabilization are effective: (i) Framework anchoring obtained by ion exchange into supercages or framework sites keeps metal ions more firmly than simple impregnation; and (ii) Encapsulation that encloses metal species in zeolite cages or core-shell structures protects them from sintering and volatilization. A good example is the single-atom Cu centres confined in FAU zeolite, which illustrate much better stability and almost no leaching in contrast to surface-deposited CuO_x, thus keeping the activity unchanged over a long period of CO_2 hydrogenation [51].

Hydrothermal stability, defined as the ability of zeolites to retain their structural integrity and active metal centres under steam-rich conditions, is a critical factor limiting their long-term catalytic performance. Framework degradation, particularly through dealumination and collapse of microporous architecture, remains a major challenge during high-temperature operation. Several strategies have been developed to enhance hydrothermal resilience, including increasing the Si/Al ratio, applying controlled steaming protocols, passivating external surfaces, and incorporating stabilizing heteroatoms such as phosphorus or transition metals. Among these, controlled dealumination and hierarchical structuring have emerged as key approaches for improving framework durability. Notably, surface-modified hierarchical zeolites have demonstrated exceptional thermal robustness, retaining over 90% of their Brønsted acidity after hydrothermal ageing at 500 °C, thereby maintaining catalytic activity and structural integrity under severe conditions [67].

Hierarchical Zeolite Durability and Resistance to Coking

Hierarchical zeolites with integrated micro-, meso-, and microporosity enhance mass transport and active-site accessibility, which is critical for CO_2 hydrogenation involving bulky intermediates. However, increased porosity can expose surface defects that promote coke formation and structural degradation if not properly controlled. Hierarchical zeolites outperform microporous analogues in continuous CO_2 hydrogenation, showing longer lifetimes (≥120 h time-on-stream) and less coke accumulation due to improved heat and mass transfer [68]. Coke resistance and regeneration capability are governed by high crystallinity, balanced acidity, and uniform mesoporosity achieved through controlled desilication, dealumination, and hard-templating synthesis [69]. These findings underscore the importance of precise structural engineering in designing durable, coke-resistant zeolite catalysts for CO_2 valorization.

Post-synthetic Modifications

Post-synthetic functionalization is one of the main methods available to change the properties of zeolites to fit the catalytic application requirements. Several methods, like ion exchange, metal impregnation, and organic grafting, are possible to create active sites and introduce functional groups that enhance the performance of CO_2-related transformations [70]. Unfortunately, these methods also bring different issues concerning the stability of the product. The use of amine-functionalized zeolites for CO_2 adsorption and cycloaddition reactions has been demonstrated to be very effective, as they can activate CO_2 and stabilize intermediates. Moreover, amine-grafted porous organic polymers greatly facilitate the selective capture of CO_2 with high efficiency in cycloaddition processes. Nonetheless, these materials are thermally and hydrolytically unstable, which makes their lifetimes in operational conditions limited [71]. On the one hand, metal impregnation is a typical method considered to elevate catalytic activity. On the other hand, it is a main reason for the presence of those weakly bound species that can be sintered and leached under hydrothermal conditions. Meanwhile, ion-exchanged or encapsulated metals can have stronger interactions with the zeolite framework and thus, offer better stability over a long time [72]. By implanting ionic liquids (ILs) or task-specific organics in the mesopores of zeolite, bifunctional catalysts are produced that have Lewis-acid and nucleophilic centres. Kumar et al. claimed that IL-functionalized β-zeolites were able to produce a CO_2–epoxide cycloaddition yield of more than 95%. However, they also noticed the degradation of IL due to the repetition of the catalytic cycles, which is a good illustration of the stability–activity compromise existing in these kinds of systems [72].

Regeneration, Lifecycle, and Industrial Integration

The catalysts of choice for industrial use would be those that can go through regeneration cycles multiple times with just a slight diminution of performance. The activity can be revived by regeneration through oxidative coke removal, mild hydrogenation, or steam treatment, but if the conditions are not right, this will lead to dealumination or metal migration. Hierarchical zeolites are characterized by a more complete regeneration and lower residual coke owing to their improved pore connectivity. However, long-term oxidative or steam treatments may gradually decrease Brønsted acidity if framework Al is mobile [68]. For the large-scale production, certain catalyst structures like extrudates, wash-coated monoliths, or zeolite membranes facilitate the management of pressure drop and the dissipation of heat. Removing products continuously and thus shifting the equilibrium, membrane reactor configurations, in turn, can raise methanol yields further. The analyses of techno-economics put the factors of active metal costs, regeneration ease, and hydrothermal degradation resistance as the main determinants of market entry [73].

Practical Recommendations for Durable and Scalable Zeolite Catalysts

1. To prevent leaching and sintering under reactive and hydrothermal environments, framework anchoring or encapsulation of metal sites should be implemented most effectively [46].

2. The creation of hierarchical porosity should involve the gentle desilication or templating so that a compromise between diffusion improvement and structural strength can be achieved [74].

3. The post-synthetic functionalization method should be represented by covalent grafting, which is more robust than physisorbed molecules, thus providing improved thermal and hydrolytic stability [75].

4. Regeneration methods ought to be confirmed through testing under representative conditions to avoid damage to the framework that can accumulate from oxidative or steam cycles [76].

5. Testing of realistic feeds, i.e., including impurities, steam, and pressure fluctuations, should go hand in hand with standard catalytic metrics, and leaching analyses ought to be reported for reproducibility and fair benchmarking [7].

Critical Evaluation and Research Gaps

Despite notable advancements in zeolite-based catalysts for CO_2 activation and hydrogenation, several unresolved challenges continue to hinder their industrial deployment. Mechanistic ambiguities persist, particularly regarding the role of metal–zeolite interfaces and the pathways involving formate or CO intermediates. Product selectivity in downstream reactions such as methanol-to-hydrocarbons (MTH) is highly dependent on zeolite topology. H-ZSM-5 favours aromatics due to its medium-pore channels, while SAPO-34 promotes light olefins via its CHA-type cages. However, a molecular-level understanding of confinement effects remains incomplete, necessitating integrated theoretical and operando approaches.

A major limitation is the absence of standardized benchmarking protocols. Performance metrics such as turnover frequency, selectivity, and space–time yield vary widely due to differences in reactor design, feed composition, and gas hourly space velocity (GHSV). Inconsistent reporting of key catalyst properties—acidity, metal dispersion, Si/Al ratio—further complicates cross-study comparisons. Establishing unified testing frameworks is essential for reproducible evaluation and rational catalyst design.

While computational tools like DFT and microkinetic modelling offer mechanistic insights, experimental validation under industrial conditions is limited. Advanced in situ and operando techniques (e.g., DRIFTS, XAS, solid-state NMR) enable real-time monitoring of CO_2 adsorption and intermediate evolution, but achieving high spatial and temporal resolution at relevant pressures and temperatures remains challenging. Long-term operando studies are particularly valuable for understanding deactivation pathways such as coking, sintering, and dealumination under fluctuating CO_2/H_2 ratios and humid feeds.

Finally, balancing activity, selectivity, and stability remains a core challenge. High metal loading and small particle size enhance activity but increase susceptibility to sintering and coke formation. Excess acidity or micropore confinement can trigger secondary reactions and diffusion limitations. Hierarchical zeolites with interconnected micro–mesopores improve mass transport and reduce coking without compromising crystallinity. Nonetheless, reproducibility, scalability, and hydrothermal durability over extended operation still require systematic optimization.

FUTURE PERSPECTIVES

After 2025, converting CO_2 with the use of zeolites will highly depend on operando spectroscopy, computational modelling, and rational catalyst design to achieve predictable activity and durability. Single-atom zeolite catalysts (SAZCs) containing single-atom ruthenium (Ru_1) or copper (Cu_1) metal centres stabilized in zeolites have become a prominent area of research because of their atomic efficiency and the adjustable electronic structure that makes it possible to selectively activate CO_2 and increase the stability. Besides, amino, hydroxyl, or carboxyl groups can be incorporated not only into the linker but also into the framework functionalization to improve the CO_2 adsorption and catalytic turnover by acid–base cooperativity and by strengthening the framework–CO_2 interactions. Membrane reactors based on zeolite catalysts are another revolutionary direction, where the reaction and separation are integrated to go beyond the equilibrium limits and increase the selectivity of methanol or dimethyl ether. Moreover, innovation in the future will require benchmark standard protocols and data-driven approaches in which AI and machine learning can expedite the discoveries of the best

metal zeolite interfaces and operating conditions. In brief, the combination of atomic-level engineering, functionalized frameworks, and integrated reactor designs is going to be the main driver of the new generation of zeolite catalysts that are efficient, durable, and scalable for CO_2 hydrogenation and other related transformations.

DESIGN PRINCIPLES FOR CATALYSTS LEARNED FROM THE LITERATURE

An additional aim of this review is to identify some general guidelines and catalyst design principles, derived from studying zeolite-based systems for CO_2 activation and conversion.

CO_2 Activation Usually Requires More Than Just Brønsted Acidity

High-performance catalysts for CO_2 activation include materials containing Lewis-acidic ions, redox-active metals or metal–oxide interactions that can polarize and stabilize bound CO_2. While Brønsted acidity plays an important role, it is insufficient by itself and merely tunes intermediate stability and proton transfers.

Size and Dispersion of Metals Impact Selectivity Greatly

Metallic sites with low coordination numbers or very small metal particles tend to favour oxygenate products by limiting over-hydrogenation. On the other hand, higher coordination numbers or larger particles could lead to RWGS, sintering, or non-selective hydrogenation.

Catalyst Efficiency Depends on Acid–Base Balance Rather Than Maximum Acidity

While many efficient catalysts include high densities of acid sites, their performance improves only up until a certain point, after which it plateaus, or even drops due to side reactions, deactivation, etc. In particular, excessive acidity may result in unwanted secondary processes.

Confinement Effects Become Disadvantageous Once Transport Limitations Arise

Micropores in zeolites help maintain intermediates, concentrate reactants locally and provide transition state control. However, once diffusion becomes a limiting factor, pore space within a zeolite will actually hinder catalysis. Hierarchical porosity then becomes highly desirable for tandem catalysis involving bulk intermediates and water generation.

Relative Positioning of Functionalities Is Just as Crucial as Their Presence

In catalysts combining several different functionalities, the distance between a metal hydrogenation center and the acidic environment of the zeolite framework will impact the degree to which intermediates are relayed from one to another. This means that catalyst design must not consider only which functionalities to use, but also how close together they will be arranged.

Catalyst Stability Must Be Considered at The Design Stage

For practical application, a catalyst should be stable in the sense of not being easily altered by processing, restructured in operation or subject to deactivation. This implies including framework-stabilized metals, robust structures, and regeneration-friendly architecture into catalyst design at an early stage.

CONCLUSION

This review demonstrates that zeolites cannot be considered only as acidic porous materials in terms of CO_2 activation and conversion, but should be regarded as programmable catalysts where the interplay between composition of the zeolite framework, metal speciation, acid-base functionality, and pore topology collectively dictates their performance. High-efficiency zeolitic catalysts capable of transforming CO_2 are achieved through the synergistic integration of CO_2 activation, intermediate stabilization, and product formation processes, irrespective of hydrogenation, cycloaddition, and amine coupling reaction families. Among others, the key point of discussion is the importance of Lewis acidic metal centers, redox metal sites, and metal-zeolite interface for primary activation of CO_2 molecules, in contrast to Brønsted acid sites, which primarily stabilize intermediates and contribute indirectly by promoting proton transfer reactions. The above observation is critical for avoiding oversimplified structure-activity relationships. As an additional point, high catalytic efficiency is not guaranteed by a single parameter but relies on the optimization of the number of metal atoms, acid-base balance, confinement effects, and accessibility. Four fundamental principles can be extracted from the current knowledge of zeolitic catalysts for CO_2 activation and conversion processes: (1) selective pathways are achieved through highly dispersed metal atoms; (2) high catalytic activity should not result in maximum acidity due to increased susceptibility to deactivation and side reactions; (3)

hierarchical structures are beneficial for multistep processes since they facilitate better diffusion, prevent coking, and preserve access to catalytic interface sites; and (4) the distance between the hydrogenation and zeolite catalysis regions is the decisive factor in tandem catalyst architecture. At the same time, several issues need to be addressed within the existing literature. The ambiguity around mechanistic questions such as the true nature of the rate-limiting step, the effect of confinement on the intrinsic elementary-step energetics, and restructuring of the catalyst surface in terms of steam-rich and impure feedstocks are among them. Furthermore, the progress in the field is slowed down by the lack of standardized testing procedures, inconsistent data on active-site descriptors, and insufficient operando studies. Future development may involve the introduction of atomically precise metal moieties, hierarchical and hydrothermally stable zeolites, advanced operando studies combined with microkinetic modelling, and intensified reactor-level strategies such as tandem beds and membrane reactors. Most importantly, future generations of highly efficient catalysts should combine selectivity, durability, activity, and manufacturing scalability under industrial-relevant conditions. Ultimately, the field would benefit from moving beyond isolated performance reporting toward **standardized, mechanism-aware catalyst benchmarking**, in which activity, selectivity, stability, and active-site identity are evaluated under more comparable and technologically relevant conditions. Without such normalization, apparent advances in catalyst design will remain difficult to interpret and even harder to translate into scalable CO_2 valorisation strategies.

CONFLICT OF INTEREST

The authors declared no conflict of interest, financial or otherwise.

REFERENCES

1. World Meteorological Organization. (2024.). Carbon dioxide levels increase by record amount, reach new highs in 2024 [Internet].
2. Nunes LJR. (2025). The rising threat of atmospheric CO_2: A review on the causes, impacts, and mitigation strategies. Environments. 10(4):66.
3. Alotaibi AM. (2025). An overview of zeolites: from historical background to diverse applications. Molecules. 30(20):4036.
4. Khodadadpour M, Bahmanzadegan F, Ghaemi A, Bazyari A. (2025). A review of the performance of zeolitic compound catalysts for CO_2 conversion into valuable hydrocarbons. Journal of CO2 Utilization. 96:103093.
5. Álvarez A, Bansode A, Urakawa A, Bavykina AV, Wezendonk TA, Makkee M, et al. (2017). Challenges in the greener production of formates/formic acid, methanol, and DME by heterogeneously catalyzed CO_2 hydrogenation. Chemical Reviews. 117(14):9804-9838.
6. Mambetova M, Dossumov K, Baikhamurova M, Yergaziyeva G. (2024). Sorbents based on natural zeolites for carbon dioxide capture and removal of heavy metals from wastewater. Processes. 12(10):2071.
7. Cutad MB, Al-Marri MJ, Kumar A. (2024). Recent developments on CO_2 hydrogenation performance over structured zeolites. Catalysts. 14(5):328.
8. Čejka J, Millini R, Opanasenko M, Serrano DP, Roth WJ. (2020). Advances and challenges in zeolite synthesis and catalysis. Catal Today. 345:2-13.
9. Shamzhy M, Gil B. (2025). Acidity of zeolites. In: Zeolites and Related Materials. Cambridge: Royal Society of Chemistry. 197–231.
10. Liu T, Liu Z, Jiang S, Peng P, Liu Z, Dutta Chowdhury A, et al. (2025). Selectivity control by zeolites during methanol-mediated CO_2 hydrogenation. Chem Soc Rev. 54:2726–2761.
11. Zhao X, Xu J, Deng F. (2020). Solid-state NMR for metal-containing zeolites: from active sites to reaction mechanism. Front Chem Sci Eng. 14(2):159-187.
12. Cánovas MA, Gracia A, Sayós R, Gamallo P. (2024). CO_2 hydrogenation on Ru single-atom catalyst encapsulated in silicalite. The Journal of Physical Chemistry C. 128(39):16551-16562.
13. Tan L, Jiao N, Bai X, Wang H, Wang J, Wang H, et al. Methods for preparing hierarchical zeolites by chemical etching and their catalytic applications. Eur J Inorg Chem. 2023;26(24):e202300314.
14. Ren M, Zhang Y, Wang X, Qiu H. (2022). Catalytic hydrogenation of CO_2 to methanol: a review. Catalysts. 12(4):403.

15. Xie J, Olsbye U. (2023). Oxygenate-mediated conversion of COx to hydrocarbons: role of zeolites in tandem catalysis. Chemical Reviews. 123(20):11775–11816.

16. Megías-Sayago C, Bingre R, Huang L, Lutzweiler G, Wang Q, Louis B. (2019). CO_2 adsorption capacities in zeolites and layered double hydroxides. Frontiers in Chemistry. 7:551.

17. Montejo-Valencia BD, Pagán-Torres YJ, Martínez-Iñesta MM, Curet-Arana MC. (2017). DFT study of M-exchanged MFI zeolites for CH_4 and CO_2 conversion. ACS Catalysis. 7(10):6719–6728.

18. Fehr SM, Nguyen K, Krossing I. (2022). Operando-DRIFTS studies on Cu/ZnO catalysts for CO_2 hydrogenation to methanol. ChemCatChem. 14(3):e202101500.

19. Kattel S, Ramírez PJ, Chen JG, Rodriguez JA, Liu P. (2017). Active sites for CO_2 hydrogenation to methanol on Cu/ZnO catalysts. Science. 355(6331):1296-1299.

20. Ticali P, Salusso D, Ahmad R, Ahoba-Sam C, Ramirez A, Shterk G, et al. (2021). CO_2 hydrogenation over bifunctional Zn-doped ZrO_2/zeolite catalysts. Catalysis Science & Technology. 11(4):1249-1268.

21. Wang M, Luo L, Wang C, Du J, Li H, Zeng J. (202). Heterogeneous catalysts toward CO_2 hydrogenation for sustainable carbon cycle. Accounts of Materials Research. 2;3(6):565–571.

22. Ozorio LP, Henrique FJ, Comerford JW, North M, Mota CJ. (2021). Zeolite-mediated production of cyclic organic carbonates. Reaction Chemistry & Engineering. 6(4):672–678.

23. Tyagi P, Singh D, Malik N, Kumar S, Malik RS. (2023). Metal catalysts for CO_2 capture and cyclic carbonate synthesis. Mater Today. 65:133-165.

24. Liang J, Liang Z, Zou R, Zhao Y. (2017). Heterogeneous catalysis in zeolites, mesoporous silica, and metal–organic frameworks. Advanced Materials. 29(30):1701139.

25. Marciniak AA, Lamb KJ, Ozorio LP, Mota CJA, North M. (2020). Heterogeneous catalysts for cyclic carbonate synthesis from CO_2 and epoxides. Current Opinion in Green and Sustainable Chemistry. 26:100365.

26. Sabet M, Johnson A, Roberts K. (2021). Zeolite-mediated CO_2/amine coupling. Catalysis Today. 368:80–92.

27. Choi M, Lee J, Kim H. (2022). Amine-functionalized zeolite adsorbents under humid conditions. Environmental Research. 214:113855.

28. Zimmerman T, Smith D. (2023). Dehydrative transformation of carbamates to isocyanates. J Catal. 421:1–10.

29. Luk J, Goodfellow AS, More ND, Bühl M, Kumar A. (2024). Selective routes to urea derivatives via formamide coupling. Chem Sci. 15:16594–16604.

30. Chai Y, Dai W, Wu G, Guan N, Li L. (2021). Confinement in zeolite catalysis. Accounts of chemical research. 54(13):2894–2904.

31. Zhang Y, Wang Y, Li X, Liu Z, Zhang J. (2023). Non-reductive transformation of CO_2 into urea derivatives. ChemCatChem. 15(18):e202301342.

32. Chen D, Liu J, Li L, Gao B, Zhang X, Gao W, et al. (2025). Zeolite-based catalysts for CO_2 hydrogenation. Catalysis Science & Technology.

33. Shi L, Song J, Yang Y, Yang L, Dai Z, Yao L, et al. (2025). Bimetallic electrocatalysts for CO_2 reduction. Journal of Materials Chemistry A.;13(4):2478–2504.

34. Ramirez A, Gong X, Caglayan M, Nastase SA, Abou-Hamad E, Gevers L, et al. (2021). Selectivity descriptors in zeolite-mediated bifunctional catalysis. Nature Communications. 12:5914.

35. Yan T, Liu H, Zeng ZX, Pan WG. (2023). Catalysts for cyclic carbonate synthesis from CO_2. The Journal of CO2 Utilization. 68:102355.

36. Ye RP, Ding J, Gong W, Argyle MD, Zhong Q, Wang Y, et al. (2019). CO_2 hydrogenation to high-value products. Nature Communications. 10:5698.

37. Shah DR, Tucker A, Xie Z, Chen JG, Jones CW. Evolution of Fe sites in tandem CO_2 conversion. CCS Chem. 2024;6(12):2895–2907.

38. Gao B, Li W, Chai Y, Wu G, Li L. (2025). Heteroatom-containing zeolites for CO_2 cycloaddition. ChemCatChem. 17(1):e202401385.

39. Ahmed M, Sakthivel A. (2017). Cyclic carbonate synthesis using amine-functionalized SAPO-34. The Journal of CO2 Utilization. 22:392–399.

40. Iliuta MC, Gutiérrez-Ortiz FJ, Urakawa A, Klemm E. (2022). Zn-exchanged ZSM-5 catalysts in epoxide/CO_2 cycloaddition. Chem Eng J. 430:137900.

41. Bezerra DP, Chen CC, Yang RT. (2014). CO_2 adsorption in amine-grafted zeolite 13X. Microporous Mesoporous Mater. 195:42–49.

42. Truong CC, Nguyen TT, Do TH, et al. (2020). Recent advances in catalytic fixation of CO_2: carbamate and urea formation routes. Journal of CO2 Utilization. 40:101265.

43. Stagel K, Qin H, Zeng H, et al. (2023). Continuous synthesis of carbamates from CO_2 and amines over heterogeneous catalysts. ACS Omega. 8(32):29215–29225.

44. Ding J, Li R, Wang T, He Y, Wu Y, Zhang Y, et al. (2023). Direct synthesis of urea from carbon dioxide and ammonia under mild conditions. Nature Communications. 14:4896.

45. Sun DL, Yang FF, Li J, et al. (2016). Green synthesis of N, N′ -dialkylureas from CO_2 and amines via catalytic carbonylation. Ind Eng Chem Res. 55:10606-10613.

46. Yarulina I, Kapteijn F, Gascon J. (2016). Importance of heat effects in the methanol-to-hydrocarbons reaction over ZSM-5: role of mesoporosity on catalyst performance. Catal Sci Technol. 6:5320–5325.

47. Wang X, Li R, Bakhtiar SULH, Yuan F, Li Z, Zhu Y. (2018;). Excellent catalytic performance for methanol-to-olefins over SAPO-34 synthesised by controlling hydrothermal temperature. Catalysis Communications. 108:64-67.

48. Al Hussami R, Ghavipour M, Nasser G, Duah C, Yousef S, Kopyscinski J, et al. (2025). A review of methanol-to-olefins conversion over SAPO-34: catalyst design, mechanisms, and kinetics. Journal of Materials Chemistry A. 14:90-179.

49. Shi H. (2014). Synthesis of SAPO-34 zeolite membranes with the aid of crystal growth inhibitors for CO_2–CH_4 separation. New J Chem. 38(11):5276-5278.

50. Budianto GP. (2021). Modification of natural zeolite to ZSM-5 as CO_2 adsorber. Eksergi.18(2):60–64.

51. Chai Y, Qin B, Li B, Dai W, Wu G, Guan N, et al. (2023). Zeolite-encaged mononuclear copper centres catalyze CO_2 selective hydrogenation to methanol. Natl Sci Rev. 10(7):nwad043.

52. Cui WG, Li YT, Yu L, Zhang H, Hu TL. (2021). Zeolite-Encapsulated Ultrasmall Cu/ZnOx Nanoparticles for the Hydrogenation of CO2 to Methanol. ACS Applied Materials & Interfaces. 14;13(16):18693-703.

53. Ozorio LP, Henrique FJ, Comerford JW, North M, Mota CJ. (2021). Zeolite-mediated production of cyclic organic carbonates: reaction of CO2 with styrene oxide on zeolite Y impregnated with metal halides. Reaction Chemistry & Engineering. 6(4):672-678.

54. Shvets O, Kurmach M, Yaremov P, Shcherban N. (2022). Hierarchical zeolite catalysts with basic properties for CO_2 cycloaddition to epoxides. Materials Today Proceedings. 62:7677–7680.

55. Ahmed M, Sakthivel A. (2017). Preparation of cyclic carbonate via cycloaddition of CO2 on epoxide using amine-functionalized SAPO-34 as catalyst. Journal of CO2 Utilization. 1;22:392-399.

56. Stagel K, Ielo L, Bica-Schroder K. (2023). Continuous synthesis of carbamates from CO2 and amines. ACS Omega. 8(50):48444-48450.

57. Zhu J, Wang Y, Yao J, Li H. (2024). Highly selective customized reduction products for hydrogenation of CO2-derived urea derivatives or carbamates. Chemical Science. 15(48):20534-20544.

58. Zhou C, Shi J, Zhou W, Cheng K, Zhang Q, Kang J, et al. (2019). Highly active ZnO-ZrO2 aerogels integrated with H-ZSM-5 for aromatics synthesis from carbon dioxide. ACS catalysis. 10(1):302-310.

59. Liu Y, Zhang X, Wang Z, Li J, Lv Q, Wang D, et al. (2026). Zeolite-Anchored Single-Atom Catalysts for Enhanced Hydrogenation and Dehydrogenation Reaction Process. Advanced Materials. 38(4):e13175.

60. Mishra V, Peter SC. (2024). A comprehensive overview of the catalytic pathway for CO2 utilization with epoxide to cyclic carbonate. Chem Catalysis. 18;4(1).

61. Xia Y, Cha X, Yan X, Wang X, Cai Y, Tan KB, et al. (2025). Fine regulation of Cu-ZnO interfaces for enhanced CO2 hydrogenation to methanol by atomic layer depositing thin ZnO films on copper phyllosilicates. Applied Catalysis B: Environment and Energy. 361:124620.

62. Shang S, Shao W, Luo X, Zuo M, Wang H, Zhang X, et al. (2022). Facet engineering in constructing Lewis acid-base pairs for CO2 cycloaddition to high value-added carbonates. Research.

63. Henrique FJ, Barbosa PA, Grisolia LM, Silva RJ, Mota CJ. (2022). Evidence for supramolecular catalysis in the synthesis of cyclic organic carbonates over zeolite Y impregnated with metal iodides. Molecular Catalysis. 522:112216.

64. Albertini PP, Calderon Mora J, Guskova M, Rodlamul P, Hicks N, Leemans J, et al. (2025). Active sites under electronic effect are more sensitive to microenvironment in CO2 electroreduction. Journal of the American Chemical Society. 147(29):25517-25526.

65. Li W, Wang K, Zhan G, Huang J, Li Q. (2021). Design and Synthesis of Bioinspired ZnZrO x &Bio-ZSM-5 Integrated Nanocatalysts to Boost CO2 Hydrogenation to Light Olefins. ACS Sustainable Chemistry & Engineering. 27;9(18):6446-6458.

66. Shi X, Lin X, Luo R, Wu S, Li L, Zhao ZJ, et al. (2021). Dynamics of heterogeneous catalytic processes under operando conditions. Journal of the American Chemical Society. 1(12):2100–2120.

67. Simancas R, Chokkalingam A, Elangovan SP, Liu Z, Sano T, Iyoki K, et al. (2021). Recent progress in the improvement of hydrothermal stability of zeolites. Chemical Science. 12(22):7677–7695.

68. Lee S, Park Y, Choi M. (2024). Cooperative Interplay of Micropores/Mesopores of Hierarchical Zeolite in Chemical Production. ACS Catalysis. 14(3):2031-2048.

69. Zhang M, Huang J, Meng F, Zhang C, Zhang Z. (2025). Coke-induced deactivation in zeolite catalysts. Dalton Trans.

70. Hack J, Maeda N, Meier DM. (2022). Review on CO_2 capture using amine-functionalized materials. ACS Omega. 7(44):39520–39530.

71. Farrusseng D, Tuel A. (2016). Zeolite-encapsulated metal nanoparticles in catalysis. New J Chem. 40(5):3933–3949.

72. Durak O, Zeeshan M, Habib N, Gulbalkan HC, Alsuhıle A, Çağlayan P, et al. (2022). Composites of porous materials with ionic liquids: Synthesis, characterization, applications, and beyond. Microporous and Mesoporous Materials. 332(1):111703.

73. Asgari M, Albacete P, Menon D, Lyu Y, Chen X, Fairen-Jimene D. (2025). Structuring porous reticular materials for energy applications. Chemical Society Review. 54:4701-4744.

74. Hijazi N, Bavykina A, Yarulina I, Shoinkhorova I, Ramos-Fernandez EV, Gascon J, et al. (2025). Chemical engineering of zeolites via hierarchical design. Chemical Society Review. 54:6335-6384.

75. Sosa JD, Bennett TF, Nelms KJ, Nelms KJ, Liu BM, Tovar RC, et al. (2018). Metal–organic framework hybrid materials. Crystals. 8:325

76. Anekwe IM, Isa YM. (2025). Catalyst deactivation pathways and regeneration technologies. Energy Advances. 4(9):1075–1113.